Electron Probe Microanalysis of Trace Sulfur in Basaltic Glasses and Silicate Minerals

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Abstract

Sulfur (S) in the mantle is conventionally assumed to be exclusively stored in accessory sulfide phases, but recent work shows that the major silicate minerals that comprise >99% of the mantle could be capable of hosting trace amounts of S. Assessing the incorporation of trace S in nominally S-free mantle minerals and determining equilibrium S partitioning between these minerals and basaltic melt requires analyzing small experimental phases with low S contents. Here, we develop a protocol for EPMA analysis of the trace levels of S in silicate phases. We use a suite of natural and experimental basaltic glass primary and secondary standards with S contents ranging from 44 ppm to 1.5 wt.%. The effects of beam current and counting time are assessed by applying currents ranging from 50 to 200 nA and total counting times between 200 and 300 seconds at 15 kV accelerating voltage. We find that the combination of 200 nA beam current with a 200 second counting time (80 second peak, 60 seconds each for upper and lower background, respectively) achieves precise yet cost-effective measurements of S down to a calculated detection limit of ~5 ppm and a blank-derived, effective detection limit of ~17 ppm. Close monitoring of the S peak intensity and position throughout the duration of each spot also
shows that high currents and extended dwell times do not compromise the accuracy of measurements, and even low S contents of 44 ppm can be reproduced to within one standard deviation. Using our developed recipe, we analyzed a small suite of experimental clinopyroxenes (cpx) and garnets (gt) from assemblages of silicate partial melt + cpx ± gt ± sulfide, generated at 1.5 to 3.0 GPa and 1200 to 1300 °C. We find S contents of up to 71 ± 35 ppm in cpx and 63 ± 28 ppm in gt, and calculate mineral-melt partition coefficients \( D_{\text{cpx/melt}} \) of up to 0.095 ± 0.064 and 0.110 ± 0.064 for \( D_{\text{cpx/melt}} \) and \( D_{\text{gt/melt}} \), respectively. The sulfur capacity and mineral-partitioning for cpx are in good agreement with SXRF measurements in a prior study by Callegaro et al. (2020), serving as an independent validation of our EPMA analytical protocol.

**Keywords:** Electron probe microanalyzer, sulfur solubility, mantle, silicate glass, clinopyroxene, garnet, partitioning

1. **Introduction**

Sulfur (S) is a critical element for planetary differentiation, formation of many ore deposits, chemical habitability of planets, and complex life. Geologists have long sought an accurate understanding of planetary sulfur cycles, particularly as pertaining to S storage in the Earth’s mantle (Lorand, 1990; von Gehlen, K. 1992; McDonough and Sun, 1995; Saal et al., 2002; Nielsen et al., 2014; Tsuno and Dasgupta, 2015; Zhang et al., 2016; Ding and Dasgupta, 2017, 2018; Sun et al., 2020; Dasgupta et al., 2022), a significant reservoir of volatile storage making up 67% of the planet by mass. This task is complicated by sulfur’s volatile nature and by extraction of S-bearing magmas from their sulfide-bearing sources, which obfuscate the pre-melting, sub-solidus source sulfur content. Previous studies have established the concentration of mantle S at a range of values between 100 and 300 ppm (e.g. Nielsen et al., 2014; Ding and
Dasgupta, 2017; Sun et al. 2020), based on the assumption that S is hosted exclusively in accessory sulfide phases such as mono-sulfide solid solution (MSS) or mono-sulfide liquid solution (MLS) (Lorand, 1989, 1990; Bockrath et al., 2004; Zhang and Hirschmann, 2016).

Recent work, however, has claimed that major silicate mantle minerals—which have thus far been assumed to be S-free—may contain trace amounts of S (Anzures et al., 2019; Callegaro et al., 2014, 2020). Here, we define a trace element as a non-stoichiometric component of a mineral that is present in its crystalline lattice at levels of <0.1 wt.% (1000 ppm). Trace elements may be incorporated into minerals by filling vacancies in the lattice or substituting for elements of similar charges/ionic radii. For example, clinopyroxene has the general formula (Ca,Mg,Fe,Na)(Mg,Fe,Al)(Si,Al)₂O₆, but S has been shown to be present at concentrations of up to approximately 50 ppm (Callegaro et al., 2014), hypothetically substituting for bridging oxygen in the M2 cation site (Callegaro et al., 2020). Considering that silicate minerals such as olivine, clinopyroxene, orthopyroxene, garnet, and high-pressure polymorphs of these species comprise >99% of the mantle, the absolute amount of S they could contribute to the estimated bulk Earth S inventory of ~1.8×10²³ kg may be non-negligible, no matter how dilute their concentration within the minerals. Furthermore, not accounting for storage of trace S in nominally sulfur-free minerals may lead to serious underestimation of the bulk mantle S budget. Additionally, incorporation of sulfur into silicate minerals may have an impact on how S is partitioned as the mantle undergoes partial melting or mantle-derived melts undergo differentiation. All current models assume that S is perfectly incompatible after exhaustion of the accessory sulfide phase during mantle melting (e.g. Ding and Dasgupta, 2017; Dasgupta et al. 2022) or until sulfide precipitates during magmatic differentiation (e.g. Lee et al., 2012; Ding
and Dasgupta, 2017). Comprehensive studies of the sulfur in mantle minerals are, therefore, crucial for better understanding volatile storage and cycling within Earth and other rocky planets. The three prior studies analyzing S in silicate minerals were conducted using secondary ionization mass spectrometry (SIMS) (Anzures et al., 2019) and synchrotron X-ray microfluorescence (SXRF) (Callegaro et al., 2014 and 2020). While both techniques are well-established for the analysis of trace elements, they have the disadvantages of low spatial resolution and high analytical cost/limited availability. In contrast, the electron probe microanalyzer (EPMA), particularly the field emission electron probe microanalyzer (FE-EPMA), offers high spatial resolution with <1 µm³ analytical volume, which is especially advantageous for fine-grained, polymineralic, and heterogeneous samples. Furthermore, EPMA is more widely available and has significantly lower operational costs.

Conventionally, EPMA has been used highly effectively for major and minor element analysis, but at less frequency for trace elements due to numerous challenges presented by the trace realm. For example, trace element analyses require higher beam currents and longer counting times than for routine major element analyses, in order to generate a sufficient quantity of X-rays to resolve the target peak from the background. However, prolonged exposure to high current densities can excessively heat up the irradiated volume and lead to degassing and/or redox change of the target element, which is particularly challenging while analyzing a volatile and multivalent element like sulfur (Hughes et al., 2020). Count precision is directly tied to the accelerating voltage; increased overvoltage allows the beam electrons to penetrate further into the sample, ionizing a greater volume of material but compromising the spatial resolution of the analysis (Reed, 2000; Carpenter and Jolliff, 2015). Trace elements are also more sensitive to various error sources that accompany EPMA analysis, including fluctuation of X-ray emissions,
incorrect background characterization due to peak interferences, coating effects, calibration
effects, and improper matrix correction (Williams et al., 2007). Finally, collection efficiency was
a challenge in the past that has now been largely resolved by advances in spectrometer
technology (Jercinovic et al., 2012).

Despite these difficulties, EPMA-based studies of trace elements have been attempted
from as far back as the 1980’s (Bodinier et al., 1987, achieving detection limits of titanium down
to 5 ppm in orthopyroxene and 4 ppm in olivine), and an increasing volume of work in the past
two decades has shown the technique to be capable of highly precise and accurate measurement
of trace levels in a range of geologic materials (e.g. Pyle and Spear, 2000; Jercinovic, 2005;
Sobolev et al., 2005; Williams et al., 2007; Weiss et al., 2008; Agangi et al., 2015; Korolyuk and
Pokhilenko, 2016; Jia et al., 2022; Sørensen et al., 2023). In this study, we develop an EPMA
analytical protocol for trace sulfur in silicates, by calibrating the analytical conditions on a series
of low-S natural and synthetic glasses. We improve measurement precision by applying a range
of high beam currents and counting times to lower detection limits (D.L.) and analytical
uncertainty, while checking for any negative irradiation effects and secondary fluorescence. We
also assess potential background interferences to characterize the continuum properly for an
accurate peak to background ratio that yields correct concentrations, and analyze San Carlos
olivine to compare the signal yielded by an assumed blank against the calculated D.L. Finally,
we apply the protocol to experimental clinopyroxene and garnet that have been grown in
equilibrium with a sulfide phase to ensure maximal uptake of S in the minerals. We validate the
recent findings that at shallow upper mantle conditions, non-negligible S may be incorporated
into dominant mantle minerals such as clinopyroxene and garnets, with mineral-melt partition
coefficients of <0.110.
2. Methods

2.1. Standard selection

A series of synthetic and natural basaltic glasses with decreasing S content were selected as primary and secondary standards with which to optimize analytical conditions for measuring trace levels of sulfur using FE-EPMA (Table 1). Although our main goal is to analyze silicate minerals, S-bearing glasses are ideal candidates for assessing the interplay of instrument conditions, due to uniform distribution of S in homogenous media and the varying concentrations that can be attained through controlled synthesis. Furthermore, because S concentrations in silicate minerals have yet to be extensively studied with other methods and no matrix-matched standards exist yet, basaltic glasses offer the closest major element profile to mafic minerals. For example, the average atomic number (Z) in our secondary standard FRND6001 is ~16.4, approaching the typical experimental clinopyroxene average Z of ~15.8 and garnet average Z of ~17.2.

Our primary standard is the Smithsonian standard NMNH 113716-1, a natural basaltic glass with a documented S content of 1200 ppm (Jarosewich et al., 1980; National Museum of Natural History, 2019). Because the protocol is developed mainly for sulfide-added samples, we calibrate the peak position to S\(^2\) at approximately 172.072 mm using a natural pyrite (FeS\(_2\)) standard. Synthetic secondary standards G669, B502, B503, and T120 were produced in the Rice University Experimental Petrology Laboratory (procedure detailed below) as nominally-anhydrous basaltic glasses doped with 180-1500 ppm S. One natural basalt is also used as a secondary standard (FRND6001), previously measured as 44 ± 1 ppm using SIMS by Lloyd et al. (2013).
2.2. Sample and standard synthesis

2.2.1. Starting mix. Synthetic glass standards were produced by mixing the BCR-1 natural basalt standard with sulfur in the form of pulverized natural pyrite to produce a range of S concentrations: 0.1 wt.% (G669), 0.05 wt.% (B503), 0.02 wt.% (B502), and 0.01 wt.% (T120).

For generating experimental mineral-melt assemblages containing sulfur, we chose a synthetic basalt composition used in literature and known to yield major upper mantle minerals clinopyroxene and garnet (Chowdhury and Dasgupta, 2019), and doped the mix with pyrite or reagent-grade FeS powder to produce low-S (0.10 wt.% S) starting mix HAB1 and high-S (6.08 wt.% S) starting mix HAB2 (Table 2).

2.2.2. Experiments. All experiments were performed using end-loaded piston cylinder apparatuses at the Rice University Experimental Petrology Laboratory, using half-inch BaCO₃ pressure medium and internal crushable MgO spacers to house the sample capsules. An outer Pb foil was used as lubricant and to contain friable assembly parts. Temperatures were monitored and controlled using Type-C (W5%Re-W26%Re) thermocouple placed within 1.5 mm of the top of the samples. The pressure and temperature calibrations of this assembly were given in Tsuno and Dasgupta (2011) and have been adopted in a number of subsequent studies including several on the synthesis of S-bearing glasses in equilibrium with sulfide or sulfate (e.g., Ding et al., 2014, 2018; Chowdhury and Dasgupta, 2019, 2020).

For the synthesis of standard glasses, the starting mix was placed in graphite capsules, heated to 1600 °C at 100 °C/minute at 1.8 GPa, and were kept for 1 h to produce a homogenous melt. For the synthesis of experimental mineral-melt assemblages, the starting mix was packed
into 2 mm deep graphite crucibles with 1.7 mm inner diameter, 3 mm height, and 3.1 mm outer

diameter. The graphite crucibles with 1 mm thick circular graphite lids were then loaded into

platinum outer capsules, which were subsequently welded shut. Outer platinum capsules were

included to minimize physical ingress of volatiles during the experiments, while the inner

graphite containers were placed to prevent iron loss to the outer Pt capsule and set the oxygen

fugacity to approximately FMQ-1.5 (Medard and Grove, 2008; Bataleva et al., 2018). Five

separate experiments were performed at $P$ and $T$ conditions reflective of the shallow upper

mantle, at 1.5 GPa/1200 °C (T124, low-S) and 1.5-3.0 GPa/1200-1300 °C (high-S experiments

T131, T154, T155, and T168), with run durations of 72 hours. All experiments were pressurized

close to the desired target pressures at room temperature and then heated at a rate of

100 °C/minute to reach the target experimental temperature. At the end of the desired duration,

the samples were rapidly cooled to room temperature by turning off power to the graphite heater

and slowly depressurized. Extracted capsules were then cut and polished to expose the resulting

phase assemblages (Fig. 1).

2.3. Sample preparation and instrument specifications

Trace element analysis requires highly polished sample surfaces, as excessive surface

topography and coating deficiencies can lead to charge buildup and fluctuations in absorbed

current that introduce significant error in the accuracy of measurements (Jercinovic et al., 2012).

Therefore, all standards and samples in this study were polished with progressively higher grit

sandpaper, and finally, 0.3 μm alumina slurry on a velvet cloth. The synthesized samples were

also impregnated with low viscosity superglue under vacuum prior to polishing, to prevent grain

pluck-outs. All standards and samples were then coated with a 25-30 nm thick layer of carbon.
Analyses were conducted at the Rice University EPMA laboratory, using a field emission JEOL JXA 8530F Hyperprobe. Voltage was set to 15 kV for all sessions, with a take-off angle of 40°, and a beam diameter of 20 µm for glasses and fully focused spots for minerals. Sulfur was measured on the PETH and PETL crystals, with the S\textsuperscript{2} peak position calibrated on pyrite and the low and high backgrounds set to -5 mm and +5 mm of the peak. The separate measurements by each crystal, as well as the combination of the two, were compared for reproduction of the primary standard NMNH 113716-1, and PETL was selected as the sole spectrometer for all subsequent analyses due to yielding lower analytical errors and D.L., and reproducing 1200 ppm S to within 1% (Table 3). Major elements were measured concurrently with sulfur (at the same beam current and accelerating voltage) with a 10 second peak counting time and 5 seconds for each background, using TAP (Si, Al, Mg, Na), PETJ (K, Ca), LIFH (Fe), and LIFL (Mn, Ti) crystals. All phases shared jadeite as the standard for Na, rhodonite for Mn, and rutile for Ti. For experimental glasses, the basaltic glass Smithsonian standard NMNH-113716-1 was used for Si, Al, Mg, and Ca, synthetic glass NMNH-117218-3 for K, and olivine for Fe. For experimental clinopyroxenes, diopside was used for Si, Ca, and Mg, olivine for Fe, biotite for K, and plagioclase for Al. Finally, for experimental garnets, almandine was used for Si, Fe, and Al, olivine for Mg, biotite for K, and plagioclase for Ca.

### 3. Results

#### 3.1. Optimized beam conditions for trace S analysis in silicate materials

In this section we assess varying beam currents and total counting times to identify the combination that produces a clearly resolved peak signal, minimal detection limit, and reduced analytical error. Furthermore, factors that can negatively affect the accuracy of EPMA
measurements of major and minor elements impart an even greater impact on trace element analyses. Here, we specifically examine the effects of background continuum, matrix corrections, beam damage, and secondary fluorescence on our protocol.

### 3.1.1. Resolution of peak signal

Successful trace element analysis on EPMA fundamentally depends on the ability to resolve X-ray emissions of a target wavelength (peak) from background emissions. Increased beam current produces more X-ray counts at both the peak and background wavelengths, and improves this resolution, expressed as $I_{\text{net}}$ in Equation 1 (JEOL, 2020):

$$I_{\text{net}} = I_{\text{peak}} \frac{I_{\text{PBH}} - I_{\text{PBL}} + I_{\text{PBL}} - I_{\text{PBH}}}{L_{\text{PBL}} + L_{\text{PBH}}}$$  

where $I_{\text{peak}}$ is the intensity of the peak position (average counts per second/beam current), $I_{\text{PBH}}$ and $I_{\text{PBL}}$ are the intensity of the backgrounds above and below the peak position, and $L_{\text{PBL}}$ and $L_{\text{PBH}}$ are the distances between the peak position and the low and high background positions. In our study, the S Kα position at an L-value of 172.072 mm is bounded by ±5 mm lower and upper offsets of background, at 167.072 mm and 177.072 mm, respectively. Our first-order goal in beam current selection, therefore, was to improve the resolution as expressed by net intensity. Peak scans at 50, 100, 150, and 200 nA (Fig. 2) demonstrated the effect of increased current in improving peak resolution for all standards. Although the improvement is not apparent from Figure 2 for the most dilute glass FRND6001 (44 ppm S), it is important to note that these peak scans were generated by continuously scanning from 171.0 mm to 173.0 mm without dwelling at any point. Therefore, Figure 2 does not capture the extended counting times at peak and background positions that produce resolvable emissions even for concentrations as low as that of
FRND6001. Background characterization and the peak resolution of FRND6001 are discussed further in section 3.1.3.

### 3.1.2. Detection limit and uncertainty

Probe current and counting time are critical not only to improving the net intensity, but also to analytical precision as expressed by D.L. and analytical error. The detection limit is calculated as a function of standard and background measurements, with the following equation (JEOL, 2020):

\[
\text{Detection limit} = \frac{\text{mass(\%)}_{\text{STD}}}{I_{\text{net STD}}} \sqrt{\frac{2 \times I_{\text{back}}}{t_{\text{back}}}}
\]

where mass(\%)_{STD} is the mass concentration of the element of interest in the standard, \(I_{\text{net STD}}\) is its net intensity as measured on the standard, \(I_{\text{back}}\) is the average intensity of background X-rays, and \(t_{\text{back}}\) is the total background counting time. The D.L. is lowered by increasing \(I_{\text{net STD}}\) and \(t_{\text{back}}\). Given a primary standard with well-established S concentration such as our primary standard Smithsonian glass NMNH 113716-1 (1200 ppm S), increasing the \(I_{\text{net STD}}\) by increasing beam current (as detailed in section 3.1.1) allows the concentration to intensity ratio to be minimized. While each background counting time is typically set to half of the peak dwell time for major element analysis, we extend the background times to 70-75% of the peak time to further lower the D.L. As an added benefit, the longer background dwell times allow for improved background characterization to resolve any interferences that may compromise the accuracy of results (Jercinovic et al., 2012).

Counting times and probe current also factor into minimizing analytical uncertainty, calculated as one standard deviation by the following equation (JEOL, 2020):

\[
S.\ D.\ (\%) = \frac{100}{I_{\text{net}}} \sqrt{\frac{I_{\text{peak}}}{t_{\text{peak}}} + \left(\frac{L_{\text{PBL}}}{L}\right)^2 \frac{I_{\text{PBL}}}{t_{\text{PBL}}} + \left(\frac{L_{\text{PBL}}}{L}\right)^2 \frac{I_{\text{PBL}}}{t_{\text{PBL}}}}
\]
where \( t_{\text{peak}} \) is the peak counting time on the sample, \( t_{PBH} \) and \( t_{PBL} \) are the counting times at high and low background positions, \( L \) is the sum of the background distances, and all other variables are as defined above. As with D.L., we lower the uncertainty by increasing beam current and background counting time, and furthermore increase the peak counting time.

To minimize D.L. and uncertainty, as well as compare the effects of beam current and counting times on these parameters, we analyzed our glass standards NMNH-113716-1 (1200 ppm S), B503 (599 ppm), T120 (183 ppm), and FRND6001 (44 ppm) at a range of conditions: beam currents of 50, 100, 150, and 200 nA, and total counting times of 200 seconds (80 s peak/60 s per background), 240 seconds (100 s peak/70 s per background), and 300 seconds (120 s peak/90 s per background). At these conditions, we observe that the primary control on D.L. is beam current (Fig. 3), approximately halving the limit from 10 ppm to 5 ppm at a total counting time of 200 seconds, while increasing the time to 300 seconds further improves the limit by only <2 ppm. Furthermore, the D.L. at a given set of conditions is identical for all secondary standards, regardless of their S content, since Equation 2 is a function of primary standard concentration and background conditions, and background intensity is roughly constant for any sample at a given beam current (Fig. 2). Analytical uncertainty is also primarily controlled by beam current, displaying a roughly exponential decrease when increasing the current from 50 to 200 nA (Fig. 4), while increased counting time for a given beam current only minimally improves the uncertainty, particularly at higher currents. For example, for the primary standard NMNH-113716-1 (1200 ppm S) at 50 nA, increasing dwell time from 200 to 300 seconds improves uncertainty by 0.4%, while the same increase at 200 nA entails a 0.1% improvement (Fig. 4a). Meanwhile, an increase from 50 to 200 nA with a total dwell time of 200 seconds enables a full 1% improvement in analytical uncertainty. This becomes much more significant
for extremely low sulfur concentrations such as FRND6001 (44 ppm S), with a >50% reduction in error by increasing beam current from 50 to 200 nA at a total counting time of 200 seconds (Fig. 4b), while longer counting times do not necessarily yield lower uncertainty for a given beam current. This is encouraging as shorter dwell times reduce instrument time and accordingly the cost of analysis.

To compare the calculated D.L. with how a “blank” signal (i.e. background continuum) may manifest, we apply the optimized beam conditions of 200 nA and 200 s total counting time to measure San Carlos olivine as an analytical blank for sulfur. Although a D.L. as low as 5 ppm is calculated by Equation 2 at these conditions, San Carlos olivine yields an apparent S concentration of 17 ± 5 ppm (Table 3; derived from 49 replicate measurements ranging from <5 to 25 ppm, averaging 47 values that exceed the calculated D.L.). We consider two possible causes for this non-zero measurement: 1) no sulfur is present (i.e. the olivine is a true “blank”), or the amount present is insufficient to resolve a peak from the background signal, so the value of 17 ± 5 ppm is an artifact of the background intensity being converted to concentration via matrix correction; 2) the olivine contains trace amounts of sulfur. In the case of 1), regardless of whether the olivine contains S, a peak cannot be resolved and therefore 17 ± 5 ppm should be selected as the D.L. over the calculated value of 5 ppm. On the other hand, the possibility of olivine containing measurable sulfur should also not be easily dismissed. While Callegaro et al. (2020) report a concentration of ≤1 ppm S in experimental olivine, Lambart et al. (2022) observe high variability of trace phosphorous in San Carlos olivine that may be attributable to metasomatism. Although sulfur is not investigated in the Lambart et al. (2022) study, it is possible that secondary processes could have produced similar variability, and 17 ± 5 ppm reflects the true sulfur content of the grains available at the Rice University EPMA lab.
However, lacking systematic and independent verification by a different *in situ* analytical technique, we have decided to consider the San Carlos olivine to be a sulfur “blank” for the purposes of our protocol, and take $17 \pm 5$ ppm to be the effective D.L. As such, sulfur values reported for all standard reproductions in Table 3 and experimental results in Table 4 are blank-corrected values, from which 17 ppm is subtracted and 5 ppm is propagated through the standard deviation.

### 3.1.3. Peak over background

Properly characterizing the background signal can be critical to clearly resolving the characteristic X-ray peaks of trace elements from the noise of the continuum. Neglecting subtleties in the background may lead to under- or over-estimating the element of interest, particularly when a peak signal is of lower magnitude than the background (Reed, 2000). Although recent studies have developed sophisticated methods of background analysis (e.g. Allaz et al., 2019), here we focus on directly observing the background and peak counts across the analytical duration (Fig. 5). For glass standard T120 with 180 ppm S, the S Kα peak is distinctly resolved from the -5 mm and +5 mm background signals (Fig. 5a). However, at 44 ppm S (FRND6001, Fig. 5b) the peak is not resolved from the low background at -5 mm, which may be a consequence of overlap with a third-order Fe Kβ peak at approximately 167 mm, or simply an effect of spectrometer geometry. To resolve such asymmetries, the JEOL software takes the average of the two backgrounds in the net intensity calculation (Equation 1). If the peak intensity is equal to or less than one of the backgrounds, the net intensity—and by extension, the concentration—will be underestimated. While this compromises the strict accuracy of our measurements at <100 ppm levels, we consider an underestimation to be acceptable as a conservative estimate. Despite this background asymmetry, we find that the
matrix- and blank-corrected concentration of FRND6001 of 36 ± 13 ppm (Table 3)—taken as an average of 20 points—to be within uncertainty of the literature value of 44 ± 1 ppm as measured by SIMS (Lloyd et al., 2013). All synthetic secondary standards (T120, B502, B503, G669) are also replicated within uncertainty of the S concentrations derived by weighing the experimental starting mixes, while our primary standard NMNH 113716-1 is reproduced to within 1% of the Smithsonian value (Fig. 6).

3.1.4. Matrix correction. The accuracy of trace element analysis also depends heavily on appropriate matrix corrections, which JEOL performs with the Armstrong method PRZ model. Ideally, the primary standard closely matches the composition of the target phase to correct for average atomic number (Z) and absorption (A) as accurately as possible. Although we use a basaltic glass primary standard in this study because S is not present in sufficiently high quantities in a silicate mineral matrix to have an exact match between standard and samples, the average Z of the glass (16.05) closely resembles that of a typical clinopyroxene (16.28), and approaches that of the experimental garnets (19.60). The integrity of the correction could be improved by synthesizing S-rich glasses with major element compositions matching clinopyroxene and garnet, to better account for the contribution of heavily fluorescing, high Z elements like Fe to the overall correction.

3.1.5. Beam damage. The benefits of high beam currents and counting times on the order of hundreds of seconds must be balanced with an increased risk for beam damage. Exposing a sample to high current densities for extended periods heats the target area and can lead to factors such as volatile loss and redox change of Fe and S in glasses (Hughes et al., 2020). Both
phenomena may lead to underestimation of the S concentration in samples, the former through loss of material, and the latter by not all X-ray emissions being collected when the peak position has changed from the specified L-value (the S$^{6+}$ of anhydrite is typically located at approximately -0.1 mm with respect to S$^{2-}$). We address these concerns by verifying the stability of the S Kα counts and the peak L-value over time.

First, we recorded the intensity of S Kα X-ray emissions (counts per second) and absorbed current (nA) throughout the dwell time on each glass standard at varying currents, to assess whether our analytical conditions cause a progressive drop in S Kα peak counts that would suggest devolatilization by beam damage. Even at the highest current of 200 nA, the count rate remains constant throughout the peak and each of the backgrounds, as indicated by the flat trend in intensity fluctuations and absorbed current recorded on the 180 ppm standard T120 (Fig. 5a) and the 44 ppm standard FRND60 (Fig. 5b). From this, we conclude that devolatilization of S is not a concern with the selected conditions.

Although the stable count intensity may be sufficient to suggest that redox change is not occurring to any significant extent, we also monitored the peak position against elapsed time for any shift to a lower L-value that would indicate beam-induced oxidation. We tested for peak shift by applying a 15 kV, 200 nA beam with 20 µm spot size to the Smithsonian standard glass NMNH 113716-1 and running a peak scan twice on a single designated point. This particular test was conducted during a different analytical session from the preceding tests, and the S$^{2-}$ peak position calibrated on pyrite was 172.122 mm instead of the aforementioned 172.072 mm. The duration of each peak scan was 400 seconds total across the L-value range of 171.1 to 173.1 mm (10 µm steps, 2000 ms per step). Approximately 1/3 of the total time, or 130 seconds of each scan is spent on the peak area, allowing a high-resolution view of the effects of prolonged beam
exposure. On the first scan, a single peak is seen at 172.065 mm (Fig. 7a), suggesting the sulfur in NMNH 113716-1 is in some intermediate redox state, more oxidized than pyrite. On the second scan, after >260 seconds spent irradiating the same spot, the morphology of the peak has changed slightly but the central peak position remains the same (Fig. 7b). We conclude that no notable redox change has occurred as a result of irradiation. Furthermore, the native Peak Scan functionality of JEOL software accounts for any variability of peak position to within ±1 mm of the calibrated position, scanning for the spot-specific peak position within this range prior to beginning the dwell time.

3.1.6. Secondary fluorescence. In contrast to beam damage, which can lead to underestimation of mobile cations and volatile elements, secondary fluorescence can cause concentrations to be overestimated. Secondary fluorescence is a phenomenon in which characteristic and continuum X-rays interact with neighboring phases that contain the target element to generate secondary signals of that element (Reed and Long, 1963; Gavrilenko et al., 2023). Given that abundant sulfides are distributed throughout the fine-grained textures of our high-S experiments (Fig. 1b), the potential effects of this phenomenon need to be carefully assessed. We used the Monte Carlo program PENEPEMA (Llovet and Salvat, 2017) to model the secondary fluorescence of S in diopside from neighboring pyrrhotite, and find that at 1 µm from the boundary with a sulfide, secondary fluorescence accounts for approximately 0.17% of the K-ratio of the S measurement; this decreases to 0.017% at a distance of 10 µm and 0.004% at 20 µm. Based on these results, we can minimize the effects of any secondary fluorescence by selecting mineral grains at least 20 µm in diameter and placing spots >10 µm away from neighboring sulfides—where visible at the surface—and calculating the final S concentration of
grains in a specific experiment by taking the average of 20 spot analyses in the target silicate phases.

3.2. Experimental results

3.2.1. Textures and phase assemblages of standards and samples. All synthesized standards have a homogenous glassy texture, lacking any zoning and sulfide phases identifiable in backscattered electron (BSE) images. Natural standard FRND6001 is glassy with some <100 µm grains of orthopyroxene and plagioclase that were avoided when setting analytical spots. The low-S experiment T124 (1.5 GPa/1200 °C) yielded an assemblage of silicate partial melt and clinopyroxene. The clinopyroxenes are situated against the capsule wall in an aggregation of <10 µm diameter grains with minimal zoning visible in BSE images (Fig. 1a). One high-S experiment, T131 (1.5 GPa/1200 °C), yielded a nearly identical assemblage of silicate partial melt and clinopyroxene, with the addition <20 µm sulfide blebs densely scattered throughout the sample. The remaining high-S experiments T154 (2.5 GPa/1250 °C), T155 (3.0 GPa/1250 °C), and T168 (3.0 GPa/1300 °C; Fig. 1b) all yielded an assemblage of silicate partial melt, clinopyroxene, garnet, and sulfide melt. Garnet and clinopyroxene were present as two interconnected layers at the bottom or cooler end of the capsule (Fig. 1b), with garnet dodecahedrons measuring 5 to 30 µm in diameter, and subhedral clinopyroxene grains with dimensions of <50 µm. Some zoning and clinopyroxene inclusions are visible in the garnets. Sulfide blebs are scattered throughout the experimental samples, and increase in size and decrease in number with increasing temperature.
3.2.2. Mineral and melt compositions from phase equilibria experiments. Table 4 provides the major element and S compositions of the experimental phases. Experimental glasses range from basalt to basaltic-andesite with SiO$_2$ in the range of ~52-58 wt.% and total alkalis (Na$_2$O + K$_2$O) of 2-3 wt.%, and FeO$^T$ ranges from ~4 to 9 wt.%. Experimental clinopyroxenes in T124, T131, T154, and T155 are classified as augite to diopside, with 44-49% Wo, 34-44% En, and 13-17% Fs. Clinopyroxene in T168 classifies as pigeonite, with an increased Al$_2$O$_3$ content (~14 wt.%) reducing the cation proportion of Ca to 12% Wo. Garnets in T131 and T154 trend toward almandine-rich compositions with 38-39% Alm, 30-35% Prp, and 28-31% Grs, while garnet in T155 is pyrope-rich with 22% Alm, 48% Prp, and 29% Grs.

3.2.3. Application of EPMA for S analysis in nominally S-free, experimental silicate minerals. Having established that glass standards with S as dilute as 44 ppm are reproducible within acceptable uncertainty and an effective D.L. of 17 ± 5 ppm can be achieved using EPMA with optimized analytical conditions of 15 kV accelerating voltage, 200 nA beam current, and 200 s total counting time, here we test our protocol by analyzing S in experimental silicate phases. Given the scarcity of data in existing literature, our aim for the analytical protocol is to produce measurements that can establish the order of magnitude of S in minerals, at a minimum, with further room for improvement in the future.

For the sulfide-undersaturated sample with low bulk sulfur content (T124), we analyzed silicate melt and coexisting clinopyroxenes. The glass S content measures 802 ± 20 ppm sulfur, with all spot analyses exceeding the D.L. and no anomalously high measurements (Table 4). Considering the 0.1 wt.% bulk S content of the starting mix and expected concentration within the melt phase through the growth of nominally S-free crystals, the reduced S content suggests
some sulfur has escaped from the capsule, likely during initial heating of the experiment. Of the 20 replicate analyses of the experimental clinopyroxene, 13 spots yield S values below the effective D.L. of 17 ppm, while three spots yield anomalously high sulfur contents of hundreds ppm, suggesting the analytical volume may have incorporated a melt zone or small quench sulfide that was not visible when setting points on the surface of the sample (Fig. 8). Discarding these datapoints, the four viable measurements yield an average S of 62 ± 24 ppm in clinopyroxene. Given the point to point heterogeneity, and upward bias introduced by discarding points below the D.L., we take this as an upper bound of S in clinopyroxene in this experiment.

For the high-S bulk composition, due to the abundance of sulfides in the experimental assemblage, analyses with anomalously high S values were excluded as they may reflect contamination from tiny sulfide globules present below the sample surface, within the excitation volume of analyses. As reported in Table 4, S contents of our sulfide-saturated experimental glasses (T131, T154, T155, T168) range from 447 ± 189 to 775 ± 71 ppm. Unlike with sulfide-undersaturated T124, all sulfur analyses in minerals exceed the D.L. Clinopyroxene S contents range from 38 ± 17 to 71 ± 35 ppm, and garnets range from 47 ± 28 to 63 ± 28 ppm. To our knowledge, this is the first sulfur content determination of garnet from a sulfide-bearing experimental assemblage.

4. Discussion

4.1. Approach to equilibrium

Our high-S experiments are conducted at sulfide saturation to allow maximum uptake of sulfur by the coexisting silicate minerals and melt, thereby establishing the S content at sulfide saturation (SCSS) or S capacity of the minerals as well as the melt. Before discussing mineral S
analyses, however, it is critical to assess how closely our experiments approached equilibrium. Approach to equilibrium for the four reported experiments can be established by the following criteria. First, our experiments were run for approximately 72 h, which is comparable to or exceeds previous experimental durations employed for melt SCSS determination at similar temperatures (e.g., Ding et al., 2014, 2018). Second, to our knowledge, sulfur diffusivity in nominally S-free minerals is undetermined. However, application of a sulfur diffusivity model for $S^2$- diffusion in hydrous basaltic to andesitic melt at sulfide saturation (Freda et al., 2005), at our experimental conditions, yields values from $2.3 \times 10^{-11}$ m$^2$/s to $4.9 \times 10^{-11}$ m$^2$/s. The application of this diffusivity range suggests that S would diffuse $\sim 3$-5 mm through melts during our experiments. Given that sulfide blebs are spaced throughout the melt pool and mineral layers at intervals of $<50 \mu$m, the entire melt volume in our experiments are expected to be equilibrated with the sulfide phase. Third, the melt S content of our sulfide-saturated experiments is in good agreement with SCSS values calculated for the relevant conditions with the Smythe et al. (2017) model (using PySulfSat, Wieser and Gleeson, 2023, overlapping within one standard deviation of calculated values (e.g. $775 \pm 71$ ppm observed, compared to $740 \pm 202$ ppm calculated, for T131; Table 4), suggesting our experiments closely approached equilibration with respect to melt sulfide capacities.

4.2. Comparison with previous studies

To assess the validity of our EPMA measurements of sulfur in nominally S-free, experimental silicate minerals, we compare both the absolute S content in silicate minerals and calculated mineral-melt partition coefficients ($D_{s^{\text{in/melt}}}$) with the SXRF results of Callegaro et al. (2020). For the most apt comparison, we select from Callegaro et al. (2020) two sulfide-saturated and
four sulfide-undersaturated experiments, all bearing clinopyroxene and run at reduced conditions
with a basaltic starting mix, equilibrated at 0.8-1.0 GPa and 1000-1240 °C. The S content of
clinopyroxene in the sulfide-saturated experiments are reported as 38 ± 11 ppm and 54 ± 22 ppm
(Callegaro et al., 2020), of which all clinopyroxenes and garnets in our sulfide-saturated
experiments are within error (Fig. 9). From this, our results agree that the SCSS of clinopyroxene
is on the order of 10^1 ppm. Additionally, consistency between the SXRF results and our sulfide-rich, high-S charges suggests that the EPMA-specific concern of secondary fluorescence does
not have a notable effect when measuring trace levels of sulfur in sulfide-saturated experimental
assemblages, provided that points are placed at least 10 µm away from any visible sulfides. At
sulfide-undersaturated conditions, Callegaro et al. (2020) record clinopyroxene S contents of 25
± 11 to 31 ± 9 ppm, which are lower than those at sulfide saturation, albeit with some
overlapping range when uncertainty is considered. In contrast, the S content of our sulfide-
undersaturated clinopyroxene is fully within range of the sulfide-saturated minerals, at <62 ± 24
ppm. We emphasize that this value is an upper limit that likely reflects an upward skew in the
averaging of replicate measurements, an artifact of most measurements falling below the D.L
(Fig. 8). The effects of heterogeneity among the replicate measurements are discussed in further
detail below.

In addition to the absolute S of minerals, we also compare the \( D_{\text{s min/melt}} \) between the two
studies, calculated as follows:

\[
D_{\text{s min/melt}} = \frac{[S]_{\text{min}}}{[S]_{\text{melt}}} = \frac{SCSS_{\text{min}}}{SCSS_{\text{melt}}} \quad (4)
\]

where \([S]_{\text{min}}\) is the mineral S content and \([S]_{\text{melt}}\) is the melt S, respectively interchangeable with
\( SCSS_{\text{min}} \) and \( SCSS_{\text{melt}} \) in sulfide-saturated experiments. For sulfide-free T124, our experimental
\( D_{\text{s cpx/melt}} \) is calculated as <0.077 ± 0.030. For our sulfide-saturated experiments, \( D_{\text{s cpx/melt}} \) ranges
from 0.052 ± 0.025 to 0.095 ± 0.064 and $D_{S}^{\text{gr/melt}}$ ranges from 0.075 ± 0.045 to 0.110 ± 0.064.

The sulfide-saturated $D_{S}^{\text{min/melt}}$ are within error of the corresponding Callegaro et al. (2020) partition coefficients of 0.069 ± 0.027 and 0.075 ± 0.034 (Fig. 9). At sulfide undersaturation, the Callegaro et al. (2020) partition coefficients range from 0.023 ± 0.010 to 0.028 ± 0.008, lower than our maximum sulfide-undersaturated $D_{S}^{\text{cpx/melt}}$ by over a standard deviation. However, again we emphasize that the $[S]_{\text{min}}$ here is an upper limit, and a lower $D_{S}^{\text{cpx/melt}}$ within range of the Callegaro et al. (2020) values would likely be obtained if the majority of S measurements could be resolved below the effective D.L. of 17 ppm. These broadly consistent results suggest that at crustal and upper mantle conditions, S is incompatible in silicate minerals with partition coefficients on the order of $10^{-2}$ to $10^{-1}$.

As reflected in the large standard deviations of the mean $SCSS_{\text{min}}$ and $D_{S}^{\text{min/melt}}$ values, the sulfur content of minerals display considerable heterogeneity from spot to spot. In the case of the low-S run, this results in 65% of the mineral spot analyses falling below the effective D.L. (Fig. 8), skewing the mean $SCSS_{\text{min}}$ and $D_{S}^{\text{min/melt}}$ toward a higher value due to omission of these datapoints. Conversely, the sulfide-saturated experiments yielded some high outliers (e.g. >300 ppm) which were discarded from the mean calculations. Such heterogeneity may be caused by incomplete equilibration in terms of sulfur in the low-S experiment, or inclusion of subsurface sulfides in the excitation volume of EPMA analyses in the high-S experiments. Alternatively, or in combination with these two causes, another factor may be nanoscale inclusions of sulfides within the silicate mineral matrix, a phenomenon observed in the natural world with sulfides in diamonds (Logvinova et al., 2010) and platinum group element-rich nanocrystals in sulfides (Wirth et al., 2013). If the observed S is hosted in such nanoinclusions rather than or in addition to being structurally bound, heterogeneity of the measurements may by correlated to the
distribution of the nanoinclusions, with a higher modal abundance and density of sulfides
increasing the probability of these being captured in the e-beam excitation volume. Although the
EPMA beam can be focused down to <0.1 µm, the resolution of the BSE image at our imaging
conditions is limited to the effective beam size of 300-350 nm; any resolvable inclusions exposed
at the surface are avoided when setting the spot, but smaller features and subsurface inclusions
cannot be avoided. Similarly, the SXRF measurements by Callegaro et al. (2020) were focused
to 6 × 6 µm, and it is unknown whether element mapping was used to assess the homogeneity of
the targeted region. However, the authors do note that the natural diopside and clinopyroxene
standards used for the SXRF analyses display heterogeneous S concentrations. Given that the S
content of these standards were determined by bulk analysis (each containing 32 ppm), it is
entirely possible the sulfur is hosted primarily in nanoinclusions that manifest as heterogeneity in
spot analysis. Considering the heterogeneity of analyses and the bias toward higher values in the
low-S experiment, we consider the $[S]_{\text{min}}$ and possibly even $SCSS_{\text{min}}$ as well as corresponding
$D_s^{\text{min/melt}}$ to be maximum values that place an upper limit on sulfur incorporation in nominally S-
free silicate minerals. Further analyses should be conducted with a higher sensitivity technique
such as NanoSIMS to assess for nanoinclusions and eliminate any effects of heterogeneity to
measure the true concentration of structurally-bound sulfur. Furthermore, if NanoSIMS confirms
the presence of sulfide nanoinclusions in silicate minerals at reduced oxygen fugacity conditions,
then this would: 1) question the interpretation of Callegaro et al. (2020) regarding S$^2$- replacing
bridging oxygen in the clinopyroxene lattice; and 2) require a correction to silicate mineral-melt
partition coefficients of sulfur. Transmission Electron Microscope (TEM) investigation may also
reveal any possible nanoinclusions of sulfides in silicate mineral phases. In summary, although
electron microprobe analysis of trace sulfur is challenging, our developed EPMA protocol will
allow S analyses down to ~17 ppm if structurally-bound S in minerals reach that level of concentration.

5. Conclusions and Implications

We have developed a method of analyzing sulfur in silicate minerals using EPMA, by calibrating optimum probe current and counting time with a series of low-S, natural and synthetic glasses. We find that with a beam current of 200 nA, peak counting time of 80 seconds, and background counting time of 60 seconds (200 second total counting time), we achieve a theoretical D.L. of 5 ppm and olivine “blank”-based effective D.L. of 17 ± 5 ppm, with analytical uncertainty of approximately 11-14%. These beam conditions are capable of reproducing the concentration of a 44 ppm S glass (measured using SIMS) to within one standard deviation at 36 ± 13 ppm. Using these optimized analytical conditions, we measure the S content of nominally S-free minerals in experimentally synthesized assemblages of clinopyroxene + glass and clinopyroxene + glass + sulfide ± garnet, reporting glass S of 447 ± 189 to 802 ± 20 ppm, clinopyroxene S of 38 ± 17 to 71 ± 35 ppm, and garnet S of 47 ± 28 to 63 ± 28 ppm. We also calculate mineral-melt partition coefficients ranging from 0.052 ± 0.025 to 0.095 ± 0.064 for $D_{cpx/melt}$ and 0.075 ± 0.045 to 0.110 ± 0.064 for $D_{gt/melt}$. Although the clinopyroxene S content and $D_{cpx/melt}$ of our sulfide-undersaturated experiment T124 falls within the range of the sulfide-saturated counterparts, we consider the sulfide-free values to be strictly an upper bound due to the limited number of viable measurements, and anticipate the true value to be considerably lower if values below the D.L. could be resolved. The clinopyroxene SCSS values closely resemble prior SXRF analyses by Callegaro et al. (2020) experimental clinopyroxenes produced under similar conditions, apparently confirming their results and validating our technique, with the potential to
significantly affect our understanding of sulfur storage in the mantle. High heterogeneity is noted in the silicate mineral S contents, which we hypothesize may be caused by insufficient diffusion of S, sulfide nanoinclusions, or some combination of the two factors. Because such nanoscale heterogeneities are not resolvable by EPMA or SXRF, we recommend that the reported storage capacity and partition coefficients are considered to be maximum values that may not necessarily reflect the presence of S by trace element substitution in silicate mineral lattices. Further work by NanoSIMS may provide better and complementary information on structurally-bound S concentration in nominally S-free minerals. Despite these sample-related challenges for silicate mineral analysis, we consider our protocol to be a robust and accessible method for the analysis of trace S in homogenous silicate phases with 10’s of ppm S.

Acknowledgments

We thank Terry Plank for providing natural glasses with previously characterized S abundances, and for useful discussions on possible challenges on S analyses. Reviews by three anonymous reviewers are gratefully appreciated. The work received support from a NASA grant 80NSSC18K0828 to RD.

References


**Figure Captions**

**Figure 1.** Backscattered electron images of our experiments. A) Low-S experiment T124, with 0.1 wt.% bulk S, was conducted at 1.5 GPa and 1200 °C and yielded two phases: silicate glass and clinopyroxene. B) High-S experiment T168, with 6.08 wt.% bulk S, was conducted at 3.0 GPa and 1300 °C and yielded four phases: glass, sulfide, clinopyroxene, and garnet. Some
clinopyroxene inclusions can be seen in the garnets. <20 μm sulfide blebs are densely

distributed, both throughout the glass and among silicate mineral grains.

**Figure 2.** Sulfur peak scans at a) 50, b) 100, c) 150, and d) 200 nA beam currents, collected on
the PETH crystal. Increased current raises both the background signal and the peak signal (at
171.072 mm), improving the net intensity or resolution of the peak signal from the background.

**Figure 3.** Sulfur detection limit vs. counting time and beam current, as measured on the primary
standard NMNH 113716-1 (1200 ppm S). Beam current exerts the primary control on lowering
the detection limit for S.

**Figure 4.** Uncertainty in analysis vs. beam current and total counting time, as measured on a)
primary standard NMNH 113716-1 (1200 ppm S) and b) secondary standard FRND6001 (44
ppm S). Each datapoint is an average of 2-3 replicate measurements. Dashed lines represent
logarithmic regression fits of each counting time series. Beam current exerts the primary control
on lowering uncertainty, with counting time only having a secondary effect.

**Figure 5.** Intensity of S signal and absorbed current vs. elapsed counting time across peak
position, low background (BG-), and high background (BG+), measured for low-S secondary
standards a) T120 (183 ppm S) and b) FRND6001 (44 ppm S). Despite a high beam current of
200 nA and extended peak counting time of 120 seconds, the intensity of the S peak remains
constant, indicating no volatile loss by irradiation. In a) the S peak is clearly resolved from the
background for T120, but in b) the peak of the more dilute FRND6001 is not clearly resolved
from the low background due to either overlap with the Fe Kβ5 peak or background asymmetry arising from spectrometer geometry.

**Figure 6.** Reproduction of primary and secondary standard measurements using EPMA. All standards are reproduced to within error of reported values (Table 3). Of particular note is the 44 ppm S standard FRND6001, measured as 36 ± 13 ppm, demonstrating reproducibility of low S contents within one standard deviation.

**Figure 7.** Sulfur peak position on primary standard NMNH 113716-1 (1200 ppm), a) before extended beam exposure, and b) after >260 seconds of irradiation. The central peak position at 172.065 mm remains unchanged, despite some fluctuation in the peak shape that is of comparable magnitude to background continuum fluctuations. Pyrite (S2-) was calibrated to 172.122 mm in this session.

**Figure 8.** Normalized frequency distribution of sulfur concentrations measured in replicate analyses of clinopyroxene in low-S experiment T124. 65% of all measurements fall below the 17 ppm detection limit, while 15% are considered to be high outliers that likely reflect the incorporation of a subsurface S-rich heterogeneities in the analytical volume. When these datapoints are discarded from calculations, only 20% of replicate measurements are considered viable. Therefore, we could only bracket an upper limit of the average S contents of nominally S-free minerals for the low-S bulk composition.
Figure 9. Sulfur contents of experimental clinopyroxene (cpx) and garnet (gt) in this study and cpx from Callegaro et al. (2020), both at sulfide-saturated (closed symbols) and sulfide-undersaturated (open symbols) conditions, plotted against the calculated mineral-melt partition coefficients of S (\(D_{s}^{\text{mineral/melt}}\)). The mineral S and \(D_{s}^{\text{cpx/melt}}\) of our sulfide-undersaturated experiment represent upper limits calculated from highly heterogeneous replicate measurements in minerals (Fig. 8), as indicated by the arrows pointing left and down. Values for our sulfide-saturated silicate minerals are within error of the corresponding Callegaro et al. (2020) values, suggesting apparent consistency of S capacity despite differing experimental conditions, and consistency between EPMA and SXRF measurements. However, it remains uncertain whether the higher mineral S contents in our high bulk-S experiments are owing to structurally-bound S, or variable proportions of sulfide micro- to nano-inclusions; therefore, these may also be maximum bounds on S capacity and \(D_{s}^{\text{mineral/melt}}\), as indicated by arrows and question marks.

### Tables

#### Table 1. Composition of basaltic glass standards

<table>
<thead>
<tr>
<th>Standard</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO&lt;sup&gt;T&lt;/sup&gt;</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G669</td>
<td>54.68(21)</td>
<td>2.15(9)</td>
<td>13.82(11)</td>
<td>12.21(25)</td>
<td>0.19(3)</td>
<td>3.70(8)</td>
<td>7.27(9)</td>
<td>3.11(8)</td>
<td>1.85(4)</td>
<td>0.37(2)</td>
<td>1560(100)</td>
</tr>
<tr>
<td>NMNH 113716-1</td>
<td>51.52(112)</td>
<td>1.3</td>
<td>15.39(100)</td>
<td>9.24(94)</td>
<td>0.17</td>
<td>8.21(101)</td>
<td>11.31(83)</td>
<td>2.48(125)</td>
<td>0.09</td>
<td>0.12</td>
<td>1200</td>
</tr>
<tr>
<td>B503</td>
<td>55.55(70)</td>
<td>2.14(5)</td>
<td>13.84(20)</td>
<td>11.78(15)</td>
<td>0.19(4)</td>
<td>3.82(8)</td>
<td>6.90(10)</td>
<td>2.68(52)</td>
<td>1.78(6)</td>
<td>0.33(4)</td>
<td>600(40)</td>
</tr>
<tr>
<td>B502</td>
<td>55.55(68)</td>
<td>2.21(10)</td>
<td>13.30(15)</td>
<td>11.99(21)</td>
<td>0.18(3)</td>
<td>3.64(15)</td>
<td>7.05(13)</td>
<td>3.02(16)</td>
<td>1.75(4)</td>
<td>0.33(2)</td>
<td>300(30)</td>
</tr>
<tr>
<td>T120</td>
<td>55.38(40)</td>
<td>2.19(6)</td>
<td>12.87(15)</td>
<td>12.15(34)</td>
<td>0.19(2)</td>
<td>3.65(28)</td>
<td>7.03(12)</td>
<td>3.20(7)</td>
<td>1.79(4)</td>
<td>0.35(1)</td>
<td>180(20)</td>
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<tr>
<td>FRND6001</td>
<td>55.06(9)</td>
<td>0.46(2)</td>
<td>13.33(1)</td>
<td>8.60(4)</td>
<td>0.14(1)</td>
<td>6.37(9)</td>
<td>11.23(7)</td>
<td>1.61(4)</td>
<td>0.45(1)</td>
<td>0.09(2)</td>
<td>44(1)</td>
</tr>
</tbody>
</table>

Major oxides are in weight percent, while sulfur content is given in ppm by weight. FeO<sup>T</sup> indicates total iron content. Uncertainties are given as 1σ where available, with the last significant digit(s) reported in parentheses. For example, 54.68(21) should be read as 54.68 ± 0.21 ppm. NMNH 113716-1 is as reported by Smithsonian (National Museum of Natural History, 2019), measured by Jarosewich et al. (1980) using “classical methods” for major
elements (uncertainty only provided where available), while in-house secondary standards G669, B503, B502, and T120 are as measured using EPMA, and FRND6001 is as measured by Lloyd et al. (2013) using EPMA for major elements and SIMS for sulfur.

Table 2. Experimental starting compositions

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeOᵀ</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>S</th>
<th>Total</th>
<th>H₂O</th>
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<tr>
<td>HAB1</td>
<td>47.87</td>
<td>0.75</td>
<td>17.95</td>
<td>9.82</td>
<td>0.20</td>
<td>5.99</td>
<td>10.97</td>
<td>0.50</td>
<td>0.10</td>
<td>96.14</td>
<td>3.86</td>
<td></td>
</tr>
<tr>
<td>HAB2</td>
<td>39.96</td>
<td>0.62</td>
<td>14.99</td>
<td>18.71</td>
<td>0.17</td>
<td>5.00</td>
<td>9.16</td>
<td>1.67</td>
<td>0.42</td>
<td>6.08</td>
<td>96.78</td>
<td>3.22</td>
</tr>
</tbody>
</table>

All values are reported in weight percent, as weighed during mixing. FeOᵀ indicates total Fe content. Sulfur was introduced to HAB1 as pyrite (FeS₂) powder, and to HAB2 as reagent-grade FeS powder. H₂O content is calculated as the deficiency from the sum of oxides.

Table 3. Major element oxide and sulfur concentrations of standards measured using EPMA

<table>
<thead>
<tr>
<th>Standard</th>
<th>N</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeOᵀ</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>S (ppm)</th>
<th>Total</th>
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<tr>
<td>G669</td>
<td>18</td>
<td>54.61(48)</td>
<td>2.14(6)</td>
<td>13.56(45)</td>
<td>12.06(21)</td>
<td>0.18(2)</td>
<td>3.52(9)</td>
<td>7.04(13)</td>
<td>3.15(5)</td>
<td>2.06(22)</td>
<td>1482(46)</td>
<td>98.32</td>
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<tr>
<td>NMNH 113716-1</td>
<td>20</td>
<td>51.61(31)</td>
<td>1.30(4)</td>
<td>15.39(42)</td>
<td>8.91(33)</td>
<td>0.17(1)</td>
<td>8.19(17)</td>
<td>11.43(17)</td>
<td>2.58(9)</td>
<td>0.08(1)</td>
<td>1193(52)</td>
<td>99.66</td>
</tr>
<tr>
<td>B503</td>
<td>21</td>
<td>54.58(53)</td>
<td>2.19(3)</td>
<td>13.29(42)</td>
<td>12.06(16)</td>
<td>0.19(1)</td>
<td>3.63(10)</td>
<td>7.02(7)</td>
<td>3.08(5)</td>
<td>1.90(5)</td>
<td>611(32)</td>
<td>97.95</td>
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<tr>
<td>B502</td>
<td>14</td>
<td>54.91(40)</td>
<td>2.19(8)</td>
<td>13.65(65)</td>
<td>11.92(34)</td>
<td>0.19(1)</td>
<td>3.57(9)</td>
<td>7.06(6)</td>
<td>3.17(6)</td>
<td>2.20(20)</td>
<td>253(28)</td>
<td>98.86</td>
</tr>
<tr>
<td>T120</td>
<td>21</td>
<td>54.17(20)</td>
<td>2.17(3)</td>
<td>13.04(35)</td>
<td>11.80(44)</td>
<td>0.19(1)</td>
<td>4.23(34)</td>
<td>6.94(17)</td>
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<td>San Carlos olivine</td>
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<td>BDL-</td>
<td>0.04(1)</td>
<td>9.70(7)</td>
<td>0.14(1)</td>
<td>48.26(50)</td>
<td>0.09(1)</td>
<td>0.01(0)</td>
<td>BDL-</td>
<td>17(5)</td>
<td>99.13</td>
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</table>

Major oxides are in weight percent, while S content is given in ppm by weight. FeOᵀ indicates total Fe content. Uncertainties are given as 1σ where available, with the last significant digit(s) reported in parentheses. For example, 54.61 ± 0.48 wt.% is reported as 54.61(48). Sulfur concentrations are reported with the San Carlos olivine S value of 17 ± 5 ppm subtracted and the uncertainty propagated.

Table 4. Compositions of experimental phases determined using EPMA
<table>
<thead>
<tr>
<th>Run#</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>Phase</th>
<th>n</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO⁺</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Total</th>
<th>H₂O</th>
<th>S (ppm)</th>
<th>D²Hmix</th>
<th>Model SCSS</th>
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<td>T124</td>
<td>1.5</td>
<td>1200</td>
<td>gl</td>
<td>15</td>
<td>52.47(24)</td>
<td>8.58(9)</td>
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<td>4.77(5)</td>
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<td>0.17(4)</td>
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<td>100.59</td>
<td>71(35)</td>
<td>0.09(2)(46)</td>
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<td>0.075(45)</td>
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</tr>
</tbody>
</table>

Major oxides are in weight percent, while S content is given in ppm by weight. FeO⁺ indicates total Fe content. Uncertainties are given as 1σ where available, with the last significant digit(s) reported in parentheses. For example, 52.47 ± 0.24 wt.% is reported as 52.47(24). Sulfur concentrations are reported with the San Carlos olivine S value of 17 ± 5 ppm subtracted and the uncertainty propagated. Experiment T124 uses low-S starting mix HAB1 and is sulfide-undersaturated, while T131, T154, T155, and T168 are sulfide-saturated, using high-S starting mix HAB2. 15 spots were set for all glass phases and 20 for minerals, with n representing the actual number of replicate analyses used to calculate mean composition once anomalously high and below the D.L. values of sulfur were omitted. Melt H₂O (wt.%) is calculated as the deficit in total cations, to add up to a sum of 100%. Model SCSS is calculated with the Smythe et al. (2017) model, using the PySulfSat program (Wieser and Gleeson, 2023).

Figures
Figure 1

(a) graphite capsule

(b) clinopyroxene

Figure 1
Figure 2

![Graph showing data for different currents (50 nA, 100 nA, 150 nA, 200 nA) with various sample identifiers and counts vs. L-value (mm).]

- a: 50 nA
  - G669 (1560 ± 100 ppm)
  - NMNH 113716-1 (1200 ppm)
  - B503 (600 ± 40 ppm)

- b: 100 nA
  - B502 (300 ± 30 ppm)
  - T120 (180 ± 20 ppm)
  - FRND6001 (44 ± 1 ppm)

Figure 3
**Figure 4**

**Figure 5**
Figure 6
Figure 7
Figure 8

Normalized frequency vs. S (ppm)

Above effective detection limit

Figure 9

$D_{\text{mineral/melt}}$ vs. Mineral S (ppm)

This study
- cpx
- gt
Callegaro et al. (2020)
- cpx