

The thermodynamic controls on sulfide saturation in silicate melts with application to Ocean Floor Basalts.

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Abstract

A thermodynamic model to calculate the “Sulfide Content at Sulfide Saturation” or SCSS of basaltic and intermediate composition silicate melts has been built from four independently measurable thermodynamic entities, namely the standard state Gibbs free energy of the saturation reaction, the “sulfide capacity”, and the activities of FeO in the silicate melt and of FeS in the coexisting sulfide:

$$\ln [S^{2-}]_{SCSS} = \Delta G_{FeO-FeS}^o / RT + \ln C_{S^{2-}} - \ln a_{FeO}^{sil\ melt} + \ln a_{FeS}^{sulf}$$

The model was calibrated for silicate melts of basic and intermediate composition from published experimental results as a function of temperature, silicate melt composition, and sulfide matte composition in the system Fe-Ni-Cu-S-O at 1 bar. The likely effects of pressure and H₂O content on SCSS were included in an exploratory way. The model was tuned against the large dataset of S

27 contents in OFB glasses of Jenner and O'Neill (2012), giving it a precision comparable to that of
28 the S analyses themselves, which is $\sim 5\%$. All but 3% the OFB glasses were found to be sulfide
29 saturated within uncertainty; these 3% have lost S by devolatilization, revealed by their low S/Se.
30 Applying the model to other OFB datasets suggests sulfide saturation is ubiquitous, including
31 olivine-hosted melt inclusions proposed previously to be sulfide undersaturated. The sulfur fugacity
32 (fS_2) of undegassed Ocean Floor Basalts varies proportionally to fO_2 , with $\log_{10}fS_2$ typically within
33 the range -0.6 to +0.4.

34

35 **1. Introduction**

36 In the Earth sciences, quantifying the thermochemistry of sulfur dissolved in magmatic silicate
37 melts is needed for understanding the behaviour of chalcophile elements during partial melting and
38 magmatic differentiation, sulfur degassing from volcanic eruptions, core formation in the early solar
39 system, and for modelling the petrogenesis of many kinds of magmatic ore deposits. Meanwhile, in
40 the technologically directed applied sciences, the thermochemical description of sulfur dissolved in
41 the oxide-silicate melts found as slags or fluxes is needed wherever this element is present, one
42 important application being the desulfurization of steel (e.g., Schrama et al. 2017). Accordingly, the
43 thermochemistry of S in silicate melts has received considerable technological attention. While the
44 fundamental principles are obviously of mutual interest, there are aspects to the understanding of S
45 in silicate melts in the geological context that are irrelevant to technological applications, and vice
46 versa. In the technological sector, the compositional space encompassing silicate melts of practical
47 interest is vast, as well shown by the list assembled by Kang and Pelton (2009) of silicate (and
48 aluminate) melts whose “sulfide capacity” (defined below) has been determined experimentally.
49 Yet this dataset includes hardly any realistic magmatic silicate melt compositions. These tend to be
50 richer in SiO_2 (> 40 wt%), with a limited range of alumina contents, and atomic Si/Al between 2.5
51 and 4.5. Metallurgical slags are often either almost free of alumina, or alternatively have high Al/Si
52 beyond the range found in nature. Natural magmas have modest but non-negligible alkali contents,

53 with most plotting on the standard total alkali-silica diagram used for rock classification
54 ($\text{Na}_2\text{O}+\text{K}_2\text{O}$ vs. SiO_2) between 2 and 10 wt% ($\text{Na}_2\text{O}+\text{K}_2\text{O}$), whereas metallurgical slags either have
55 negligible alkalis (e.g., most steel-making slags), or, elsewhere, Na_2O as the main or even sole
56 basic-oxide constituent (e.g., Chan and Fruehan 1986, 1988). In terms of melt structure, most
57 magmatic melt compositions have NBO/T, the ratio of non-bridging oxygens to tetrahedrally
58 coordinated cations, between 0 and 1.5, whereas few of the compositions listed by Kang and Pelton
59 (2009) have $\text{NBO/T} < 2$. “Water” (H as H_2O) is a major component in many magmas, but is almost
60 absent in slags, because the dissolution of more than trace amounts of H_2O in silicate melts requires
61 geological pressures. And of course such pressures are not relevant to metallurgical processes,
62 which generally occur not far from atmospheric pressure.

63 There is a further difference. The technologist needs to predict S solubility in a slag perhaps to a
64 factor of two or so, but over the vast range of slag compositions mentioned above. For example,
65 they may need to know how much lime should be added to a slag to reduce S in the steel by a factor
66 of, say, five. To the petrologist, the precision with which sulfide solubilities need to be known is far
67 greater, albeit only within a relatively narrow range of melt compositions. For example, among
68 Ocean Floor Basalts, almost the entire range of recovered glass samples analysed for S fall within a
69 factor of three (Jenner and O’Neill 2012), so predicting S solubilities to a factor of two would be
70 useless. From the perspective of basalt petrology, the aspirational target is to predict the “Sulfide
71 Content at Sulfide Saturation”, or SCSS, which is how much S dissolved as S^{2-} there is in a silicate
72 melt in equilibrium with a sulfide phase, to somewhere approaching the analytical accuracy to
73 which S contents can be measured. In basaltic glasses, this appears to be at about $\pm 5\%$. Formidable
74 though this challenge may seem, the theme of this review is that it can now be met, thanks to the
75 efforts of many experimental petrologists over the last few decades.

76 The equilibrium that describes SCSS is:



79 As emphasised by O'Neill and Mavrogenes (2002), this equilibrium can be deconstructed into four
80 thermodynamic entities: 1) the standard-state free energy of the reaction, which is a function of
81 temperature and pressure alone; 2) the “sulfide capacity” of the melt; 3) the activity of FeO in the
82 silicate melt; and 4) the activity of FeS in the coexisting sulfide (often molten, when it is
83 appropriately called a matte). Entities 2), 3) and 4) are dependent on composition as well as
84 temperature and pressure. In principle, each one of these entities can be measured experimentally,
85 and independently of each other. In practice there are experimental limitations, but at least at
86 atmospheric pressure all four items have indeed been measured independently of each other. The
87 standard state free energy and activities of FeO in silicate melts and FeS in sulfide mattes are
88 familiar thermodynamic quantities, but the “sulfide capacity” of a silicate melt is not, which has
89 caused some confusion as to its nature, leading to uncertainty as to how it may depend on melt
90 composition. Its relationship with other potentially useful thermodynamic properties of silicate
91 melts, for example their “carbonate capacity” has also been underappreciated.

92

93 **Sulfide Capacity**

94 One area in which the technological sciences provided guidance was in establishing the notion
95 of the “sulfide capacity”, denoted $C_{S^{2-}}$ (Fincham and Richardson 1954). These authors studied the
96 solubility of S in some simple-system silicate melts (and one aluminate melt) in equilibrium with
97 SO_2 - H_2 - CO_2 - N_2 gas mixtures, which were used to control the fugacities of sulfur and oxygen (f_{S_2}
98 and f_{O_2}). While they mention steelmaking as an application of their work, they emphasized that
99 their goal was a broader understanding of silicate melt thermochemistry. They noted that “Previous
100 attempts to elucidate the chemistry of sulphur in molten silicates (e.g., Grant and Chipman 1946)
101 have been based on the measurements of the equilibrium distribution of sulphur between complex
102 slags and molten iron. Although a considerable amount of quantitative information has been
103 amassed, the results are too complicated to permit the development of a clear picture from them.” If
104 this is a reasonable view from within the restricted context of steelmaking, how much more so is it

105 for geological processes? Their call for some judicious reductionism has much influenced the
 106 approach of this present review.

107 Fincham and Richardson (1954) found that, while keeping other compositional parameters and
 108 temperature constant, the sulfur concentration in the melt changed proportionally to $(fS_2)^{1/2}$, when
 109 fO_2 was low as well as constant. Likewise, when keeping fS_2 constant, they found that S
 110 concentrations changed proportionally to $(fO_2)^{-1/2}$. These observations implied that S was dissolving
 111 only as the sulfide species, S^{2-} , and did so by replacing O^{2-} . This has sometimes been summarized
 112 by writing the reaction:

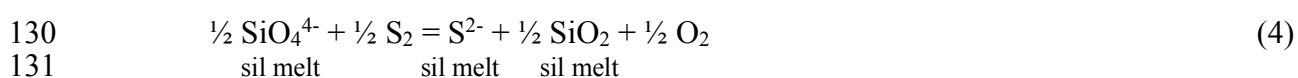


115 There is no implication that O^{2-} is an abundant species in the silicate melt, which it is not in the
 116 compositional space of natural magmas (Mysen and Richet 2005). Rather, O^{2-} should be viewed as
 117 a “structural element”, by analogy with vacancies or interstitials in the point-defect thermodynamics
 118 of crystals (e.g., Schmalzried 1995). In this formalism, the “structural elements” are treated like
 119 thermodynamic components, with chemical potentials that vary monotonically with the logarithms
 120 of their concentrations. Whether structural elements can actually have definable chemical potentials
 121 is a moot point, but this is the hypothesis. It follows from this hypothesis that a quantity resembling
 122 an equilibrium constant may be written for reaction (2), namely $[S^{2-}]/[O^{2-}](fO_2/fS_2)^{1/2}$, where the
 123 square brackets denote concentration. It is then assumed that $[O^{2-}]$ is unaffected by $[S^{2-}]$, at least for
 124 small amounts of S^{2-} to the melt, which motivates the definition of the sulfide capacity of the melt
 125 ($C_{S^{2-}}$) as the constant of proportionality between $[S^{2-}]$ and $(fO_2/fS_2)^{1/2}$:

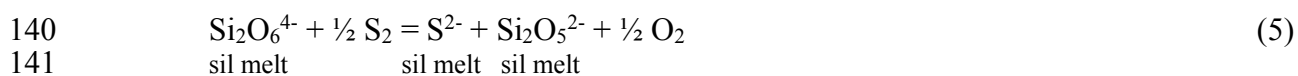
$$126 \quad C_{S^{2-}} = [S^{2-}](fO_2/fS_2)^{1/2} \quad (3)$$

127 where $[S^{2-}]$ is the sulfur content of the melt in any convenient units, like parts per million by weight.

128 O'Neill and Mavrogenes (2002) pointed out that an analogous reaction could be written using
 129 orthosilicate and framework structural units of the type actually found in silicate melts:



132 This reaction has the same dependence on $(fO_2/fS_2)^{1/2}$, also has two “structural elements” (S^{2-} and
 133 SiO_4^{4-}), and in addition one definable thermodynamic component (SiO_2). In principle, reactions that
 134 conform even more closely to silicate melt structure could be formulated. According to Mysen
 135 (1983) “three-dimensional network units are the most common in natural magmatic liquids. These
 136 units will also contain most of the aluminum. Consequently, the anionic structure of anhydrous
 137 magmatic liquids at or near 1 atm pressure may be described as a combination of nearly pure
 138 $Si_2O_6^{4-}$ (NBO/Si = 2) and $Si_2O_5^{2-}$ (NBO/Si = 1) units, together with three-dimensional units in
 139 which the aluminum is located”. This insight suggests the reaction:



142 All these ways of representing the relationship between fS_2 , fO_2 and the S^{2-} concentration of the
 143 silicate melt, denoted here as $[S^{2-}]$, come to the same thing, namely $[S^{2-}]$ is proportional to
 144 $(fS_2/fO_2)^{1/2}$, provided that $[S^{2-}]$ is sufficiently low that it does not noticeably perturb the
 145 concentrations of the other structural elements in the reactions (i.e., O^{2-} , SiO_4^{2-} , etcetera). In the case
 146 of reaction (4) this implies that $[S^{2-}]$ is too low to affect the ratio $[Si_2O_5^{2-}]/[Si_2O_6^{4-}]$. The
 147 proportionality between $[S^{2-}]$ and $(fS_2/fO_2)^{1/2}$ is critical; the concept of a sulfide capacity would not
 148 be of much use if this proportionality did not hold.

149 Fincham and Richardson (1954) went on to show that at high oxygen fugacity (obtained with
 150 SO_2 - O_2 gas mixes) the proportionality changed, from which they inferred that S was dissolving as
 151 sulfate (SO_4^{2-}), hence the definition of the sulfate capacity $C_{SO_4^{2-}}$:

$$152 \quad C_{SO_4^{2-}} = [SO_4^{2-}](fS_2)^{-1/2}(fO_2)^{-3/2} \quad (6)$$

153 At intermediate fO_2 the levels of S dissolving in the silicate melts dropped below detection
 154 limits, implying that S in oxidation states between 2- (in S^{2-}) and 6+ (in SO_4^{2-}) in the melt are
 155 unimportant. This precludes a significant role for S dissolving as S^{4+} , or sulfite (SO_3^{2-}) in silicate
 156 melts at atmospheric pressure. Whether S^{4+} may play a role at higher pressure, where it is physically
 157 possible for pSO_2 to reach values very much greater than 1 bar, remains a grey area – see Métrich et
 158 al. (2009) and the discussion on S X-ray spectroscopy below. The fact that their S solubility data

159 could be fitted to the two relationships (1) and (2) only also meant that experimentally detectable
160 roles could be precluded for S dissolved in silicate melts as elemental S, other molecular S species
161 (e.g., S₂), polysulfide species (e.g., S₃⁻), or thiosulfite, thiosulfate, and so on.

162 The range of melt compositions investigated by Fincham and Richardson (1954) was limited,
163 and they were unable to obtain reproducible results on their Fe-containing composition. They also
164 only looked at a limited range of temperatures. The task of exploring the extent of the
165 compositional space, T and fO₂ over which the Fincham-Richardson sulfide and sulfate solubility
166 laws hold was left for subsequent experimental investigation.

167 The first attempt to test the Fincham-Richardson relationship on a geologically relevant
168 composition (a komatiite) was by Shima and Naldrett (1975), using fS₂ from 10⁻⁴ to 10^{-1.4} bars and
169 just two different fO₂s at 1450°C. They confirmed that [S] ∝ (fS₂)^{1/2} at both fO₂s, but the
170 proportionality between the two fO₂s was only to the power of 0.4, so the relationship looked to fail
171 that part of the test. An even more emphatic lack of agreement was reported later (Buchanan et al.
172 1983). O'Neill and Mavrogenes (2002) then tested twelve Fe-free compositions in the system CaO-
173 MgO-Al₂O₃-SiO₂ over as wide a range of both fO₂ and fS₂ as their experimental method allowed,
174 but only at one temperature, 1400°C. The low fO₂ and high fS₂ limits were set by the CO₂-CO-SO₂
175 gas mixes that they used, and the requirement that the partial pressures of all three gases sum to 1
176 bar. (This combination of input gases does not go to as low fO₂ as the CO₂-H₂-SO₂ mixes of
177 Fincham and Richardson 1954, but has the experimental advantage that achieving the equilibrium
178 gas-phase speciation from the input gas is faster, and there is less susceptibility to thermal
179 segregation in the temperature gradients of conventional gas-mixing muffle furnaces). The high fO₂
180 and low fS₂ limits were set by the dissolved S falling below the limit of quantification feasible with
181 the electron microprobe. Contrary to the earlier studies, it was found that the Fincham-Richardson
182 relationship was followed within experimental uncertainty. O'Neill and Mavrogenes (2002) also
183 tested six Fe-containing compositions, and here again the results showed agreement with the
184 Fincham-Richardson hypothesis within experimental uncertainty. The fO₂-fS₂ range that could be

185 accessed experimentally while keeping melt composition constant was not as great as for the Fe-
186 free compositions, because the melt compositions lost some of their FeO towards lower fO_2 and/or
187 higher fS_2 , due to exsolution of FeS-rich sulfide melt. Provided the Fincham-Richardson relation
188 can be assumed to hold, this is not disadvantageous, because it throws valuable experimental light
189 on the relationship between $C_{S^{2-}}$ and melt composition (see next section).

190 All the compositions examined by O'Neill and Mavrogenes (2002) to test the Fincham-
191 Richardson relationship were broadly similar in terms of melt descriptors like optical basicity or
192 NBO/T (Non-Bridging Oxygens to Tetrahedral cations) to natural basalts, *sensu latissimo*, with
193 NBO/T from just above 0 to less than 2. Quantifying solubilities of S as S^{2-} in “acidic” melts with
194 NBO/T ~ 0 was not possible because the solubilities of S in such melts are so low under the
195 experimentally accessible conditions of fO_2 and fS_2 in gas-mixing experiments at atmospheric
196 pressure that adequately precise results cannot be obtained with the electron microprobe. At present
197 there are no unambiguous tests of the Fincham-Richardson relationship for such melts, but this
198 would be feasible with the much better limits of detection afforded by SIMS (< 1 ppm S according to
199 Hauri et al. 2002).

200 There are currently few published experiments against which to test the Fincham-Richardson
201 relationship for sulfate solubilities (Eqn. 2). An exception is the study of Holmquist (1966), who
202 verified that the relationship of Eqn. (5) generally held well in Na_2O-SiO_2 melts at $1150 - 1250^\circ C$,
203 except at very high concentrations, above several weight percent S. Results mentioned in abstract
204 (O'Neill and Mavrogenes 2019) confirm the relationship for a wide variety of more magmatically
205 relevant silicate melt compositions.

206

207 *The experimental sulfur solubility minimum*

208 One of the main ways that Fincham and Richardson (1954) chose to present their experimental
209 results has subsequently proved unfortunate. The problem that Fincham and Richardson faced was
210 how to display the way that the total amount of S dissolved in a silicate melt changes with fO_2 in

211 going from the sulfide-dominated to the sulfate-dominated regions of fO_2 . Clearly connecting the
212 two variables of dissolved S and fO_2 cannot be addressed without taking into account what a third
213 variable, most lucidly fS_2 , is doing (Eqns. 2 and 5). Illustrating their results under the specification
214 that fS_2 be kept constant was not a practical option for Fincham and Richardson, because to obtain
215 measurable S as S^{2-} in the sulfide field they needed fS_2 to be in the region of 10^{-4} bars, whereas to
216 get measurable S as SO_4^{2-} in the sulfate field, fS_2 needed to be $< 10^{-10}$ bars (depending on
217 temperature). This low fS_2 stems from the requirement for high fO_2 . So the quantity that they kept
218 constant for their plots of $[\Sigma S]$ versus $\log fO_2$ was the concentration of SO_2 in their input gas mix,
219 which was either 1% or 2%. Note, this is in the input gas mix, and is not the SO_2 concentration in
220 the gas at equilibrium in the experiments. The resulting plots showed a V-shaped dependence of
221 dissolved S on $\log fO_2$. This same representation was subsequently used by Katsura and Nagashima
222 (1974). Such a variable has no meaning outside the laboratory: for example, nature is not known to
223 meter vapour composed of unequilibrated gas species into magma chambers. Nor is the input gas
224 composition relevant to experiments that do not use gas mixing, such as those under pressure. But
225 somehow the idea that there is a minimum in the solubility of sulfur in silicate melts as a function of
226 oxygen fugacity crept into popular culture. This myth has no substance. Unless a third variable is
227 specified, such as fS_2 (or fSO_2), or the presence and composition of a saturating phase (like a sulfide
228 matte), nothing can be said about the relationship between the two variables of S content and fO_2 . In
229 nature, silicate melts with redox speciations towards the reduced end of the terrestrial spectrum, like
230 Ocean Floor basalts, have FeS-rich sulfide matte as their saturating phase, whereas the relevant
231 saturating phase under oxidizing conditions, as for some convergent margin magmatism, might be
232 anhydrite (e.g., Luhr 2008). There is no continuity in the chemical potentials of sulfur-containing
233 components between the two phases (that is, sulfide matte and anhydrite), hence S contents at phase
234 saturation cannot be conceived as a continuous function of fO_2 between such conditions.

235

236 **The thermodynamic meaning of the sulfide capacity**

237 One way of interpreting the capacities $C_{S^{2-}}$ and $C_{SO_4^{2-}}$ is as the phenomenological constants of
 238 proportionality in the relationships of (2) and (5), as established by experiment. The experiments
 239 also show that the capacities vary with the major-element composition of the silicate melt, and
 240 temperature. To get a better understanding of these dependences, particularly the functional form of
 241 the dependence on melt composition, it is necessary to look beyond the phenomenology, into the
 242 thermodynamic foundations. The principle should be the same for both $C_{S^{2-}}$ and $C_{SO_4^{2-}}$ (and indeed
 243 for other similar possible “capacities”, see Wagner 1975); here they will be addressed for $C_{S^{2-}}$.

244 Haughton et al. (1974) suggested that the sulfide capacities measured in their experiments at
 245 1200°C and atmospheric pressure using CO-CO₂-SO₂ gas mixtures could be fitted to an equation
 246 with the form:

$$247 \quad \ln C_{S^{2-}} = A_0^{S^{2-}} + \sum X_M A_M^{S^{2-}} \quad (7)$$

248 The justification for this for was supplied later by O’Neill and Mavrogenes (2002) from the
 249 theory of reciprocal solutions. The thermodynamics of such solutions with mixing on two (or more)
 250 sublattices is a well-trod path in physical chemistry (e.g., Flood et al. 1954), and has long been the
 251 common choice in the thermochemical modelling of slags (e.g., Hillert 1998, 2001). Indeed, it
 252 forms the basis of most currently used models for calculating $C_{S^{2-}}$ in metallurgical contexts (e.g.,
 253 Reddy and Blander 1987; Pelton et al. 1993; Kang and Pelton 2009).

254 In these multicomponent ionic solutions, cations mix on one sublattice, anions on the other.
 255 Consider the simplest case, the solution $(A^{x+}, B^{x+})(X^{x-}, Y^{x-})$. There exist four end-member
 256 compositions, AX, BX, AY and BY, which together define the limits of the free-energy surface in
 257 compositional space, to which all the other contributions to the free energy of the solution are
 258 additional, including that from the configurational entropy. The existence of such a free energy
 259 surface is not dependent on details of melt structure; it is more fundamental, depending only on the
 260 uncontested assumption of charge balance between electropositive elements forming cations (A and
 261 B) and electronegative elements forming anions (X and Y). With this assumption, individual ions

262 (A^{x+} etc.) and $A^{x+}B^{x+}$ or $X^{x-}Y^{x-}$ are disregarded as thermodynamic components, because they cannot
 263 be independently varied.

264 The total free energy of the solution may be visualized as being built up from this surface in
 265 multicomponent hyperspace by adding the other types of free energies, of which that contributed by
 266 the configurational entropy of mixing on each sublattice is fundamental. The free energy of the
 267 solution must consist of these two contributions at least; others may or may not be important. These
 268 others, collated here under the term “the excess free energy of mixing” include heats of mixing and
 269 deviations in the entropies of mixing from whatever model is used for the configurational entropy.
 270 The total free energy is therefore given by $G_{melt} = G_{end-members}^o + G_{config} + G_{excess}$.

271 Assuming that a silicate melt consists of cation and anion sublattices, the three contributions are
 272 evaluated as follows:

273 1) $G_{end-members}^o$ is the sum of the free energies of the pure end-member components,
 274 weighted according to the mole fractions of these components. When normalized to the
 275 single-anion basis, these components have the general formula $M_{x/z}X$, where M is a cation
 276 of valence z, and X are anions of valence x. The fundamental assumption of the reciprocal
 277 solution theory is that all possible components that fulfill the criterion of charge balance
 278 are present, such that:

$$279 \quad G_{end-members}^o = \sum_{M,X} X_M^{cat} X_X^{an} \mu_{M_{x/z}X}^o \quad (8)$$

280 Here X_M^{cat} is the mole fraction of M^{z+} cations on the cation sublattice, and likewise X_X^{an}
 281 is the mole fraction of X^{x-} anions on the anion sublattice. Note that $\sum_M X_M^{cat} = \sum_X X_X^{an} =$
 282 $\sum_{M,X} X_M^{cat} X_X^{an} = 1$. The notation for chemical potential (μ) is used rather than Gibbs free
 283 energies for convenience, including avoiding the need to define a reference state, but may
 284 be understood to be equivalent in practice (the reference state always cancel out across a
 285 balanced chemical reaction). The important point is that the standard state free energy,
 286 $\mu_{M_{x/z}X}^o$, of every possible stoichiometric component $M^{z/2}X$ enters into the model. To take
 287 an example relevant to the present discussion, the chemical potential of FeS in a

multicomponent silicate melt (μ_{FeS}) ineluctably implies something about the value of, say, $\mu_{Na_2S}^o$, unless there is no Na in the melt. The standard-state chemical potential of each possible end-member, $\mu_{M_{x/z}X}^o$, contributes to $G_{end-members}^o$ proportionally to its statistical weight, $X_M^{cat} X_X^{an}$. The logic of this is best understood by noting that the chemical potential of each and every charge-balanced component $M_{x/z}X$ can be in principle evaluated ($\mu_{M_{x/z}X} \equiv \partial G_{melt} / \partial n_{M_{x/z}X}$), and by definition $\mu_{M_{x/z}X} = \mu_{M_{x/z}X}^o + RT \ln a_{M_{x/z}X}$, therefore the free energy of the solution contains information on $\mu_{M_{x/z}X}^o$ for each and every $M_{x/z}X$, so long as some M and some X are present.

2) G_{config} is the ideal configurational entropy that accrues from mixing of cations and anions separately on each sublattice. The usual model is:

$$G_{config} = -RT[\sum_M n X_M^{cat} \ln(X_M^{cat}) + \sum_X X_X^{an} \ln(X_X^{an})] \quad (9)$$

here n_{cat} and n_{an} are the fraction of sites available for mixing of the cations and anions respectively.

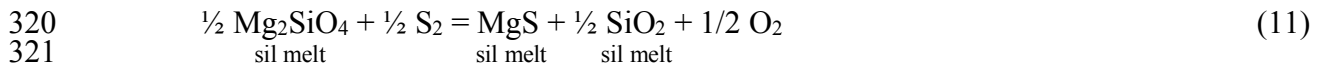
3) G_{excess} is the excess free energies of mixing, which accounts for heats of mixing, deviations from the ideal configurational free energy of mixing, and the free energy from any non-configurational entropy of mixing. G_{excess} is conventionally expressed using activity coefficients for cations and anions separately on each sublattice (γ_M^{cat} and γ_X^{an}), by analogy with the configurational free energy:

$$G_{ex} = -RT[\sum_M X_M^{cat} \ln(\gamma_M^{cat}) + \sum_X X_X^{an} \ln(\gamma_X^{an})] \quad (10)$$

O'Neill and Mavrogenes (2002) presented the next stage of the argument using oxide and sulfide components $M_{z/2}O$ and $M_{z/2}S$, but, as they pointed out, a similar argument could be developed using silicate anion structural elements, such as, for example, orthosilicate units SiO_4^{2-} and polymerized SiO_2 units, as for reactions (4) and (5) above. Given our present understanding of the structure of silicate melts (e.g., Mysen and Richet 2005), choosing such structural units might only yield a tractable model between the orthosilicate-equivalent composition at $NBO/T = 4$, and a fully polymerized melt at $NBO/T \sim 0$. In actuality, most of the experimental studies of S^{2-} solubility

314 in the geological literature are on melt compositions with NBO/T between 0.05 and 2, and, as noted
 315 above, there are few if any precise measurements of $C_{S^{2-}}$ on compositions with NBO/T at or about
 316 0 because the low levels of S^{2-} in such melts are near to the analytical limits of quantification by
 317 EMPA under experimentally accessible conditions.

318 With orthosilicate and silica components, the relationship between $[S^{2-}]$ in the silicate melt and
 319 fO_2 and fS_2 is given by:



322 The selection of Mg^{2+} as the cation used to describe the equilibrium is arbitrary; for example,
 323 Fe^{2+} or Ca would do as well. It is essential to acknowledge this point: the reciprocal theory of
 324 mixing on sublattices is not merely an hypothesis, but is mandated by the requirement of internal
 325 consistency. This internal consistency means that writing Eqn (11) using Ca or Fe^{2+} (etc.) rather
 326 than Mg should end up giving exactly the same result, which reciprocal solution theory ensures that
 327 it does. Other attempts that try to define the activity of FeS in silicate melts without invoking
 328 reciprocal solution theory do not meet the requirement of internal consistency and are accordingly
 329 wrong. There may be some misconception in petrological thermodynamics, carried over from
 330 pioneering days, that an astute choice of components in a multicomponent phase can circumvent
 331 having to know the thermodynamic properties of other components in the phase. This has much
 332 truth in simple crystalline solutions where there is mixing on only one crystallographic site, but in
 333 more complex solutions with mixing on multiple sites, it is a fallacy. Because of the reciprocal
 334 solution effect, one cannot choose to define, for example, the activity of FeS in a silicate melt,
 335 without implying information about the activity of, say, MgS; this in turn means implying
 336 information about the standard state properties of MgS. Hence it is inescapable that the standard
 337 state properties of MgS and all other charge-balanced end members must be contained within the
 338 model.

339 All the components in Eqn. (11) are valid thermodynamic components, because they can be
 340 independently varied. In formal terms, $(\partial G_{\text{melt}}/\partial n_i)_{T,P,n_j}$ ($n_j \neq n_i$) is definable, and, moreover,

341 experimentally measurable. This is not the case for charged species, or “structural elements” in the
 342 jargon of point-defect theory (Schmalzried 1995), like O^{2-} and S^{2-} , because $(\partial G_{melt}/\partial n_{O^{2-}})_{T,P,n_j}$ is
 343 not independently variable due to the charge-balance constraint, and is not definable in
 344 conventional chemical thermodynamics where only temperature, pressure and composition are the
 345 variables. There is no implication in Eqn. (11) that a gas phase need be present, as S_2 and O_2 refer to
 346 the components of the system, which may be defined without specifying the phases in the system.

347 At equilibrium:

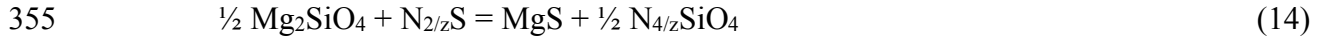
$$348 \quad \mu_{MgS} - \frac{1}{2} \mu_{Mg_2SiO_4} = \frac{1}{2} RT \ln(fS_2/fO_2) - \frac{1}{2} \mu_{SiO_2} \quad (12)$$

349 The evaluation of μ_{MgS} and $\mu_{Mg_2SiO_4}$ from Eqns. (7) to (9) gives:

$$350 \quad \mu_{MgS} = \mu_{MgS}^o + \sum_{N \neq Mg} (-X_N^{cat} X_{SiO_4}^{an} \Delta \mu_{rec}^o[S - SiO_4]) + RT \ln(X_{Mg}^{cat}) + RT \ln(X_S^{an})$$

$$351 \quad + RT \ln(\gamma_{Mg}) + RT \ln(\gamma_S) \quad (13)$$

352 This equation contains a term in X_S^{an} , which is the concentration of S^{2-} in the melt expressed as
 353 a mole fraction. The term $\Delta \mu_{rec}^o[S - SiO_4]$ is the change in free energy of the homogeneous
 354 equilibrium in the melt; such equilibria are often known as reciprocal reactions:



$$356 \quad \Delta \mu_{rec}^o[S - SiO_4] = (\mu_{MgS}^o - \frac{1}{2} \mu_{Mg_2SiO_4}^o) - (\mu_{N_{2/z}S}^o - \frac{1}{2} \mu_{N_{4/z}SiO_4}^o) \quad (15)$$

357 Likewise for $\mu_{Mg_2SiO_4}$:

$$358 \quad \mu_{Mg_2SiO_4} = \mu_{Mg_2SiO_4}^o + \sum_{N \neq Mg} (X_N^{cat} X_S^{an} \Delta \mu_{rec}^o[S - SiO_4]) + 2 RT \ln(X_{Mg}^{cat}) + RT \ln(X_{SiO_4}^{an})$$

$$359 \quad + 2 RT \ln(\gamma_{Mg}) + RT \ln(\gamma_{SiO_4}) \quad (16)$$

360 Substituting (12) to (15) into (11), putting $X_{SiO_4}^{an} = 1$ (that is, X_S^{an} is small, and the SiO_2 units do
 361 not mix with the charged species S^{2-} and SiO_4^{2-} on the anion sublattice) and rearranging gives:

$$362 \quad \ln X_S^{an} = \sum_M X_M^{cat} \left(\frac{1}{2} \mu_{M_{4/z}SiO_4}^o - \mu_{M_{2/x}S}^o \right) / RT - \frac{1}{2} \ln a_{SiO_2}$$

$$363 \quad - \ln \gamma_S + \frac{1}{2} \ln \gamma_{SiO_4} + \frac{1}{2} \ln (fS_2/fO_2) \quad (17)$$

364 This shows that the S content of the melt depends proportionally on $(fS_2/fO_2)^{1/2}$, as in the definition
 365 of the sulfide capacity, $C_{S^{2-}}$, in Eqn. (2). Eliminating the term in $(fS_2/fO_2)^{1/2}$ between (17) and (3)
 366 gives:

$$367 \quad \ln C_{S^{2-}} = B_0^{S^{2-}} + c \ln a_{SiO_2} + \sum X_M B_M^{S^{2-}} \quad (18)$$

368 where the term $B_0^{S^{2-}}$ also accounts for the conversion from mole fractions on the anion sublattice to
 369 weight fractions (conveniently parts per million by weight, while $B_M^{S^{2-}} = k(\frac{1}{2} \mu_{M_{4/z}SiO_4}^o -$
 370 $\mu_{M_{2/x}S}^o)/RT$, where k is a constant, the same for all M. The activity coefficients, γ_S and γ_{SiO_4} , will
 371 for simplicity be assumed to vary only with the M^{x+} cation fractions in the melt composition, but
 372 this is likely only within a limited range of melt compositions, say with NBO/T between 0.2 and 2,
 373 which covers most silicate melt compositions apart from the granite/rhyolite extreme. The average
 374 values of γ_S and γ_{SiO_4} within this range are implicitly incorporated in the $B_0^{S^{2-}}$ term.

375 Equation (18) also contains a term in the activity of silica, a_{SiO_2} , which may be expected to be a
 376 function of the cation mole fractions in the melt. Assume that over a reasonably limited range of
 377 silicate melt compositions, it has the functional form $\ln (a_{SiO_2})^n = C_0 + X_M C_M$. This permits
 378 simplification, to Eqn. (6): $\ln C_{S^{2-}} = A_0^{S^{2-}} + \sum X_M A_M^{S^{2-}}$, where $A_0^{S^{2-}} = B_0^{S^{2-}} + C_0$, and $A_M^{S^{2-}} =$
 379 $B_M^{S^{2-}} + C_M$. In order to achieve a good fit to the data, the cations M include the usual ones that form
 380 the basic oxide components important in natural-composition silicate melts (Na^{1+} , Mg^{2+} , K^{1+} , Ca^{2+} ,
 381 Mn^{2+} , and Fe^{2+}), but also Al^{3+} and Ti^{4+} , whose structural positions in the melts are thought to be
 382 different, and in different ways (Mysen and Richet 2005). Si is not included in the sum of these M
 383 cations explicitly, because it is implicitly included from the closure condition, $\sum X_M = 1$. The mole
 384 fractions are defined on the single-cation basis ($NaO_{0.05}$, MgO , $AlO_{1.5}$, SiO_2 , etc.), despite Eqns.
 385 (10) to (16) being developed with mole fractions on the single-anion basis; for some reason, this
 386 way gives a noticeably better fit.

387 The importance of this derivation of $C_{S^{2-}}$ from solution thermodynamics is that it establishes
 388 that the logarithm of the sulfide capacity $C_{S^{2-}}$ should vary linearly with the mole fractions. This

theoretical relationship was subjected to detailed experimental scrutiny by O'Neill and Mavrogenes (2002), who investigated nearly 200 different melt compositions covering various proportions of the above cations, with NBO/T ranging from 0 to 2 (the mean NBO/T of the compositions they measured is 0.85, with a standard deviation of 0.3), at 1400°C. Such a high experimental temperature was necessary to access a wide range of melt compositions, and was not meant to mimic magmatic temperatures. The tests included experiments adding progressive amounts of one component to a base composition, the particularly important case being the addition of FeO to a CaO-MgO-Al₂O₃-SiO₂ composition, with results shown in Fig. 13 of O'Neill and Mavrogenes (2012). The reason that this example is so important is that it refutes the notion that there are thermodynamically relevant Fe²⁺ - S²⁻ “complexes” in the silicate melts. Rather, the simple log-linear Eqn. (7) performs well, except at very high FeO contents where FeO loses some of its potency for dissolving S²⁻ (the opposite trend to that which would come from complex formation). This interesting phenomenon will be addressed further below.

The model may be tested from a different perspective, namely the magnitudes of the different $A_M^{S^{2-}}$ terms compared to those expected from standard thermodynamic data. An enabling assumption is that the C_M terms used to parameterize a_{SiO_2} are relatively small, such that neglecting them for the present exposition allows the approximation $A_M^{S^{2-}} \propto (\frac{1}{2}\mu_{M_4/zSiO_4}^o - \mu_{M_2/xS}^o)/RT$, where the latter is the difference between the free energies of the orthosilicates and the sulfides. This is an important insight, because if this relationship is valid, it would enable estimates of the effects of melt composition on other “capacities” – sulfate, carbonate, phosphate, etcetera, providing a thermodynamically based alternative to other concepts like NBO/T or “optical basicity” that have been invoked to predict melt thermodynamic properties. The relationship is tested in Fig. 1, using the values of $A_M^{S^{2-}}$ from O'Neill and Mavrogenes (2002) plus that for $A_{Mn}^{S^{2-}}$ from Evans et al. (2008). For the free energies of formation of the orthosilicate and sulfide components, the data for the solid phases at 1400 K were used as a proxy for what is actually required, which is the free energies of the components in the liquid phase in silicate melts extrapolated to infinite dilution at the

415 temperature of interest (here 1673 K). At least this proxy has the merits of consistency for all
416 components. These data are from the JANAF tables (Chase et al. 1998) or Robie and Hemingway
417 (1995).

418 The reason for not trying to build a model from reaction (5), which may be a more realistic
419 approximation to the structure of most silicate melts of geological interest, is that the analogous
420 thermodynamic data for crystalline substances proxying for the $M^{2/x}Si_2O_5$ units are mostly not
421 available, and for the $Si_2O_6^{4-}$ dimer units in the melt ($NBO/Si = 2$), the equivalent crystalline
422 stoichiometry corresponds to that of the chain silicates (e.g., pyroxenes), which seems dubiously
423 appropriate as structural proxies. The orthosilicate stoichiometry has the same SiO_4^{4-} structural units
424 in crystals as in melts.

425 There is a fair positive correlation ($R = 0.80$) between $A_M^{S^{2-}}$ and $(\frac{1}{2}\mu_{M_{4/z}SiO_4}^o - \mu_{M_{2/x}S}^o)/1400R$.
426 O'Neill and Mavrogenes (2002) pointed out that there was no such correlation between the values
427 of $A_M^{S^{2-}}$ and the analogous terms $(\mu_{M_{2/z}O}^o - \mu_{M_{2/x}S}^o)/RT$, indicating that the ability of a basic oxide
428 component $M_{x/2}O$ to contribute to the sulfide capacity of a silicate melt is lessened by the strength
429 of the chemical bonding of the M^{x+} cation to the silicate units in the melt. Thus Ca^{2+} is less effective
430 at enhancing $C_{S^{2-}}$ than Fe^{2+} because $Ca^{2+} - SiO_4^{4-}$ interactions are far stronger than $Fe^{2+} - SiO_4^{4-}$
431 interactions in silicate melts, well known from the thermodynamics of the simple binaries CaO -
432 SiO_2 and FeO - SiO_2 (e.g., Mysen and Richet 2005).

433 This correlation also shows that the large magnitude of $A_{Fe}^{S^{2-}}$ relative to the other $A_M^{S^{2-}}$, except
434 $A_{Mn}^{S^{2-}}$, is not an anomaly, but is that expected from the reciprocal solution theory, given the relative
435 magnitudes of the free energies of formation of Fe_2SiO_4 and FeS . There is no reason to postulate
436 complexes between Fe^{2+} and S^{2-} in the silicate melts. The correlation predicts that the effects of Ni^{2+}
437 and Cu^{1+} on $C_{S^{2-}}$ should be even larger than those of Fe^{2+} and Mn^{2+} . Evans et al. (2008) found that
438 $A_{Ni}^{S^{2-}}$ and $A_{Cu}^{S^{2-}}$ could not be measured experimentally with available methods, because at the fS_2 -
439 fO_2 conditions needed to achieve measurable S^{2-} in the silicate melt, the Ni and Cu were stripped
440 out into immiscible sulfide melts. It is the same strength of the Ni^{2+} - S^{2-} and Cu^{1+} - S^{2-} chemical

441 bonding in the silicate melts compared to the rather feeble $\text{Ni}^{2+}\text{-SiO}_4^{4-}$ and $\text{Cu}^{1+}\text{-SiO}_4^{4-}$ bonding,
442 causing the large values of $A_{\text{Ni}}^{S^{2-}}$ and $A_{\text{Cu}}^{S^{2-}}$, that also causes the immiscible sulfide melts to form;
443 two sides of the same coin. The correlation in Fig. 1 suggests $A_{\text{Ni}}^{S^{2-}} \approx 30$ and $A_{\text{Cu}}^{S^{2-}} \approx 60$; to estimate
444 the latter the free energy of formation of the non-existent orthosilicate Cu_4SiO_4 from the oxides was
445 taken to be zero.

446 This information on the likely values of $A_{\text{Ni}}^{S^{2-}}$ and $A_{\text{Cu}}^{S^{2-}}$ is somewhat nugatory, as the stripping
447 out of Ni and Cu into a sulfide melt keeps Ni and Cu concentrations in the silicate melt to the 10^2
448 ppm level, at which they have no discernible effect on $C_{S^{2-}}$ (Evans et al. 2008). Put another way,
449 the atomic ratios of Ni and Cu to Fe in terrestrial basalts are both about 10^{-3} , therefore given these
450 values of $A_{\text{Ni}}^{S^{2-}}$ and $A_{\text{Cu}}^{S^{2-}}$, neglecting Ni and Cu has an equivalent effect to decreasing the
451 concentration of FeO in the silicate melt by 0.1 and 0.2 % relative, well below the best analytical
452 precision. The effect of Ni and Cu on SCSS is entirely through their obvious influence on the
453 activity of FeS in the sulfide melt. If NiO in the silicate melt has negligible effect on S^{2-} solubility,
454 then the corollary is that S^{2-} has negligible effect on the activity of NiO in the silicate melt, for
455 example, in the context of the partitioning of Ni between olivine and silicate melt. This point is
456 addressed in Tuff and O'Neill (2010).

457

458 *The Fe^{3+} problem*

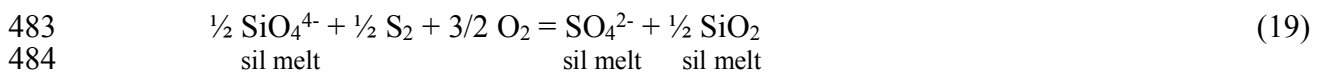
459 Given that the direct measurement of sulfide capacities requires knowing both $f\text{O}_2$ and $f\text{S}_2$, it
460 can be done most easily and also precisely at atmospheric pressure in gas-mixing experiments,
461 where the sum of the partial pressures of all gas species are limited to 1 bar. Unfortunately,
462 increasing $f\text{O}_2$ to where $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ in the silicate melt is more than a couple of percent enters
463 the regime of the experimental S solubility minimum, where S solubilities fall below the limit of
464 quantification of the electron microprobe. Thus only the effect of Fe^{2+} on $C_{S^{2-}}$ is known, and the
465 influence of Fe^{3+} is currently completely mysterious. The correlation used to guestimate $A_{\text{Ni}}^{S^{2-}}$ and
466 $A_{\text{Cu}}^{S^{2-}}$ (Fig. 1) is useless, because thermodynamic data for the non-existent sulfide $\text{Fe}^{3+}\text{S}_{1.5}^{2-}$ are not

467 available, unsurprisingly. A couple of thoughts arise. One possibility is that the electron
 468 configurations of Fe^{3+} is the same as that of Mn^{2+} ($\text{Ar}3d^5$), and size differences between cations are
 469 less important in the environment of silicate melts where cation-anion interatomic distances are not
 470 influenced by crystal symmetries, suggesting that $A_{\text{Fe}^{3+}} \sim A_{\text{Mn}}$. As the latter is similar to $A_{\text{Fe}^{2+}}$
 471 (Evans et al. 2008), changing $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ would have no effect on $C_{\text{S}^{2-}}$. Alternatively, on the
 472 grounds that Fe^{3+} may play a similar structural role to Ti^{4+} in silicate melts, $A_{\text{Fe}^{3+}}$ may be similar to
 473 A_{Ti} , and increasing $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ would decrease $C_{\text{S}^{2-}}$ accordingly. That changing the oxidation
 474 state of a key cationic component of a silicate melt may have a huge effect on $C_{\text{S}^{2-}}$ has been
 475 claimed for vanadium. Allertz et al. (2016) showed that increasing $f\text{O}_2$ by six orders of magnitude
 476 at 1600°C increased $C_{\text{S}^{2-}}$ by over two orders of magnitude in CMAS-based melts with 3.6 to 9.5
 477 wt% V; the increase is presumably due to the V changing from predominantly $2+$ to predominantly
 478 $3+$. Is V a trustworthy analogue for Fe?

479

480 *Sulfate capacities, $C_{\text{SO}_4^{2-}}$*

481 Following the same logic, the equilibrium between orthosilicate and framework structural units
 482 that defines the sulfate capacity, $C_{\text{SO}_4^{2-}}$, would be:



485 This suggests that the dependence of $C_{\text{SO}_4^{2-}}$ on silicate melt composition should take the same form
 486 as that for $C_{\text{S}^{2-}}$, namely:

$$487 \quad \ln C_{\text{SO}_4^{2-}} = A_0^{\text{SO}_4^{2-}} + \sum X_M A_M^{\text{SO}_4^{2-}} + \quad (20)$$

488 where $A_0^{\text{SO}_4^{2-}} = B_0^{\text{SO}_4^{2-}} + C_0$, $A_M^{\text{SO}_4^{2-}} = B_M^{\text{SO}_4^{2-}} + C_M$, with $B_M^{\text{SO}_4^{2-}} = k(\frac{1}{2} \mu_{\text{M}_{4/2}\text{SiO}_4}^{\text{O}} - \mu_{\text{M}_{2/x}\text{SO}_4}^{\text{O}})/RT$.

489 The difference between the coefficients for of each M cation for $C_{\text{SO}_4^{2-}}$ and $C_{\text{S}^{2-}}$ is therefore:

$$490 \quad A_M^{\text{SO}_4^{2-}} - A_M^{\text{S}^{2-}} = k(\mu_{\text{M}_{2/x}\text{S}}^{\text{O}} - \mu_{\text{M}_{2/x}\text{SO}_4}^{\text{O}})/RT \quad (21)$$

491 In taking the difference, most of the approximations used in deriving the individual values of
 492 $A_M^{S^{2-}}$ and $A_M^{SO_4^{2-}}$ would cancel out, like the effect of the activity of silica. This then further suggests
 493 that the dependence of $C_{SO_4^{2-}}$ on silicate melt composition could be predicted from the experimental
 494 measurements on $C_{S^{2-}}$, together with the readily available standard-state thermodynamic data on
 495 sulfates and sulfides.

496 The ratio of sulfide to sulfate dissolved in a silicate melt follows from the definitions of $C_{S^{2-}}$
 497 and $C_{SO_4^{2-}}$:

$$498 \quad [SO_4^{2-}] / [S^{2-}] = C_{SO_4^{2-}} / C_{S^{2-}} (fO_2)^2 \quad (22)$$

499 The fO_2 at which $[SO_4^{2-}] / [S^{2-}]$ is 1, denoted here as $(fO_2)_{S_6+/S_2-}$, is therefore $(C_{S^{2-}} / C_{SO_4^{2-}})^{1/2}$. For
 500 present purposes, the anion complex SO_4^{2-} may be taken as equivalent to S^{6+} . Substituting Eqns. (7)
 501 and (20) into (22) gives:

$$502 \quad \ln ([SO_4^{2-}] / [S^{2-}]) = + 2 \ln fO_2 + (A_0^{SO_4^{2-}} - A_0^{S^{2-}}) + \sum X_M (A_M^{SO_4^{2-}} - A_M^{S^{2-}}) \quad (23)$$

503 where the effect of silicate melt composition is contained in the last term on the right-hand side,
 504 whose thermochemical significance is given by Eqn. (21).

505 From this, it may be predicted that, at a given T, P and fO_2 , increasing FeO in the melt would
 506 increase $(fO_2)_{S_6+/S_2-}$, while increasing CaO and Na₂O would decrease $(fO_2)_{S_6+/S_2-}$.

507 The value of $(fO_2)_{S_6+/S_2-}$ is not well constrained for anhydrous basaltic melts. The inescapable
 508 experimental problem is that it falls in the region of the ambient-pressure experimental S solubility
 509 minimum. It has been approximately located at about the fO_2 of the quartz-fayalite-magnetite
 510 equilibrium (QFM) by Fincham and Richardson (1954) and Katsura and Nagashima (1974) from
 511 extrapolation of solubilities measured at higher and lower fO_2 . (Oxygen fugacities are conveniently
 512 discussed relative to some isobarically invariant “buffer” such as QFM because condensed-phase
 513 redox equilibria all tend, to a first approximation, to have similar slopes in $1/T$ -log fO_2 space. For
 514 reference, QFM is given by $\log_{10} fO_{2(QFM)} = 8.58 - 25050/T$ at 1 bar (O'Neill 1987), and $\Delta QFM =$
 515 $\log_{10} (fO_2 / fO_{2(QFM)})$).

516 Recently this approach has been expanded upon by Nash et al. (2019), who exploited the lower
 517 limits of detection afforded by SIMS to investigate the solubilities of S in the region of the
 518 solubility minimum. Their experiments were at 1300°C, and used CO-CO₂-SO₂ gas mixes. They
 519 assumed that total S solubilities at higher fO₂ in excess of those predicted for S²⁻ from the Fincham-
 520 Richardson relation at low fO₂, were due to additional S⁶⁺. This they corroborated by S K-edge
 521 XANES spectroscopy. They found that values of (fO₂)_{S6+/S2-} for six melt compositions lay in the
 522 range ΔQFM 0 to +0.6, concordant with the earlier studies. Increasing (fO₂)_{S6+/S2-} correlated
 523 qualitatively with increasing FeO in the melt, although the effect was smaller than expected from
 524 the sensitivity of C_{S2-} to FeO (O'Neill and Mavrogenes 2002).

525 Other information on where (fO₂)_{S6+/S2-} lies in silicate melts comes from X-ray spectroscopic
 526 characterization of S⁶⁺/S²⁻ in quenched glasses prepared under pressure, and necessarily containing
 527 H₂O in order to control fO₂. These measurements have been problematic because of beam-damage
 528 issues, see Wilke et al. (2008, 2011), Métrich et al. (2009) and Jugo et al. (2010). The majority view
 529 is that S⁴⁺ (that is, sulfite, SO₃²⁻) found spectroscopically by XANES is caused by beam damage, at
 530 least in glasses of low-pressure provenance (both natural and synthetic). The probability is that most
 531 X-ray fluorescence measurements of S oxidation state obtained with the electron microprobe are
 532 badly affected by beam damage (Wilke et al. 2008), but because this technique only gives the
 533 average oxidation state of S, S⁴⁺ is not itself distinguished (unlike with XANES), making it difficult
 534 to judge exactly what is going on. Because of this knowledge gap, the test for beam damage is
 535 whether the measured S⁶⁺/S²⁻ follows the theoretical dependence on (fO₂), which is that [S⁶⁺]/[S²⁻]
 536 ∝ (fO₂)² (Eqn. 22), provided that the assumption of negligible S⁴⁺ is accepted. At present, among
 537 studies that cover a sufficiently meaningful range of fO₂, the only experiments to pass this test to
 538 date are those of Jugo et al. (2010) and Botcharnikov et al. (2011), who used XANES to quantify
 539 S⁶⁺/ΣS in a series of glasses quenched from hydrated basaltic and andesitic melts with about 5 wt%
 540 H₂O at 1050°C and 0.2 GPa, and those of Nash et al. (2019), described above. Jugo et al. (2010)

541 fitted their results to an equation with the stoichiometry of the speciation constrained at the
542 theoretical value:

$$543 \quad S^{6+}/\sum S = 1/(1 + 10^{(2.1-2 \Delta QFM)}) \quad (24)$$

544 Hence $(fO_2)_{S^{6+}/S^{2-}}$ is at $\Delta QFM+1.05$. Botcharnikov et al. (2011) then found that this equation
545 described their results on their andesitic composition within uncertainty.

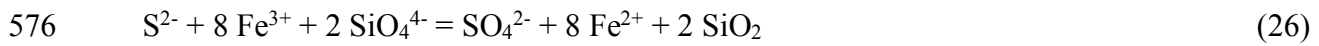
546 For comparison, the change in oxidation state of the main redox-variable element in basalts, Fe,
547 given by Berry et al. (2018) is:

$$548 \quad Fe^{3+}/\sum Fe = 1/(1 + 10^{(1.0575-0.25 \Delta QFM)}) \quad (25)$$

549 The relationship between $S^{6+}/\sum S$ and $Fe^{3+}/\sum Fe$ from combining these two equations to eliminate
550 ΔQFM is shown in Fig. 2. On the face of it, the range of $Fe^{3+}/\sum Fe$ measured in MORB glasses
551 coincides with $S^{6+}/\sum S$ going from zero to as much as 30%, but this depends on the rather dubious
552 equivalence between hydrated basalts at 1050°C and the natural MORB glasses, which are quenched
553 from ~ 1200°C and contain little H₂O (see below).

554 A different view emerges from the recent study of Nash et al. (2019), who calculated Fe^{3+}/Fe^{2+}
555 for the experiments at 1300°C in which they had estimated S^{6+}/S^{2-} (as described above), and also for
556 those of Jugo et al. (2010) and Botcharnikov et al. (2011) at 1050°C. They then fitted these data to
557 an expression also constrained to the theoretical stoichiometry, which included a dependence on
558 temperature. To constrain this latter variable better (given that the available data are from only two
559 temperatures and those at 1050°C are hydrous melts) they invoked thermochemical data for
560 crystalline-phase analogues of the melt components. As regards the effect of melt composition, their
561 data were too scattered to resolve any (see their Fig. 6). The relationship between $S^{6+}/\sum S$ and
562 $Fe^{3+}/\sum Fe$ from their equation, calculated at 1190° (the average for anhydrous MORB glasses in
563 equilibrium with olivine according to the magmathermometer of Putirka 2008), is also shown in
564 Fig. 2. With their formulation, even the more oxidized MORB glasses would contain only a few
565 percent $S^{6+}/\sum S$. As will be shown below, the evidence from the SCSS of MORB glasses is more
566 concordant with this view.

567 The temperature-dependence of S speciation relative to QFM in silicate melts remains
 568 somewhat contentious. Nash et al. (2019) inferred that decreasing temperature shifts $(fO_2)_{S^{6+}/S^{2-}}$ to
 569 higher ΔQFM (i.e., decreasing temperature stabilizes S^{2-} relative to S^{6+} at a given ΔQFM), which is
 570 in the opposite direction to that anticipated by Métrich et al. (2009). That S^{6+} forms an anionic
 571 complex, SO_4^{2-} , may seem at first sight to endow this speciation with low configurational entropy,
 572 but as the effects of entropy are always relative, the entropies of the alternative arrangements need
 573 to be considered. Assuming the same orthosilicate and framework species as for modeling of $C_{S^{2-}}$,
 574 the two alternatives for redox speciation in a melt containing both Fe and S could be described by
 575 the homogeneous equilibrium:



577 From the point of view of configurational entropy, both sides of this reaction contain the same
 578 number of species, but two of the 11 species on the right-hand side (RHS) are polymerized SiO_2
 579 units in the melt, which might be expected to have lower entropy, implying that the speciation
 580 might proceed towards the RHS with decreasing temperature.

581 The experiments of Luhr (1990) on sulfur solubilities in hydrous melts as a function of
 582 temperature and fO_2 (at 0.2 and 0.4 GPa) show that at 900°C and above, total S in the oxidized
 583 experiments was higher than experiments at QFM (see Fig. 10 of Luhr 1990), whereas at 800 and
 584 850°C it was the same in the oxidized experiments as in the pyrrhotite-saturated experiments at
 585 QFM. This is suggestive that, contrary to the entropy argument, increasing temperature favours the
 586 RHS of reaction (26), but it is not definitive as the oxidized experiments did not contain pyrrhotite.

587 The isochemical redistribution of species according to reaction (26) involves only electron
 588 hopping between atoms with coordination changes on the scale of interatomic distances, and is
 589 therefore likely very fast, arguably so fast as to be unquenchable from liquidus temperatures (cf.
 590 Berry et al. 2003). If the right-hand side of (26) were favoured on cooling (the opposite to the
 591 inference from the experiments of Luhr 1990), it might explain the small amounts of sulfate

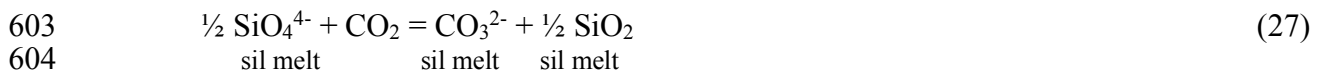
592 identified by XANES spectroscopy in some natural basaltic glasses (Métrich et al. 2009; Jugo et al.
593 2010).

594 The only available indication of the effect of pressure on the S^{2-}/SO_4^{2-} transition is the study of
595 Matjuschkin et al (2016), which indicates that increasing pressure may move $(fO_2)_{6+/2}$ to higher
596 ΔQFM . Measurements of $S^{6+}/\Sigma S$ and $Fe^{3+}/\Sigma Fe$ on the same melt compositions over a range of fO_2
597 (probably from QFM-1 to QFM+2) as a function of temperature and pressure are much needed. But
598 this is a formidable experimental challenge.

599

600 *Other capacities for anions and anion complexes in silicate melts*

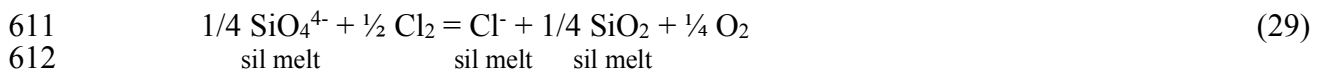
601 The “capacity” idea could be extended to other anionic substitutions in silicate melts, for
602 example, CO_2 dissolving as carbonate, CO_3^{2-} :



605 for which the carbonate capacity would be given by:

$$606 \quad C_{CO_3^{2-}} = [CO_3^{2-}]fCO_2 \quad (28)$$

607 with $A_0^{CO_3^{2-}} - A_M^{S^{2-}} = k(\mu_{M_{2/x}S}^o - \mu_{M_{2/x}CO_3}^o)/RT$. Likewise, to predict the effect of composition on
608 chlorine in silicate melts, which is difficult to measure experimentally because Cl_2 gas volatilizes
609 most of the oxide components in one-atmosphere experiments, the chloride capacity would be
610 defined as:



$$613 \quad C_{Cl^-} = [Cl^-](fCl_2)^{1/2}(fO_2)^{1/4} \quad (30)$$

$$614 \quad \text{and } A_0^{Cl^-} - A_M^{S^{2-}} = k(1/2\mu_{M_{2/x}S}^o - \mu_{M_{1/x}Cl}^o)/RT.$$

615 A suggestion to relate the various “capacities” of silicate melts to one another was made by Carl
616 Wagner in one of his last contributions (Wagner 1975). Wagner, who has been called the “Father of
617 Solid-state Chemistry” (Martin 2001), defined a “basicity” for a silicate melt of a specified
618 composition using carbonate capacities:

$$B_{\text{carb}} = C_{\text{CO}_3^{2-}} / C_{\text{CO}_3^{2-}}^* \quad (31)$$

where $C_{\text{CO}_3^{2-}}^*$ is the carbonate capacity of a reference melt (he suggested one with composition 0.4 CaO, 0.4 SiO₂ and 0.2 Al₂O₃). Wagner (1975) also discusses how such a definition of “basicity” for a silicate melt provides a more rational measure than the “activity” of O²⁻, which, despite its appearance as a “structural element” in definitions of capacities like Eqn (2), is not, as Wagner pointed out, a usefully definable quantity, thermodynamically.

Wagner (1975) then proposed that the capacities of other anionic species Zⁿ⁻ (e.g., S²⁻, SO₄²⁻, Cl⁻ among many others) could be related to this basicity by:

$$C_{Z^{n-}} = C_{Z^{n-}}^* (B_{\text{carb}})^{2/n} \quad (32)$$

One of the benefits of deriving the thermochemical meaning of these “capacities” from reciprocal solution theory with mixing on sublattices is that it goes straight to the heart of the problem with Wagner’s suggestion (which he alluded to himself): it implicitly assumes that the quantities $(\frac{1}{2} \mu_{\text{M}_{4/2}\text{SiO}_4}^0 - \mu_{\text{M}_{v/x}\text{Z}}^0)$ are the same for all anionic species Z, and for all relevant elements M. A few minutes perusing a thermochemical database would reveal that this is obviously not the case. The escape clause is that in a majority of basic slag compositions these M cations are dominated by only two, namely Mg and Ca, and it is possible to get away with taking the difference $[(\mu_{\text{Ca}_{v/x}\text{Z}}^0 - \mu_{\text{Mg}_{v/x}\text{Z}}^0)]$ as being constant within limited horizons. Looking a bit further, it is the great stability of the FeS component in silicate melts compared to MgS or CaS (cf. FeCO₃ compared to CaCO₃ or MgCO₃), with the consequence for sulfide capacities, that provides the exception disproving this rule handsomely – although MnS would do as well as FeS.

A new parameterization of sulfide capacity for basaltic melts

From the point of view of reproducing the experimental data, there are nevertheless a few ad-hoc “improvements” that can be made to the simple relationship of Eqn. (7), albeit at the cost of divorcing the parameters $A_M^{S^{2-}}$ from their thermochemical roots. O’Neill and Mavrogenes (2002)

644 showed that adding a cross term in $X_{\text{Fe}}X_{\text{Ti}}$ is needed to account for Fe^{2+} - Ti interactions in the melt
645 (see Fig. 14 of O'Neill and Mavrogenes 2002). Smythe et al. (2017) suggested a similar cross-term
646 in $X_{\text{Fe}}X_{\text{Si}}$, and in the fitting to be described below, it was confirmed that this term was very
647 effective at improving the fit of the experimental data.

648 A well known but hitherto unaddressed problem is that the linear relationship between $\ln C_{\text{S}^{2-}}$
649 and the cation mole fractions X_{M} breaks down at high FeO contents, between 15 and 20 wt% FeO
650 according to O'Neill and Mavrogenes (2002). This phenomenon has been confirmed by several
651 studies on SCSS (see section below). The deviation is in the direction of lower S^{2-} in the silicate
652 melt than the linear relationship established at < 15 wt% FeO would predict, the opposite to that
653 expected from formation of Fe^{2+} - S^{2-} complexes. The deviation becomes noticeable at S^{2-}
654 concentrations that are relatively low compared to those of Fe^{2+} , for example at ~ 3500 ppm S in
655 melt at 20 wt% FeO, which in molar proportions of S to FeO is still only less than 1 to 10 (see
656 Table 13 of O'Neill and Mavrogenes 2002). Other experiments on Fe-free compositions with high
657 CaO exceed this S^{2-} content with no such deviations apparent (e.g., nearly 6000 ppm dissolve in the
658 AD+Wo composition run 17/2/97 in Table 2 of O'Neill and Mavrogenes 2002), indicating,
659 importantly, that the Fe problem is not due to the assumption of constant “activities” of “structural
660 elements” like O^{2-} breaking down in the derivation of Eqn. 3. Another curious feature is that the
661 change of $C_{\text{S}^{2-}}$ with X_{Fe} is linear within experimental uncertainty up to ~ 15 wt% FeO, but then
662 breaks sharply to a different linear trend of $\ln C_{\text{S}^{2-}}$ vs X_{Fe} (see Fig. 15 of O'Neill and Mavrogenes
663 2002).

664 This is a peculiar phenomenon, for which there is no explanation at present, and more
665 experimental information would be useful. There seem to be no experiments that have tested the
666 Fincham-Richardson relationship in high FeO melts; for example, it would be interesting to
667 measure $C_{\text{S}^{2-}}$ at various $f\text{O}_2$ and $f\text{S}_2$, on a composition with, say, 30 wt% FeO in the melt. The
668 propensity for high FeO, high S^{2-} melts to exsolve FeS-rich sulfide microblobs on quenching
669 despite using the standard rapid-quenching techniques (Métrich et al., 2009; Wykes et al. 2015), has

so far prevented obtaining samples suitable for spectroscopy (Métrich et al, 2009). The departure from the simple theory at high FeO has hindered applying sulfide solubility models to many extraterrestrial basalts, which often have FeO > 15 wt%. In view of the lack of theoretical insight but the need for something to be done, it seems expedient to forgo a thermodynamically based model, and find a parameterization of $C_{S^{2-}}$ as a function of melt composition that includes FeO-rich basaltic melts. The shape of the departure from linearity suggests the arctangent function or the error function; the latter was used here. With these three additions to the simple Eqn. (7), all the data from O'Neill and Mavrogenes (2002), including the high FeO compositions, plus those at 1400°C from Tuff and O'Neill (2010), were fitted by weighted least squares regression. The function minimized was $[(\ln(C_{S^{2-}})_{\text{obs}} - \ln(C_{S^{2-}})_{\text{calc}})/s(\ln C_{S^{2-}})]^2$, where the weight $s(\ln C_{S^{2-}})$ was obtained by propagating the uncertainty in measured S, $s([S]_{\text{obs}})$ as observed, or 3%, whichever was larger, plus uncertainties in log fO₂ and log fS₂ of 0.05 each. Typically $s(\ln C_{S^{2-}})$ is about 0.1 (that is, 10%), except for experiments with very low S contents (< 500 ppm), which may have substantially larger uncertainties, and the 12 CMAS and one CMAS+Ti compositions from Table 1 of O'Neill and Mavrogenes (2002), in which the multiple measurements produce a lower uncertainty of 0.03 to 0.05. The regression gave:

$$\begin{aligned} \ln C_{S^{2-}}(1673\text{K}, 1 \text{ bar}) = & -5.330 + 6.7 (X_{\text{Na}} + X_{\text{K}}) + 1.8 X_{\text{Al}} + 4.9 X_{\text{Mg}} + 8.1 X_{\text{Ca}} \\ & + 8.9 X_{\text{Fe}^*} - 22.2 X_{\text{Fe}^*} X_{\text{Ti}} + 7.2 X_{\text{Fe}^*} X_{\text{Si}} - 2.06 \text{erf}(-7.2 X_{\text{Fe}^*}) \end{aligned} \quad (33)$$

where X_{Fe^*} is $(X_{\text{Fe}} + X_{\text{Mn}})$, and mole fractions are defined on the single cation basis (NaO_{0.05}, MgO, AlO_{1.5}, SiO₂, etcetera). The agreement between the parameterization and the input data (n = 228) is shown in Fig. 3a. The reduced chi-squared (χ^2_{ν}) is 1.2, indicating a good fit to the data, apart from two CMAS compositions. One is the CMAS7E composition from Table 1 of O'Neill and Mavrogenes (2002). It is a challenge to model the compositional dependence of $C_{S^{2-}}$ for the twelve CMAS compositions from that Table, because of the small uncertainty in $C_{S^{2-}}$ that comes from the multiple experiments (10 or 12 on each composition). Whilst this challenge is mostly met, the misfit to CMAS7E is a notable failure. The parameterization also fails to fit an anomalous datum from

696 Tuff and O'Neill (2010), N81B1, which was discussed in that paper. Due to the large number of
 697 data, these two outliers have negligible effect, but they were removed from the fitting procedure
 698 anyway.

699

700 *Temperature dependence of $C_{S^{2-}}$*

701 Because the compositional terms come from reciprocal reactions, they are likely to be
 702 dominated by enthalpy changes, hence the form of the parameterization for other temperatures is
 703 proposed to be:

$$704 \quad \ln C_{S^{2-}}(T, 1 \text{ bar}) = A^H/T + A^S + (1673/T) [6.7 (X_{Na}+X_K) + 1.8 X_{Al} + 4.9 X_{Mg} + 8.1 X_{Ca} \\ 705 \quad + 8.9 X_{Fe^*} - 22.2 X_{Fe^*}X_{Ti} + 7.2 X_{Fe^*}X_{Si}] - 2.06 \operatorname{erf}(-7.2 X_{Fe^*}) \quad (34)$$

706 where $A_0 = A^H/T + A^S$. With $(A^H/1673 + A^S)$ constrained to -5.330 to meld with the 1400°C fit,
 707 these parameters were evaluated to be $A_H = -23590$ and $A_S = 8.77$, obtained as follows.

708 The experimental study of Haughton et al. (1974), being ambitious in scope, has had much
 709 influence on previous petrologically focused reviews of the behavior of S^{2-} in silicate melts
 710 (Poulson and Ohmoto 1990; Wallace and Carmichael 1992; Ariskin et al. 2013). The study
 711 consisted of 100 experiments at 1200°C, divided into two groups: Series I experiments ($n = 37$)
 712 investigated a single base composition at different fO_2 and fS_2 , with the composition varied in its
 713 FeO from addition of Fe_2O_3 and/or separation of immiscible sulfide. Their Series II experiments (n
 714 $= 63$) investigated different starting compositions at the same fO_2 and fS_2 , with all compositions
 715 designed to be saturated FeS-rich melt. As pointed out in O'Neill and Mavrogenes (2002), their
 716 results show a lot of scatter. For example, replicate experiments agree poorly, and the results of the
 717 Series I experiments are incommensurate with those of Series II. Two causes are likely,
 718 equilibration problems and difficulties analyzing S at relatively low levels by electron microprobe.
 719 The silicate melts were held in alumina crucibles, which results in continuous reaction with the
 720 crucible during the experiment, because the original melt compositions are not saturated in alumina.
 721 This effect also biases the melt compositions studied to high Al_2O_3 . In addition, some precipitation

722 of FeS during the quenching might be anticipated, given the relatively slow quenching rates
723 possible with the alumina crucibles. The S content in one experiment in Series I, 4F1, which was
724 run at a higher fO_2 than any other experiment in the study, was reported at 270 ppm, which,
725 although low, is far higher than any value that would reasonably be expected for any extrapolation
726 (< 50 ppm), attesting to analytical difficulties. The scatter of the data has meant that attempts to
727 parameterize the results of Haughton et al. (1974) have led to complicated scenarios involving
728 hypothetical Fe-S species or complexes in the silicate melt (Poulson and Ohmoto 1990; Ariskin et
729 al. 2013), or to the idea that SCSS varies with fO_2 and fS_2 at constant melt composition (Wallace
730 and Carmichael 1992), which it does not, apart from second order effects like changing Fe^{3+}/Fe^{2+}
731 (Mavrogenes and O'Neill 1999). These points are discussed further below. Here, the results of
732 Haughton et al. (1974) were used only to obtain an estimate of A_0 at 1200°C. To do this, both series
733 were fitted to Eqn. (34), with the result shown in Fig. 3b. Together with some additional
734 information from the author's own preliminary results at 1300°C and 1500°C, these results were
735 used to estimate $A_H = -23590$ and $A_S = 8.77$.

736 More data over a wider range of temperatures are needed to decrease the considerable
737 uncertainty on these values. The effects of pressure and volatile contents (with H_2O of particular
738 interest) on $C_{S^{2-}}$ cannot at present be measured to useful accuracy by existing experimental
739 methods directly, but their contributions to SCSS is accessible experimentally and will be reviewed
740 below.

741

742 **Sulfide content at sulfide saturation (SCSS)**

743 The term “sulfur content at sulfide saturation”, meaning the amount of sulfur dissolved in a
744 silicate melt in equilibrium with a sulfide phase (usually but not necessarily a FeS-rich sulfide
745 melt), and acronymed as SCSS, was introduced by Shima and Naldrett (1975). Because some non-
746 negligible proportion of the sulfur dissolved in silicate melts in equilibrium with some sulfides will
747 be SO_4^{2-} towards the high end of the range of oxygen fugacities of natural magmas, and there are

possibly other S species present at high pressure or hydrous melts (for example HS⁻), the quantity is less ambiguously labelled “sulfide content at sulfide saturation”. This is the meaning of SCSS that will be used here.

The equilibrium between a silicate melt and a sulfide matte (Eqn. 1) gives the relationship:

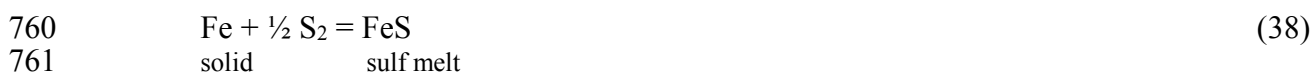
$$-\Delta G_{FeO-FeS}^o/RT = -\ln a_{FeO}^{sil\ melt} + \ln a_{FeS}^{sulf} + \ln (fO_2/fS_2)^{1/2} \quad (35)$$

Substituting Eqn. (3), the definition of $C_{S^{2-}}$, into (35) to eliminate (fO_2/fS_2) gives:

$$\ln [S]_{SCSS} = \Delta G_{FeO-FeS}^o/RT + \ln C_{S^{2-}} - \ln a_{FeO}^{sil\ melt} + \ln a_{FeS}^{sulf} \quad (36)$$

Therefore, SCSS depends on four quantities:

1) the standard state free energy of the reaction (1), $\Delta G_{FeO-FeS}^o$, which is the difference between the two free energies of formation from the elements:



The free energy of reaction (37), $\Delta G_{FeO}^{o,sil\ melt}$, is taken from Holzheid et al. (1997), who combined the data for crystalline but non-stoichiometric “FeO” in equilibrium with Fe metal from O’Neill and Pownceby (1994) with those for the melting of FeO from Barin (1989), which gave:

$$\Delta G_{FeO}^{o,sil\ melt} \text{ (J mol}^{-1}\text{)} = -244118 + 115.559 T - 8.474 T \ln(T) \quad (39)$$

The data for $\Delta G_{FeS}^{o,sulf\ melt}$ are less accurately known, with different assessments or tabulations of thermodynamic data differing by up to 10 kJ mol⁻¹ at relevant temperatures, reflecting different measurements reported in the literature, see Waldner and Pelton (2005) for a review. Here it was assumed that $\Delta G_{FeS}^{o,sulf\ melt} = \Delta H_{FeS}^o - T \Delta S_{FeS}^o$, with the values of ΔH_{FeS}^o and ΔS_{FeS}^o to be optimized in the fitting. Whether these optimized values fall within the range of experimentally measured values provides a critical test of the modelling. The effect of pressure on $\Delta G_{FeS}^{o,sulf\ melt}$ could in principle be evaluated from the partial molar volumes of FeO in silicate melts (Lange and Carmichael 1990) and of FeS in sulfide melts (e.g., Kress et al. 2008). However, for the purpose of calculating SCSS this information is insufficient because the effects of pressure on the other quantities in Eqn. (36) are not

775 known. Henceforward the effects of pressure will be regarded as having to be parameterized
776 empirically from the SCSS data.

777 2) The sulfide capacity $C_{S^{2-}}$ has been evaluated above as a function of composition and
778 temperature, however, its pressure dependence, and the compositional effects of H₂O and other
779 volatile species, remain unknown. An hypothesis to explain the currently available experimental
780 data on the effect of H₂O on SCSS will be proposed later, but first only supposedly anhydrous
781 experiments will be considered.

782 3) The activity of FeO in silicate melts is related to its mole fraction by $a_{FeO}^{sil\ melt} = X_{FeO}^{sil\ melt}$
783 $\gamma_{FeO}^{sil\ melt}$. The activity coefficients, $\gamma_{FeO}^{sil\ melt}$, have been measured by equilibration with Fe metal
784 according to reaction (37) at atmospheric pressure, using gas-mixing methods, from 1150 to
785 1500°C. The upper temperature limit is an experimental one, set by the melting point of Fe metal
786 (1538°C). Achieving good accuracy is relatively easy in such measurements compared to most
787 matters in the world of experimental petrology, and studies on silicate melts with compositions of
788 geological relevance are available from Roeder (1974), Doyle and Naldrett (1986), Doyle (1988,
789 1989), O'Neill and Eggins (2002), Borisov et al. (2004, 2006) and Borisov (2007). In addition,
790 Holzheid et al. (1997) obtained measurements in equilibrium with Fe-Ni-Co alloys. These studies
791 provide over 600 experimental observations, dominated by the Doyle datasets (512 data, all at
792 1327°C), but the coverage of melt composition is not even. Although the Doyle opus is of great
793 value, it does show a marked predilection for melts high in K, also in Ti, an aversion to Na, and
794 almost a dismissal of Mg; in fact, high MgO compositions are generally lacking in all the studies,
795 and high SiO₂ compositions, such as relevant to rhyolites (say, $X_{SiO_2} > 0.65$), are not represented at
796 all. On the plus side, there is good agreement among all these studies, as noted by O'Neill and
797 Eggins (2002), and by Borisov (2007). When referenced to the standard state of Eqn. (37), the
798 experimental data show that $\gamma_{FeO}^{sil\ melt}$ varies between 0.7 and 2 for most compositions (e.g., Fig. 4).
799 Although this is a relatively small variation compared to activity coefficients of other oxide
800 components in silicate melts (O'Neill and Eggins 2002; Wood and Wade 2013), this factor of three

maps on to a factor of three for $[S]_{\text{scss}}$ (Eqn. 36). It therefore needs to be taken into account, by parameterizing $\gamma_{\text{FeO}}^{\text{sil melt}}$ as a function of melt composition and temperature. The experimental observations show that $\gamma_{\text{FeO}}^{\text{sil melt}}$ increases with alkali content (Na and K), and decreases with Ti, with a minimum in plots against X_{SiO_2} near 0.55 (O'Neill and Berry 2006; Borisov 2007). As well as reproducing these features, a parameterization needs to ensure that $\gamma_{\text{FeO}}^{\text{sil melt}} \rightarrow 1$ as $X_{\text{FeO}} \rightarrow 1$. To take these factors into account, the experimental data were fitted to the equation:

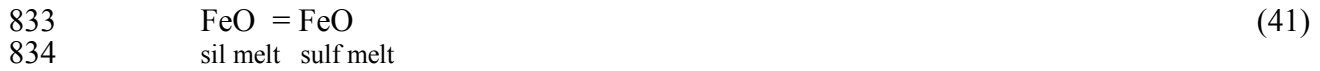
$$\begin{aligned} \text{RT ln } \gamma_{\text{FeO}}^{\text{sil melt}} = & (1-X_{\text{FeO}})^2 [W_0 + W_{\text{Mg}}X_{\text{MgO}} + W_{\text{Ca}}X_{\text{CaO}} + W_{\text{Na}}X_{\text{NaO}1.5} + W_{\text{K}}X_{\text{KO}1.5} + W_{\text{Ti}}X_{\text{TiO}_2}] \\ & + (1-X_{\text{FeO}}) [U_1X_{\text{SiO}_2} + U_2(X_{\text{SiO}_2})^2] \end{aligned} \quad (40)$$

(the W terms are not Margules coefficients, just ad-hoc parameters). All the experimental data were recalculated to the same standard state using Eqn. (37), with all compositions converted to mole fractions on the single-cation basis. An initial best fit was obtained, but to aid internal consistency a further refinement was done in conjunction with the fitting of the SCSS data, see below.

4) The activity of FeS in sulfide melts presents a somewhat different problem to that of FeO in silicate melts, simply because FeS will be the dominant component in the envisaged applications of Eqn. (36). For example, in Ocean Floor Basalts, X_{FeO} is only about 0.1, whereas $a_{\text{FeS}}^{\text{sulf}}$ varies from about 0.7 to 0.9 (see below). The contributing factors are dilution by O substituting for S, and, in part of the experimental database but ubiquitously in natural systems, dilution by other chalcophile elements, of which Ni and Cu are predominant in nature. There is continuous miscibility between liquid FeS and liquid Fe above the melting point of the latter (e.g., Waldner and Pelton 2005), such that with decreasing $f\text{O}_2$, and/or decreasing $f\text{S}_2$, Fe-S melts become increasingly metal-rich ($\text{Fe/S} > 1$). However, below $\text{Fe/S} = 1$, the contours of $f\text{S}_2$ vs. mole fraction of FeS on the join Fe-FeS are quite flat (Waldner and Pelton, their Fig. 5), indicating, incidentally, that liquid immiscibility would develop at lower temperatures, were it possible to undercool Fe-S melts. Hence $a_{\text{FeS}}^{\text{sulf}}$ is rather insensitive to changes to composition in this range. For example, Mavrogenes and O'Neill (1999) calculated that $a_{\text{FeS}}^{\text{sulf}}$ was ~ 0.5 in sulfide melts in their experiments in the limiting case of equilibrium with solid Fe metal (see also Ballhaus et al. 2017). Sulfide melts with large metal

827 excesses ($Fe/S \gg 1$) were not included in the experimental database considered here, so this aspect
 828 of the a_{FeS}^{sulf} problem was ignored.

829 The amount of oxygen dissolved in liquid sulfide mattes is a function of fO_2 , fS_2 , and both Ni
 830 and Cu contents, and temperature (Fonseca et al. 2008), indicating considerable complexity.
 831 However, switching from system variables (fO_2 , fS_2) to focus on the composition of a coexisting
 832 silicate melt suggests that the equilibrium between silicate and sulfide melts may be:



835 Hence the amount of the FeO component in the sulfide matte should vary with $a_{FeO}^{sil\ melt}$. Kiseeva
 836 and Wood (2013) showed that on a mole fraction basis, $X_{FeO}^{sulf} \simeq X_{FeO}^{sil\ melt}$, which is confirmed
 837 here, more-or-less, from the data used in the SCSS fitting that reported oxygen contents of the
 838 sulfide melt, although there is considerable scatter (Fig. 5). Measuring the oxygen content of sulfide
 839 melts is difficult, because of the complex textures produced on quenching (Kress 1997; Fonseca et
 840 al. 2008), and the task is made harder when silicate melt is present, because this phase provides a
 841 refuge for oxygen fleeing the sulfide melt during its crystallization on quenching.

842 For Ni and Cu, it has been proposed from available partitioning data that these elements may be
 843 treated as inert diluents (Smythe et al. 2017). By this hypothesis, a_{FeS}^{sulf} may be approximated in
 844 sulfide mattes that are not metal-rich (that is, their atomic $M/(S+O)$ do not differ greatly from unity)
 845 in equilibrium with silicate melts by:

$$846 \quad a_{FeS}^{sulf} = (1 - k_{Ox} X_{FeO}^{sil\ melt}) \left[\frac{Fe}{Fe+Ni+Cu+\dots} \right]_{sulf} \quad (42)$$

847 Here k_{Ox} is an equilibrium constant for reaction (41), and $\left[\frac{Fe}{Fe+Ni+Cu+\dots} \right]_{sulf}$ is the atomic ratio of
 848 Fe to other cationic diluents in the matte. In natural terrestrial basalts, only Ni and Cu are
 849 significant, but other chalcophile elements are present in the sulfide of a few of the experimental
 850 studies used as input to the model (Table 1), and all were treated similarly. Trials showed that using
 851 the simpler $X_{FeO}^{sil\ melt}$ rather than the more logical $a_{FeO}^{sil\ melt}$ in the above expression returned a
 852 slightly better result. A linear least-squares best fit found $k_{Ox} = 1.20 \pm 0.04$ (Fig. 5), but given the

scatter in the data, k_{Ox} was put at 1 following the suggestion of Kiseeva and Wood (2013), which made no perceptible difference to the SCSS fitting.

By splitting the SCSS problem up in this four-fold way, a better understanding is achieved of how SCSS responds to the different variables (T, P, silicate and sulfide melt compositions). This will enable a quantitative sensitivity analysis. The four-fold way is also useful in divining where model inadequacies may lie, and what further work would be most beneficial.

859

Fitting the experimental data on SCSS on anhydrous compositions

The experimental studies from which the data used to model SCSS were taken are listed in Table 1. These experiments are all at relatively low fO_2 , where SO_4^{2-} should be negligible. Only nominally anhydrous experiments were considered; the effect of H_2O will be addressed briefly below. Experiments at > 5 GPa were also not considered, due to the large changes in silicate melt structure expected at higher pressures and high liquidus temperatures introducing extra experimental uncertainty. Given the lack of experimental information on $\gamma_{FeO}^{sil melt}$ at high SiO_2 , so were compositions with $X_{SiO_2} > 0.62$. The limited information available hints at a large increase in $\gamma_{FeO}^{sil melt}$ with X_{SiO_2} at higher SiO_2 (O'Neill and Berry 2006; Borisov 2007). Data on compositions with < 1 wt% FeO were also excluded for reasons described later. To account for the effect of pressure in Eqn. (36), two terms were added, the usual one in P/T but modified by a second term in $\text{erf}(P)/T$, to allow for coordination changes in the silicate melt. This extra term will be discussed in detail below. The model to which the data were fitted was:

$$\begin{aligned} \ln [S]_{SCSS} = & [\Delta G_{FeO}^{o, sil melt} + \Delta H_{FeS}^o - T\Delta S_{FeS}^o] / RT + \ln C_{S^{2-}} - \ln X_{FeO}^{sil melt} - \ln \gamma_{FeO}^{sil melt} \\ & + (1 - X_{FeO}^{sil melt}) \left[\frac{Fe}{Fe+Ni+Cu+\dots} \right]_{sulf} + (C_1 P + C_2 \text{erf}(C_3 P)) / T + \end{aligned} \quad (43)$$

where the parameters to be determined are ΔH_{FeS}^o , ΔS_{FeS}^o , C_1 , C_2 and C_3 from the SCSS experiments, plus the coefficients in Eqn. (40) for $\gamma_{FeO}^{sil melt}$ from the entirely separate $a_{FeO}^{sil melt}$ vs. X_{Fe} experiments.

878 The fitting was by weighted least squares, minimizing the objective function $((\ln [S]_{\text{SCSS}(\text{obs})} -$
 879 $\ln[S]_{\text{SCSS}(\text{calc})})/s(\ln[S]_{\text{SCSS}}))^2$, subject to the constraint that a second objective function for the
 880 optimization of $\gamma_{\text{FeO}}^{\text{sil melt}}$, namely $((T \ln \gamma_{\text{FeO}}^{\text{sil melt}})_{\text{obs}} - (T \ln \gamma_{\text{FeO}}^{\text{sil melt}})_{\text{calc}})/s(T \ln \gamma_{\text{FeO}}^{\text{sil melt}}))^2$, did
 881 not increase by more than 2.5% above its best fit value obtained independently of the SCSS data.
 882 The 2.5% limit corresponds to less than a percent change in the level of significance. This
 883 procedure ensures internal consistency between the different parts of the model. It also has the
 884 beneficial effect of bringing more of the relevant compositional space for silicate melts into the
 885 parameterization of $\gamma_{\text{FeO}}^{\text{sil melt}}$, and the fact that this can be done within the 2.5% limit chosen shows
 886 that, despite the 600 experimental observations, more data are needed on a wider compositional
 887 range (particularly towards high MgO, and as pointed out above, high SiO₂). For the weighting,
 888 $s(RT \ln \gamma_{\text{FeO}}^{\text{sil melt}})$ was taken as 800 J mol⁻¹ for every datum. This value corresponds approximately
 889 to $s(\log f\text{O}_2) = 0.03$ and 5% relative uncertainty in $X_{\text{FeO}}^{\text{sil melt}}$. The value of $s([S]_{\text{SCSS}})$ was taken as
 890 reported, or 5%, whichever was larger. This uncertainty dominates the other uncertainties in the
 891 SCSS measurements, namely temperature, pressure, major-element composition, and the minor
 892 amounts of H₂O expected to contaminate most high-pressure experiments but which are usually not
 893 measured. The exception is at very low $X_{\text{FeO}}^{\text{sil melt}}$, where $s(X_{\text{FeO}}^{\text{sil melt}})$ becomes dominant as $[S]_{\text{SCSS}}$
 894 rises sharply (Wykes et al. 2015). For this reason, and because the composition of the sulfide liquid
 895 in equilibrium with such compositions is somewhat uncertain (possibilities include M/S >> 1 and the
 896 presence of normally lithophile components), the data with < 1wt% FeO were filtered out of the
 897 input.

898 A major problem with combining experimental datasets from different experimental studies
 899 performed in different laboratories and addressing different volumes of T-P-compositional space is
 900 the way that systematic error can translate into misleading effects. For example, consider a study
 901 that reports S contents that are systematically too high, perhaps due to instrument calibration. If that
 902 study provided most of the data at, say, high pressure, then this systematic error in S analysis would
 903 translate into the modeling as an effect of pressure. For analytical aspects, the effects of this type of

904 problem can be ameliorated by reporting analyses of widely available standards. Many of the input
 905 studies listed in Table 1 have done this using the natural glass VG2 (USNM 111240/52; Jarosewich
 906 1980) with c. 1400 ppm S, which provides a valuable point of comparison (Table 2). The inter-
 907 laboratory differences are considerable in some cases. The homogeneity of VG2 is unknown, and
 908 the amount of S, although typical of Ocean Floor Basalt glasses, is well below that found in some
 909 reduced glasses let alone in oxidized ones with S as SO_4^{2-} . It would be helpful to have inter-
 910 laboratory comparisons available for other standard glasses, perhaps synthetic, with tested
 911 homogeneity and higher sulfur contents, one with S as S^{2-} and another with S as SO_4^{2-} .

912 Of all the initially included studies, only the data of Holzheid and Grove (2002) could not be
 913 well fitted, consistently returning calculated values of $[\text{S}]_{\text{scss}}$ higher than observed. This may be
 914 due to failure to account for $\gamma_{\text{FeO}}^{\text{sil melt}}$ adequately in these high MgO compositions, alternatively the
 915 effect of pressure on depressing $[\text{S}]_{\text{scss}}$ appears higher in these experiments than in others.
 916 Although there is no independent reason to do so, the data of Holzheid and Grove (2002) were
 917 removed from the fitting, except for their four experiments with high Ni in the sulfide.

918 The numerical value of C_3 was found to be insignificantly different from 1 (units in GPa^{-1}), so it
 919 was fixed at this value, which then gave $C_1 = -291 \text{ GPa K}^{-1}$ and $C_2 = 351 \text{ K}^{-1}$. For reaction (38), the
 920 optimization produced:

$$921 \quad \Delta G_{\text{FeS}}^{o, \text{sulf melt}} (\text{J mol}^{-1}) = -106340 + 23.893 T \quad (44)$$

922 This gives $-70.5 \text{ kJ mol}^{-1}$ at 1500 K, in between the values tabulated by Barin (1989) and Robie
 923 and Hemingway (1995), namely - 70.0 and -73.4 kJ mol^{-1} , respectively. This agreement is a notable
 924 affirmation of the model, because the determination of $G_{\text{FeS}}^{o, \text{sulf melt}}$ is independent of anything to do
 925 with silicate melts. The free energy for reaction (35) is therefore:

$$926 \quad \Delta G_{\text{FeO-FeS}}^o (\text{J mol}^{-1}) = 137778 - 91.66 T + 8.474 T \ln(T) \quad (45)$$

927 The reduced chi-squared for the regression, χ_v^2 , was 3.7 ($n = 407$, four refined parameters).
 928 Including the term for pressure in $\text{erf}(P)/T$ decreased χ_v^2 from 4.8, a significant improvement since a
 929 third of the experiments are at ambient pressure. The rather high value of χ_v^2 is explicable at least in

part by inter-laboratory differences in determining S (cf. Table 2), pressure, temperature, oxidation state, unanalyzed H₂O in high pressure experiments, and other factors that may differ between studies, and which were not included in the uncertainties used for weighting.

The parameterization of $\gamma_{FeO}^{sil\ melt}$ gave:

$$\begin{aligned} RT \ln \gamma_{FeO}^{sil\ melt} = & (1 - X_{FeO}^{sil\ melt})^2 [28870 - 14710 X_{MgO}^{sil\ melt} + 1960 X_{CaO}^{sil\ melt} \\ & + 43300 X_{NaO_{0.5}}^{sil\ melt} + 95380 X_{KO_{0.5}}^{sil\ melt} - 76880 X_{TiO_2}^{sil\ melt}] \\ & + (1 - X_{FeO}^{sil\ melt}) [-62190 X_{SiO_2}^{sil\ melt} + 31520 (X_{SiO_2}^{sil\ melt})^2] \end{aligned} \quad (46)$$

with $\chi^2_v = 2.9$. Note the large effect that the alkalis, Na and even more so K, have on increasing $\gamma_{FeO}^{sil\ melt}$. The comparison between the measured values of $\gamma_{FeO}^{sil\ melt}$ and those calculated from this parameterization is shown in Fig. 4.

Fe³⁺/ΣFe in the silicate melts in the experiments that measured $\gamma_{FeO}^{sil\ melt}$ would be insignificantly different from zero, because all these experiments were in equilibrium with metallic Fe. No provision for Fe³⁺ was made in the fitting of the SCSS experiments, either. Because of the constraints on how experiments are done, Fe³⁺/ΣFe in the silicate melts of the SCSS database are < 0.02 for atmospheric-pressure experiments (see Tuff and O'Neill 2010, their Table 5), but likely a little more in many of the higher-pressure experiments, which, because of the prevalence of graphite in the pressure assemblies if not the sample capsules, usually return redox conditions about a log unit in log fO₂ below the graphite-CO₂ buffer, hence two log units below the quartz-fayalite-magnetite equilibrium (Frost and Wood 1997), corresponding to approximately 0.03 in Fe³⁺/ΣFe at atmospheric pressure.

The effect of pressure on SCSS

Experimental studies have established that SCSS decreases substantially with increasing pressure at high pressures (Wendlandt 1982; Mavrogenes and O'Neill 1999; Holzheid and Grove 2002; Smythe et al. 2017), as shown in Fig. 6. The important consequence is that “primary” magmas should erupt undersaturated in sulfide, if the temperature decrease during their ascent is no

956 more than adiabatic (Mavrogenes and O'Neill 1999). However, Liu et al. (2007) found no
 957 difference in SCSS between 0.5 and 1 GPa in two pairs of experiments, although the uncertainty
 958 was large (see their Fig. 2). The present fitting exercise showed that this view has merit. If only the
 959 data in the interval from 0 to 1.5 GPa were considered, there would appear to be little or no effect of
 960 pressure. The possibility exists that the effect of pressure changes with pressure. This is not
 961 surprising; previously, it has been assumed in fitting experimental data that the relevant $\int VdP$
 962 terms in the four quantities in Eqn (36) could be approximated by a constant: that is, $\ln [S]_{\text{SCSS}}$
 963 varied linearly with P/T (Mavrogenes and O'Neill 1999). This simplification has long been
 964 accepted as a viable first-order approximation in solid-state reactions, where, in essence, it assumes
 965 that the effects of the thermal expansivities and bulk moduli of the individual crystalline phases in
 966 the reaction cancels out across the reaction. But silicate melts have different P-V characteristics
 967 from crystalline phases. With increasing pressure, the main aluminosilicate structural units change,
 968 while the average coordinating number of the nearest-neighbour anions forming the coordination
 969 polyhedra around the M^{x+} cations tends to increase. Possibly the coordination environment of the
 970 S^{2-} anions also change with pressure. Such changes are more akin to order-disorder phenomena or
 971 even phase transitions than to the effects of compressibility on the $\int VdP$ terms in crystals, so
 972 carrying over an approximation from experience with crystals may not be such a good idea. Trials
 973 fitting the data with polynomials, such that $\ln [S]_{\text{SCSS}}$ varied with terms in $C_n P^n/T$, produced a
 974 marked hump in $[S]_{\text{SCSS}}$ vs. P in the range 0 to 1 GPa, where there are almost no data to constrain
 975 reality. As a hump seems implausible, compared to no change in $[S]_{\text{SCSS}}$ vs. P in this range, the
 976 relationship was described using an error function in Eqn. (43), despite reservations about
 977 employing this function twice in one paper. The form of the suggested pressure-dependence is
 978 compared to the conventional views in Fig. 6. Above ~ 1 GPa, there is little difference from the
 979 conventional assumption.

980 With increasing pressure above ~ 5 GPa, SCSS becomes very low (e.g., Li and Agee 2001),
 981 confirming the trend in Fig. 6, but precise experimental measurements are difficult because of the

982 high silicate liquidus temperatures, and the fact that the melts do not quench to glasses, making it
983 difficult to know if the tiny sulfide globules commonly encountered are exsolved on quenching or
984 not.

985 Experimental studies to date have not been designed to cope with the possibility that the
986 pressure dependence of SCSS may be non-linear. For example the classic study of Wendlandt
987 (1982) investigated pressures only between 1.25 and 3 GPa, completely missing the hypothetical
988 low-pressure inflection shown in Fig. 6. A more detailed look at the pressure-dependence of SCSS
989 between 0 and 1 GPa is needed.

990

991 *The dependence of SCSS on FeO*

992 SCSS depends on the FeO content in the silicate melt mainly in two ways (Eqn. 36). The $C_{S^{2-}}$ -
993 term causes a linear increase of SCSS with increasing $X_{FeO}^{sil\ melt}$, except, as reviewed above, at high
994 FeO (> 15 wt%), whereas the $a_{FeO}^{sil\ melt}$ term causes a logarithmic decrease of SCSS with increasing
995 $X_{FeO}^{sil\ melt}$ (modulated somewhat by changes in $\gamma_{FeO}^{sil\ melt}$ with X_{FeO}). These competing effects may
996 conveniently be studied by measuring SCSS on a compositional pseudo-binary between a FeO-free
997 “matrix” composition and FeO, with temperature and pressure kept constant. Such a series
998 eventuates anyway in 1-atmosphere experiments conducted over a range of fO_2 and fS_2 , when FeO
999 is removed from an initial composition by exsolution of an FeS-rich matte in response to decreasing
1000 fO_2 and/or increasing fS_2 (Haughton et al. 1974; O'Neill and Mavrogenes 2002). The result is that
1001 graphs of SCSS vs. FeO (wt%) for these pseudo-binaries should have an asymmetric U shape.
1002 Demonstrating this with 1-atmosphere experiments has been unconvincing, because sufficiently
1003 high fS_2 cannot be imposed to access much of the left-hand side of the “U” (Haughton et al. 1974;
1004 O'Neill and Mavrogenes 2002). To get around this, Wykes et al. (2015) performed a series of
1005 experiments at 1400°C and 1.5 GPa. The results are compared to the present model in Fig. 7. The
1006 fix of parameterizing $C_{S^{2-}}$ at high FeO with an error-function term (Eqns. 33 and 34) works well in
1007 describing the data to the highest FeO measured (30 wt%). For a comparison of these data against

1008 previous models, see Wykes et al. (2015), their Fig. 9. The model also works well for the data at < 1
1009 wt% FeO, which were not used in the SCSS fitting. Also plotted on this diagram are some
1010 previously unpublished data (Table 3), using the same starting composition and Re capsules as
1011 described in Wykes et al. (2015), but with water added. The Re capsules did not hold the H₂O
1012 quantitatively, but some H₂O was found in the recovered glasses, as determined by FTIR. The
1013 concentration of H₂O actually increased from the added amount in one run (G76). The major
1014 elements and S analyses were obtained by EMPA, as described in O'Neill and Mavrogenes (2002),
1015 but as the major elements were only determined by Energy Dispersive Spectrometry (EDS), they
1016 have been recalculated to 100% taking into account the analysed S and H₂O contents. The latter
1017 were measured as described in Liu et al. (2005).

1018

1019 *The effect of H₂O*

1020 Naldrett and Richardson (1967) showed that H₂O had no perceptible effect on the melting point
1021 of pyrrhotite-magnetite assemblages at 0.2 GPa, implying that this component has negligibly small
1022 solubility in Fe-S-O melts at these conditions. This is supported by the experiments of Moune et al.
1023 (2009), who report pyrrhotite, not sulfide melt, at 1045°C, ~ 0.3 GPa. Thus the effect of H₂O can be
1024 isolated to what happens in the silicate melt. In the context of the four-fold way, two variables, $C_{S^{2-}}$
1025 and $\alpha_{FeO}^{sil\ melt}$, will be affected by adding H₂O, but the presence of H in the system could perhaps
1026 also result in S dissolving as anionic species in addition to the species that predominate in dry
1027 systems (S²⁻ and SO₄²⁻), for example HS⁻, or perhaps, by analogy with OH⁻/H₂O speciation, as
1028 molecular H₂S in high-SiO₂ melts (Clemente et al. 2004). At present there is no compelling
1029 evidence for HS⁻ in FeO-containing hydrous basic or intermediate melts (Wilke et al. 2011; Wykes
1030 et al. 2015), and the following discussion will assume that only S²⁻ is present in the relevant fO₂
1031 range.

1032 Adding H₂O to silicate melts is thought to break up framework silicate units, which decreases
1033 the activity of SiO₂. From reaction (10), this should increase S²⁻ in the silicate melt. However,

potential additional anion units like OH⁻ or SiO₃OH³⁻ (the hydroxylated orthosilicate unit), add complexity to the anion sublattice, with input into the reciprocal solution formalism that cannot be predicted at present. But there is a simpler effect that first needs to be addressed. It is dilution. Adding H₂O to a silicate melt adds oxygen anions to the anion sublattice, and when converted into mole fractions, petrologically reasonable amounts can be seen to be large: for typical basaltic compositions, 5 wt% H₂O correspond to about 0.25 in $X_{HO_{0.5}}^{sil\ melt}$ (mole fraction on the single-cation basis). The mole fractions of all the other oxide components $X_{MO_{x/2}}^{sil\ melt}$ are lowered, by a factor of $(1 - X_{HO_{0.5}}^{sil\ melt})$. By itself, this dilution effect should influence SCSS in two ways: 1) by lowering $a_{FeO}^{sil\ melt}$; 2) by lowering all the $X_{MO_{x/2}}^{sil\ melt}$ (M≠H) in the model for $C_{S^{2-}}$ (Eqn. 34).

Potentially, H₂O could change $\gamma_{FeO}^{sil\ melt}$. Not much is known about how H₂O effects individual activity coefficients in silicate melts, but a qualitative judgment can be made from the observation that H₂O has only a minimal influence on the partitioning of Fe²⁺ and Mg between olivine and silicate melt (Toplis 2005). This indicates that any effect of H₂O cancels out in the ratio $\gamma_{FeO}^{sil\ melt} / \gamma_{MgO}^{sil\ melt}$, which would be unlikely if the effect of H₂O on either activity coefficient were huge. Therefore, it is assumed that $\gamma_{FeO}^{sil\ melt}$ may be evaluated as per Eqn. (46), with no additional terms.

This “dilution” hypothesis was tested against the available experimental database for SCSS in H₂O-containing silicate melts, as follows. Only experiments at sufficiently low fO₂ that S⁶⁺/S²⁻ should be near zero were considered: Moune et al. (2009); Fortin et al. (2015); D’Souza and Canil (2018); and Table 3. The sulfide capacities of hydrous melts may conceptually be divided into two parts, that due to the anhydrous oxide components, taking account of their dilution by the factor of $(1 - X_{HO_{0.5}}^{sil\ melt})$, called here $C_{S^{2-}}^{dil}$, and that due to terms in $X_{HO_{0.5}}^{sil\ melt}$, called here $C_{S^{2-}}^H$, such that $C_{S^{2-}} = C_{S^{2-}}^{dil} C_{S^{2-}}^H$. The calculated SCSS due only to dilution is then:

$$\ln [S]_{SCSS(dil)} = \Delta G_{FeO-FeS}^0 / RT + \ln a_{FeS}^{sulf} + \ln C_{S^{2-}}^{dil} - \ln X_{FeO}^{sil\ melt} - \ln \gamma_{FeO}^{sil\ melt} \quad (47)$$

and the difference between the measured S and this calculated [S]_{SCSS(dil)} is given by:

$$\ln C_{S^{2-}}^H = \ln [S]_{obs} - \ln [S]_{SCSS(dil)} \quad (48)$$

1059 The calculated values of $\ln C_{S^{2-}}^H$ from the input experiments are plotted against $X_{HO_{0.5}}^{sil\ melt}$ in Fig.
 1060 8a, which shows that they scatter around a fairly well defined curve of somewhat parabolic shape.
 1061 Some scatter would be expected from the effect of H₂O on the activity of SiO₂. D'Souza and Canil
 1062 (2018) also proposed a strong effect of Na and K, from the difference between the two
 1063 compositions studied by them. With these considerations, the experimental data were fitted by non-
 1064 linear least-squares regression assuming uncertainties in both S and H₂O contents, with $s([S])$ taken
 1065 as 5% or as reported, whichever is larger, and $s(H_2O)$ as 0.1 wt% + 0.05[H₂O], to parameterize $C_{S^{2-}}^H$
 1066 as:

$$1067 \quad \ln C_{S^{2-}}^H = X_{HO_{0.5}}^{sil\ melt} (6.4 + 12.4 X_{HO_{0.5}}^{sil\ melt} - 20.3 X_{HO_{0.5}}^{sil\ melt} + 73 X_{HO_{0.5}}^{sil\ melt}) \quad (49)$$

1068 The uncertainties in the reported H₂O contents have almost as much influence on the regression as
 1069 those on the S contents, and cannot be neglected; they must also be propagated through the entire
 1070 model, because of their effect on calculating the mole fractions of the other components. The
 1071 reduced chi-squared for the fit was 5.0, indicating that the model is too simplistic, if the weighting
 1072 of the data is reasonable; but as the four experimental studies address different compositions at
 1073 different temperatures and pressure, to use more variables could be misleading. The experiments of
 1074 Moune et al. (2009), all at 1045°C, ~ 0.3 GPa, were saturated with pyrrhotite, not FeS-rich matte,
 1075 requiring calculation of the activity of FeS relative to the standard state of liquid FeS. This was
 1076 done using the enthalpy of melting and the melting temperature of pure FeS of 32.34 kJ mol⁻¹ at
 1077 1468 K from Robie and Hemingway (1995), to give $a_{FeS}^{sulf} = 1.35$, with X_{FeO}^{sulf} taken to be zero (no
 1078 dissolved O in pyrrhotite. No correction was attempted for the stoichiometry of the pyrrhotite (i.e.,
 1079 deviations from atomic Fe/S = 1), as this was not reported. Pyrrhotite in comparable experiments is
 1080 only a little metal-deficient, with Fe/S ~ 0.96 (Luhr 1990). The concentrations of S calculated from
 1081 the model (Eqns. 47 to 49) are compared to the observed values in Fig. 8b. Most of the data are
 1082 reproduced to within ± 10%.

1083 The net effect of adding H₂O to a silicate melt is a tradeoff between the dilution effect (where
 1084 obviously $C_{S^{2-}} > C_{S^{2-}}^{dil}$) and the increase in $C_{S^{2-}}$ due to the addition of the $C_{S^{2-}}^H$ term. The dilution

effect depends to a large extent on the FeO content of the melt, hence there should be a substantial difference in the net effect of adding H₂O between high and low FeO compositions. For low FeO compositions, adding H₂O should increase $C_{S^{2-}}$, and vice versa. Presumably, for the effect of H₂O on the sulfate capacity, $C_{SO_4^{2-}}$, the same principle would apply ($C_{SO_4^{2-}} = C_{SO_4^{2-}}^{dil} - C_{SO_4^{2-}}^H$).

At present, nothing seems to be known about the effects on the solubilities of either S²⁻ or SO₄²⁻ of CO₂, whose own solubility in silicate melts becomes considerable above ~ 2 GPa, nor of other volatile species.

Application to mid-ocean ridge and similar basalts

The geochemistry of ocean floor basaltic (OFB) magmatism has been intensively studied from the perspective of the glassy rinds on erupted pillows. These glasses typically contain ~10³ ppm total sulfur (Mathez 1976; Czamanske and Moore 1977), which is in the range quantifiable by electron microprobe to about 5% precision with a bit of care. Métrich et al. (2009) used XANES spectroscopy to show that the oxidation state of nearly all the S in three representative glasses was S²⁻, with 4 to 8% as SO₄²⁻, which they proposed was produced on cooling. Many of the glasses contain globules of quenched sulfide mattes, often nearly spherical in shape, with diameters mostly in the range 10 to 100 μm, with an average of 27 μm according to Patten et al. (2012), although some up to 600 μm have been reported elsewhere (e.g., Czamanske and Moore 2007). The textures of the phase assemblages in the globules vary, at least in part due to differences in cooling rates (e.g., Patten et al. 2012). Bulk compositions of the globules are more reliably estimated for those with finer-grained textures, and are fairly rich in Ni and Cu. For example, the average Ni and Cu contents of 14 fine-grained globules from Patten et al. (2012) are 6.1 ± 2.9 and 8.5 ± 4.0 wt% respectively, with atomic Fe/(Fe+Ni+Cu) being 0.78 ± 0.05 .

The existence of these globules has been attributed to the erupted basalts being at sulfide saturation (Mathez 1976; Czamanske and Moore 1977), hence the S contents of their host basalt glasses should correspond to their SCSS at their eruption temperature and pressure. Several

1111 attempts have been made to compare their measured S contents against models for the SCSS, but
1112 this requires knowing the temperature of the basalt at the time the sulfide matte separated from the
1113 silicate liquid, plus correction for its Ni and Cu contents. Only the recent work of Smythe et al.
1114 (2017) has addressed this issue quantitatively, although Ariskin et al. (2013) did consider Ni.
1115 Another issue is that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in OFB glasses is typically about 10% (Berry et al. 2018), which
1116 must lower $a_{\text{FeO}}^{\text{sil melt}}$ by about this amount compared to calculations that assume all Fe in the silicate
1117 melt to be Fe^{2+} .

1118 The model for SCSS derived from experimental data in this contribution may be tested against
1119 the global dataset of Ocean Floor Basaltic glasses of Jenner and O'Neill (2012), for which S
1120 concentrations in 329 samples were determined by EMPA. The advantages of this dataset for
1121 present purposes is that it is eclectic in geographical locations and tectonic nuances, and that the
1122 determination of S concentrations was standardized against the OFB glass VG2 (Table 2). The S
1123 concentrations are the means of at least five individual analyses on each sample, with standard
1124 deviations giving an indication of sample homogeneity. In order to apply the SCSS model, some
1125 enabling assumptions need to be made, as follows.

- 1126 1) Sample temperatures were estimated using the magmathermometer of Putirka (2008), his
1127 Eqn. (15), with H_2O put to zero. This thermometer assumes the presence of olivine, hence
1128 is inappropriate for the most evolved OFB glasses, but with the necessary caveat it will be
1129 used here in extrapolation for all OFB glasses with > 4 wt% MgO. The equilibrium
1130 pressure was taken to be the pressure from which the samples were recovered, or 0.03
1131 GPa if this was not known, but the effects of pressure are trivial with the present model.
- 1132 2) The H_2O content of OFB glasses is generally < 0.5 wt% (e.g., Michael 1995; Le Voyer et
1133 al. 2015; Shimizu et al. 2016), and in view of the absence of experimental data on the
1134 effect of H_2O at the relevant pressures and temperature, the low sensitivity of SCSS to
1135 H_2O in this range (Fig. 8), and the lack of direct determination of H_2O in the dataset of

Jenner and O'Neill (2012), H₂O has initially been assumed to be zero. This assumption will be examined subsequently (see below).

3) The approximation used in modelling the experimental data, that Fe³⁺ in the silicate melts is low enough to be neglected, is not valid for OFB glasses. During OFB petrogenesis Fe³⁺ behaves as a Lightly InCompatible trace Element (LICE), whose concentration as the oxide component in wt% is given by $\ln[\text{Fe}_2\text{O}_3] = 1.46 - 0.177 [\text{MgO}]$ (Berry et al. 2018; O'Neill et al. 2018). Because Fe³⁺/Fe²⁺ has been measured in only a subset of the samples analysed for S by Jenner and O'Neill (2012), it was estimated from the above relationship against MgO. Potentially, Fe²⁺-Fe³⁺ interactions in the melt could also effect $\gamma_{\text{FeO}}^{\text{sil melt}}$, so an extra term, $W_{\text{Fe}^{3+}} X_{\text{Fe}^{3+}\text{O}_{1.5}}^{\text{sil melt}}$, was added to Eqn. 46, with $W_{\text{Fe}^{3+}}$ to be determined by fitting to the natural data, as described below. As discussed previously, there is no information at all on how Fe³⁺ affects $C_{\text{S}^{2-}}$, so for the calculation of this quantity, Fe²⁺O was put equal to total FeO.

4) Although the composition of the sulfide is not known, it should be specified by the composition of the silicate melt, assuming equilibrium. As diluents of FeS, only Ni, Cu and O are present in sufficient amounts to affect $a_{\text{FeS}}^{\text{sulf}}$. For Ni, the equilibrium between sulfide and silicate melts is:



Hence the atomic ratio Ni/Fe in the sulfide is given by:

$$\text{Ni/Fe (atomic)} = K_{\text{Ni/Fe}}^* [\text{Ni}]/[\text{Fe}^{2+}\text{O}] \quad (51)$$

The concentrations of Ni and Fe²⁺O in the silicate melt are input in ppm and wt% respectively, where $[\text{Fe}^{2+}\text{O}] = [\text{FeO}_{\text{tot}}] - 0.8998 [\text{Fe}_2\text{O}_3]$. The equilibrium constant $K_{\text{Ni/Fe}}^*$ includes implicitly the ratio of the activity coefficients of NiO and Fe²⁺O in the silicate melt ($\gamma_{\text{NiO}}^{\text{sil melt}}/\gamma_{\text{Fe}^{2+}\text{O}}^{\text{sil melt}}$). The change of $\gamma_{\text{NiO}}^{\text{sil melt}}$ with silicate melt composition parallels that of $\gamma_{\text{Fe}^{2+}\text{O}}^{\text{sil melt}}$ (O'Neill and Eggins 2002), so that this ratio is relatively insensitive to composition and may be approximated as a

constant. The stoichiometry of the equivalent Cu-Fe²⁺ exchange reaction is not so convenient, because the oxidation state of Cu is 1+ in the silicate melt and potentially a mixture of CuS_{0.5} and CuS components in the sulfide matte, depending on fS₂ (e.g., Ripley et al. 2002), but to keep things simple, it is proposed that Cu/Fe (atomic) may be approximated in the same way over the limited range of conditions appropriate to OFB. Hence:

$$a_{FeS}^{sulf} = (1 - X_{Fe^{2+}O}^{sil\ melt}) / (1 + K_{Ni/Fe}^* [Ni]/[Fe^{2+}O] + K_{Cu/Fe}^* [Cu]/[Fe^{2+}O]) \quad (52)$$

These enabling assumptions require three unknown parameters, $W_{Fe^{3+}}$, $K_{Ni/Fe}^*$ and $K_{Cu/Fe}^*$, the values of which were estimated by “tuning” the model to fit the data of Jenner and O’Neill (2012) by least squares, minimizing $(([S]_{obs} - [S]_{SCSS, calc})/[S]_{obs})^2$, where $[S]_{obs}$ was taken as 5% or as given by Jenner and O’Neill (2012), whichever is larger. Because Ni and Cu decrease, and Fe³⁺ increases monotonically with MgO in OFB glasses, these three parameters are highly correlated with each other.

Of the 329 OFB glasses, 11 were identified as possibly having lost S or being sulfide-undersaturated, and removed from consideration. These samples will be revisited below. Of the remaining 318 glasses, Jenner and O’Neill (2002) identified 17 in which the standard deviation of the S analyses was far above analytical precision, and this heterogeneity was confirmed by replicating the analyses in another session. Although these samples cannot be at equilibrium, their large standard deviations give them little weight in the regression, and they were retained. Initial fitting gave $W_{Fe^{3+}}$ within uncertainty of zero, so it was fixed at this value, giving $K_{Ni/Fe}^* = 0.013$, and $K_{Cu/Fe}^* = 0.025$, with a reduced chi-squared, χ_v^2 , of 1.45.

The agreement between the measured S content, $[S]_{obs}$, and the calculated SCSS, is shown in Fig. 9a. Generally, OFB glasses not occurring as melt inclusions have degassed some CO₂, with their remaining CO₂ corresponding to CO₂ solubility at the water depth at which they erupted (e.g., Dixon and Stolper 1995). On the present evidence, this degassing does not usually cause perceptible S loss. Exceptions are 11 data with low $[S]_{obs}$, which are independently distinguishable by their low S/Se ratio (Fig. 9b), implying that they have lost S by volatilization, since Se is less volatile than S

1188 (Jenner et al. 2010). None of these S-deficient samples (VG numbers 1672, 1673, 1674, 1677, 4750,
 1189 4751, 4754, 4755, 6822, 8550, 8555), were erupted at particularly shallow depths. Elsewhere,
 1190 Nilsson and Peach (1993) demonstrated a correlation between S loss and $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by
 1191 wet chemistry in back-arc basin glasses from the Lau Basin; see also Jenner et al. (2010). Here the
 1192 only glass for which $\text{Fe}^{3+}/\text{Fe}^{2+}$ has been measured is VG6822 (Berry et al. 2018), whose oxidation
 1193 state is unexceptional (Fig. 10), so in this particular case its S loss by degassing was not promoted
 1194 by an unusually high oxidation state compared to other OFB glasses. Two of the samples (VG8550
 1195 and VG8555, from the Tuzo Wilson seamounts) have significantly lower S/Se than that expected
 1196 from just S loss (Fig. 9b), which is intriguing. One possibility is if the devolatilizing magma
 1197 contained abundant sulfide globules, which were resorbed back into the silicate melt during S loss.

1198 The calculated compositions of the sulfide mattes that are assumed to be in equilibrium with
 1199 each glass provide another test of the model. Observed compositions of bulk sulfide globules from
 1200 OFB are available from Czamanske and Moore (1977) and Patten et al. (2012). As the former study
 1201 does not give the compositions of the host basalts, only their TiO_2 contents, this variable was used
 1202 in Fig. 11 to compare Ni/Fe and Cu/Fe measured in the real sulfide globules with the calculated
 1203 ratios in the hypothetical sulfide in equilibrium with each of the glasses from Jenner and O'Neill
 1204 (2012). For both Ni/Fe and Cu/Fe, the calculated values fall within the range of those observed,
 1205 indicating that the values of $K_{\text{Ni/Fe}}^*$ and $K_{\text{Cu/Fe}}^*$ from the model are reasonable. The large scatter in
 1206 the Ni/Fe and Cu/Fe ratios in the natural sulfide globules evident in these figures reflects a lack of
 1207 equilibrium between glass and sulfide and/or the difficulties of analyzing the bulk globules on
 1208 account of their crystallization to polyphase assemblages.

1209 The good agreement between $[\text{S}]_{\text{obs}}$ and $[\text{S}]_{\text{SCSS}}$ shown in Fig. 9a indicates that S^{6+} is no more
 1210 than a few percent of total S in these glasses, a possible exception being VG 614, which has the
 1211 highest $[\text{S}]_{\text{obs}}$ of any glass in the dataset, and the lowest MgO (4.85 wt%). This finding is
 1212 compatible with the model of Nash et al. (2019) for $\text{S}^{6+}/\Sigma\text{S}$ as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 2). It is
 1213 reinforced by comparing the values of $\text{Fe}^{3+}/\Sigma\text{Fe}$ that were measured by XANES spectroscopy by

1214 Berry et al. (2108) in a subset of 35 of the OFB glasses of Jenner and O'Neill (2012) with the
 1215 difference between $[S]_{\text{obs}}$ and the calculated SCSS (Fig. 10). There is almost no correlation ($R^2 =$
 1216 0.16), which also implies that the fO_2 of OFB glasses lies below the threshold at which $S^{6+}/\Sigma S$
 1217 becomes more than a few percent (see Fig. 2). That the model fits the data with the tuning
 1218 parameter $W_{Fe^{3+}} \sim 0$ is circumstantial evidence that the effect of changing Fe^{3+}/Fe^{2+} on $C_{S^{2-}}$ may
 1219 be small. The way that $Fe^{3+}/\Sigma Fe$ influences SCSS seems to be entirely through its lowering of
 1220 $X_{FeO}^{sil\ melt}$ from that which would be calculated assuming $Fe^{3+}/\Sigma Fe = 0$.

1221 An Excel spreadsheet called "SCSS_Calculator.xlsx" for calculating SCSS according to the
 1222 routine described above is included in Supporting Information.

1223

1224 *Sensitivity analysis*

1225 For each variable X, the sensitivity may be defined as $\partial[S]_{\text{SCSS}}/\partial n_X$, where n_X is a convenient
 1226 unit of the variable. The values of $\partial[S]_{\text{SCSS}}/\partial n_X$ were calculated for representative glass with a
 1227 typical composition (VG 390), and are given in Table 4.

1228 These sensitivities may be used to calculate a representative non-systematic uncertainty (i.e.,
 1229 precision) in $[S]_{\text{SCSS}}$, under the approximation of the equation for the propagation of small errors:

$$1230 \quad s([S]_{\text{SCSS}}) = [\sum (s(X)/n_X)^2 (\partial[S]_{\text{SCSS}}/\partial n_X)^2]^{1/2} \quad (53)$$

1231 Taking $s(MO_{x/2}) = 0.1$ wt% ($M = \text{Na, Mg, Al, Ca, and Fe as FeO}_t$), $s(\text{MnO})$ and $s(\text{TiO}_2) = 0.03$
 1232 wt%, $s(\text{SiO}_2) = 0.2$ wt%, $s(T) = 20$ K, $s(\text{Ni})$ and $s(\text{Cu}) = 10$ ppm, and $s(Fe^{3+}/\Sigma Fe) = 0.03$,
 1233 propagates to $s([S]_{\text{SCSS}}) = 64$ ppm, or about 5.5% of the average S content of the undegassed OFB
 1234 glasses of Jenner and O'Neill (2012), which is 1150 ppm. The largest contribution to the
 1235 uncertainty comes from temperature, followed by $Fe^{3+}/\Sigma Fe$, then FeO_t , but reasonably accurate
 1236 knowledge of the Ni and Cu contents of the silicate glass are also needed. Easy to overlook would
 1237 be the effect of MnO, which contributes to $C_{S^{2-}}$ as much as does FeO on a proportional basis, but
 1238 does not contribute to $a_{FeO}^{sil\ melt}$. Consequently, ignoring the ~ 0.2 wt% MnO typical of OFB would
 1239 alone cause an error in SCSS of 3%. The sensitivity of the model to the effect of pressure is

speculative only, given the present lack of constraints on the effects of pressure at less than 1 GPa (Fig. 6), and was therefore not included.

Is neglecting H₂O in OFB glasses justified?

Although H₂O has not been directly measured in the OFB glasses analysed by Jenner and O'Neill (2012), their H₂O contents may be estimated approximately, using the observation that H₂O/Ce in OFB glasses is reasonably constant (e.g., Michael 1995). Assuming H₂O/Ce = 200, the “tuning” procedure was repeated for the 318 undegassed glasses of Jenner and O'Neill (2012), with all mole fractions lowered by the factor $(1 - X_{H_2O,0.5}^{sil\ melt})$ to calculate $C_{S^{2-}}^{dil}$, the addition of the term in $C_{S^{2-}}^H$, the calculated temperature lowered by 12.83 K per wt% H₂O as specified by the magmathermometer of Putirka (2015), his Eqn. 15, and $W_{Fe^{3+}}$, $K_{Ni/Fe}^*$ and $K_{Cu/Fe}^*$ taken as tuning parameters. With this model, it is possible to achieve a statistically better fit ($\chi_v^2 = 1.16$), but at the expense of a very large negative $W_{Fe^{3+}}$, which seems physically unreasonable (although it could be compensating for an effect of Fe³⁺/Fe²⁺ on $C_{S^{2-}}$), and a larger $K_{Cu/Fe}^*$, which translates into higher Cu/Fe ratio in the coexisting sulfide, contrary to the inference from the analysed sulfides (cf. Fig. 11b). On the other hand, constraining $W_{Fe^{3+}} = 0$ gives $\chi_v^2 = 1.80$, only a little less good than the model assuming zero H₂O, but with lower $K_{Ni/Fe}^*$ and $K_{Cu/Fe}^*$, which give Ni/Fe and Cu/Fe in good agreement with the available sulfide analyses.

The conclusion is that while the effects of small amounts of H₂O in OFB glasses on SCSS may not be negligible, they cannot be quantified at present. However, the zero-H₂O assumption looks to be a good approximation, and will be used for the following discussions, even where H₂O is known, to ensure unbiased comparisons.

Comparison with previous models

With the exception of the recent study of Smythe et al. (2017), previous modeling of SCSS in silicate liquids of geological interest has concentrated on reproducing the available experimental

1266 data in systems without Ni and Cu (Moretti and Ottonello 2005; Moretti and Baker 2008), and are
1267 therefore not directly applicable natural systems containing Fe-Ni-Cu-S-O sulfides.

1268 The model of Smythe et al. (2017) and that of this work are compared in Fig. 12a by applying
1269 both to the dataset of Jenner and O'Neill (2012), with liquidus temperatures calculated the same
1270 way, that is, with the magmathermometer of Putirka (2008). There is excellent agreement over
1271 most of the range of $[S]_{\text{obs}}$, from 800 to 1500 ppm, but above 1500 ppm S, the model of Smythe et
1272 al. returns higher values of SCSS, which would correspond to such samples being sulfide-
1273 undersaturated. Figure 12b shows that the difference between the two models is largely due to the
1274 different ways that the effects of FeO_t are handled. The model of Smythe et al. does not include the
1275 ad-hoc adjustment made in this work for the non-linear decrease of $\ln C_{S^{2-}}$ vs. $X_{\text{FeO}}^{\text{sil melt}}$ (Eqns. 33
1276 and 34), and does not parameterize $\gamma_{\text{FeO}}^{\text{sil melt}}$ as a function of composition. On the other hand,
1277 Smythe et al. (2017) use a more sophisticated treatment of $a_{\text{FeS}}^{\text{sulf}}$. Despite this, the calculated values
1278 of Ni/Fe in the sulfide from the model of this work appear more realistic when compared to actual
1279 sulfide globule analyses (Fig. 11a). The calculated Cu/Fe ratios are similar over the range of TiO_2
1280 contents of the glass for which there are actual sulfide globule analyses (Fig. 11b).

1281

1282 *Application to other OFB glass datasets.*

1283 Some recent studies have reported sulfur contents in OFB glasses determined by SIMS together
1284 with the necessary compositional data including Ni and Cu (Le Voyer et al. 2015, 2017; Shimizu
1285 2016). The latter study presents new analyses of a number of glasses from Macquarie Island
1286 previously analysed for all relevant elements by Kamenetsky et al. (2000) and Kamenetsky and
1287 Eggins (2012), including S by EMPA. This replication is a valuable resource for ground-truthing
1288 analytical precision (not just for S), and also provides a test of accuracy, of the “necessary but not
1289 sufficient” kind. The average agreement between the S analyses by the two methods is very good
1290 (Fig. 13a). Non-linear regression of the data assuming that the relative uncertainties are the same in
1291 both methods, gives $[S]_{\text{SIMS}} = 1.01 [S]_{\text{EMPA}}$, and setting the reduced chi-squared to unity gives the

1292 most probable value of this uncertainty as 5.8%. If the SIMS analyses were more precise then the
1293 EMPA would be less precise, and vice versa, but 5.8% for EMPA seems reasonable based on the
1294 VG2 analyses (Table 2). Kendrick et al. (2014) also report replicate measurements of S by both
1295 SIMS and EMPA for some Ocean Island basaltic glasses, with fewer samples ($n = 18$) but over a
1296 wider range of S contents, because of variable S loss by degassing. There is less good agreement,
1297 with $[S]_{\text{SIMS}} = 1.07 [S]_{\text{EMPA}}$ (Fig. 13a), largely due to the samples with higher S contents, above the
1298 ~ 1400 ppm of the VG2 standard. The most probable uncertainty assuming equal uncertainties is
1299 similar, at 5.0%.

1300 In addition to their replication of the S analyses, Shimizu et al. (2016) also report analyses of the
1301 major- and trace elements in the Macquarie Island glasses that replicate those of Kamenetsky and
1302 co-workers, giving some information on the accuracy of calculated SCSS. The values of SCSS
1303 calculated from the dataset of Shimizu et al. (2016) are displaced to higher SCSS (Fig. 13b).
1304 Because of the way the model is assembled, it is easy to find the culprits: they are the Ni and Cu
1305 analyses, which are on average 7% and 14% lower respectively in the dataset of Shimizu et al.
1306 (2016). This emphasises just how important it is to know the Ni and Cu contents of a basalt liquid
1307 to judge whether it was sulfide-saturated or not. The comparison of $[S]_{\text{obs}}$ with the SCSS model is
1308 shown for both datasets in Fig. 14. The analyses of Kamenetsky et al. (2000) and Kamenetsky and
1309 Eggins (2012) scatter around the model SCSS, although a few are offset to considerably higher
1310 SCSS than $[S]_{\text{obs}}$, indicating that they may be sulfide-undersaturated. The dataset of Shimizu et al.
1311 (2016) is displaced to higher SCSS, as expected from Fig. 13b.

1312 Shimizu et al. (2016) report S and all the necessary data for the SCSS model for basaltic glasses
1313 from two other geotectonic localities, Northern East Pacific Rise (NEPR) off-axis seamounts, and
1314 the Quebrada-Discovery-GoFar (QDG) transform fault system. The comparison between $[S]_{\text{obs}}$ and
1315 SCSS is shown in Fig. 15. There is a systematic offset of 9% for both datasets, with $[S]_{\text{obs}}$ being
1316 higher than the calculated SCSS. The SCSS models of Smythe et al. (2017) give the same result,
1317 almost exactly. Given the complexity of the SCSS models, the only reasonable explanation for why

the offset is so systematic is that the calibration of the SIMS for S differs from what has been typically used for EMPA, on which the model is based. Evidence supporting this proposition is: 1) the reported value for VG2 by SIMS (Le Voyer et al. 2017) is higher than most EMPA values by ~5% (Table 2); and 2) the 7% offset of SIMS compared to EPMA analyses from Kendrick et al. (2014) shown in Fig. 13a. There is, however, the problem that the Macquarie Island glasses do not show the same offset (Fig. 13a). The offset is opposite to that expected of undersaturation in sulfide, and towards extra S as SO_4^{2-} . This seems unlikely, because if there was significant SO_4^{2-} , small but plausible variations $f\text{O}_2$ (as monitored by $\text{Fe}^{3+}/\Sigma\text{Fe}$) should cause more scatter in $[\text{S}]_{\text{obs}}$ (cf. Fig. 2). A small subset from the NEPR seamounts do seem to contain excess S beyond likely uncertainty (Fig. 15), implying non-negligible SO_4^{2-} and inviting further investigation by XANES.

For olivine-hosted melt inclusion glasses from OFB, there is fair agreement between analysed S and calculated SCSS for those samples in which the necessary Ni and Cu contents have been measured (Le Voyer et al. 2017), shown in Fig. 16a, but only if the original analyses, uncorrected for presumed post-entrapment crystallization, are used. The correction used by Le Voyer et al. (2017) hardly changes the Fe, Ni, Cu or S contents of the trapped melt from their measured values, but mainly affects MgO, hence the calculated temperature from the magmathermometer of Putirka (2008). The result is, the larger the *calculated* degree of post-entrapment crystallization, the greater the difference between $[\text{S}]_{\text{obs}}$ and the *calculated* SCSS (Fig. 16b). This emphasizes the sensitivity of SCSS to temperature. Intriguingly, here is also a correlation between the calculated percentage of post-entrapment crystallization and the uncorrected SCSS (Fig. 16b), which can be interpreted as showing that the degree of disequilibrium between the melt inclusion and its olivine host is correlated with undercooling as monitored by the difference between $[\text{S}]_{\text{obs}}$ and calculated SCSS. Olivine phenocrysts in OFB are often (perhaps mostly) not in Mg-Fe equilibrium with their host melts at any temperature (see, for example, Fig. 6 of Coogan 2014), and the very existence of a melt inclusion is evidence of rapid crystallization of its host crystal, plausibly caused by undercooling. Melt inclusions have sometimes been regarded as magic bullets to understand basalt petrogenesis,

1344 whereas the reality is that a better understanding of basalt petrogenesis is needed to understand melt
1345 inclusions.

1346

1347 *Siqueiros OFB olivine-hosted melt inclusions*

1348 Saal et al. (2002) studied olivine-hosted melt inclusions in OFB from the Siqueiros Fracture
1349 Zone, however they did not measure Ni and Cu, so their claim that some of these melt inclusions
1350 were sulfide-undersaturated needs scrutiny. To a first approximation this may be done if it is
1351 assumed that these melt inclusions had the typical Ni and Cu contents for Ocean Floor Basaltic
1352 glasses as a function of [MgO]. To implement this idea, the datasets of Jenner and O'Neill (2012)
1353 and Gale et al. (2013) were combined, to give, for glasses with [MgO] > 5 wt% (n = 1060):

$$1354 \quad \log_{10} [\text{Ni}] (\pm 0.115) = 0.692 + 0.169 [\text{MgO}] \quad (54)$$

$$1355 \quad \log_{10} [\text{Cu}] (\pm 0.103) = 1.620 + 0.037 [\text{MgO}] \quad (55)$$

1356 as shown in Fig. 17. The scatter, which is far outside analytical uncertainty, reflects real
1357 geochemical variability, which needs to be taken into account for the SCSS calculation. This may
1358 be done using the sensitivities in Table 4. The relationship between [S]_{obs} and calculated SCSS
1359 enabled by these estimates for Ni and Cu abundances for the Siqueiros inclusions is shown in Fig.
1360 18 for both the uncorrected analyses, and with their correction for post-entrapment crystallization.
1361 With the exception of four inclusions (out of 107) that have lower [S]_{obs} than calculated SCSS, the
1362 inclusions appear to be sulfide-saturated within likely uncertainty. It cannot at present be excluded
1363 that the low S in the four anomalous inclusions are due to high Ni and/or Cu or disequilibrium
1364 during trapping as inferred for other melt inclusions (Fig. 16).

1365

1366 **The sulfur fugacity (fS₂) of Ocean Floor Basalts**

1367 Given T, P and fO₂, the sulfur fugacity (fS₂) of a basalt at ambient pressure may be calculated
1368 from Eqn. (35) if it is sulfide-saturated, but this requires knowing $a_{FeO}^{sil\ melt}$ and a_{FeS}^{sulf} . More
1369 generally, at ambient pressure, given T and fO₂, fS₂ may also be calculated from its model C_{S2-} and

observed S content, sulfide-saturated or not (Eqn. 3). There is insufficient information to calculate fS_2 at higher pressures by this latter route, because the effect of pressure has been constrained experimentally only on SCSS, and not separately on the four entities that make up SCSS, including $C_{S^{2-}}$. Ambient-pressure values for fS_2 calculated from the $C_{S^{2-}}$ route are plotted against the relative oxygen fugacity ΔQFM in Fig. 19a for 35 OFB glasses whose $Fe^{3+}/\Sigma Fe$ has been determined by Berry et al. (2018) by XANES, and whose S contents were measured by Jenner and O'Neill (2012). The parameterization of O'Neill et al. (2018) was used to convert $Fe^{3+}/\Sigma Fe$ into ΔQFM . The slope of the correlation between $\log_{10} fS_2$ and ΔQFM is 0.82 ± 0.08 , somewhat less than the naïve value of 1 implied by Eqn. (3), due to the effects of silicate melt composition and temperature. This correlation flows on to one of fSO_2 with ΔQFM , since $1/2S_2 + O_2 = SO_2$ (Fig. 19b). The large increase in fSO_2 (hence pSO_2) with ΔQFM raises the possibility that some of the rare S-degassed OFB glasses (Fig. 9) may have been unusually oxidized (high Fe^{3+}/Fe^{2+}). A high oxidation state has been postulated elsewhere to lead to S degassing during submarine eruptions (Nilsson and Peach 1993; Jenner et al. 2010). Perversely, degassing of S^{2-} as SO_2 would then reduce Fe^{3+}/Fe^{2+} (Moussallam et al. 2016). The one glass with low S due to presumed degassing for which $Fe^{3+}/\Sigma Fe$ was measured, VG6822, shows no evidence of this hypothetical behavior (Fig. 10).

1386

1387 **Conclusions**

The “capacity” approach to understanding the thermodynamics of anion species in silicate melts leads to a thermodynamically based model for the “Sulfide Content at Sulfide Saturation” (SCSS) of basic to intermediate magmas. The model has a precision for calculating SCSS of better than 10%, if the composition of the sulfide can be adequately constrained. Application of this model to undegassed basaltic glasses from deep submarine eruptions show that nearly all have S contents consistent with being saturated in a Fe-Ni-Cu-S-O sulfide matte on eruption. The agreement between analysed S and SCSS indicates that such magmas contained no more than a few percent of S as S^{6+} , which is supported by the results of XANES spectroscopy on their quenched glasses (e.g.,

1396 Métrich et al. 2009). However, several uncertainties remain. There is a need to better constrain the
1397 effects of pressure relevant to the range over which many common basalts are generated and evolve
1398 (i.e., 0 to 1.5 GPa). More experimental information is needed on the effects of H₂O, especially
1399 confirmation that H-S species (e.g., HS⁻, H₂S) are negligible, as assumed here. Nothing is known
1400 about the effects of CO₂ or other volatile species. A fascinating problem in physical chemistry yet
1401 to be addressed is the kinetics of the electron-exchange interaction between Fe³⁺/Fe²⁺ and S⁶⁺/S²⁻ in
1402 silicate melts, which determines to what extent the equilibrium speciation in the silicate melt is
1403 preserved when cooled to glass.

1404

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1414

1415 **REFERENCES**

- 1416 Allertz, C., Selleby, M., & Sichen, D. (2016). The effect of oxygen potential on the sulfide
1417 capacity for slags containing multivalent species. *Metallurgical and Materials Transactions B*, 47,
1418 3039-3045.
- 1419 Ariskin, A. A., Danyushevsky, L. V., Bychkov, K. A., McNeill, A. W., Barmina, G. S., &
1420 Nikolaev, G. S. (2013). Modeling solubility of Fe-Ni sulfides in basaltic magmas: The effect of
1421 nickel. *Economic Geology*, 108, 1983-2003.

1422 Baker, D. R., Barnes, S. J., Simon, G., & Bernier, F. (2001). Fluid transport of sulfur and metals
 1423 between sulfide melt and basaltic melt. *The Canadian Mineralogist*, 39, 537-546.

1424 Baker, D. R. (2008). The fidelity of melt inclusions as records of melt composition.
 1425 *Contributions to Mineralogy and Petrology*, 156, 377-395.

1426 Ballhaus, C., Fonseca, R. O., Münker, C., Rohrbach, A., Nagel, T., Speelmanns, I. M., Helmy,
 1427 H. M., Zirner, A., Vogel, H. K. & Heuser, A. (2017). The great sulfur depletion of Earth's mantle is
 1428 not a signature of mantle–core equilibration. *Contributions to Mineralogy and Petrology*, 172, 68.

1429 Barin, I., Sauert, F., Schultze-Rhonhof, E. & Sheng, W. S. (1989). Thermochemical data of
 1430 pure substances, part I and part II. Weinheim, Germany: VCH Verlagsgesellschaft, pp. 1-1739.

1431 Bell, A. S., Simon, A., & Guillong, M. (2009). Experimental constraints on Pt, Pd and Au
 1432 partitioning and fractionation in silicate melt–sulfide–oxide–aqueous fluid systems at 800 C, 150
 1433 MPa and variable sulfur fugacity. *Geochimica et Cosmochimica Acta*, 73, 5778-5792.

1434 Berry, A. J., Shelley, J. M. G., Foran, G. J., O'Neill, H. S. C., & Scott, D. R. (2003). A furnace
 1435 design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and
 1436 temperatures to 1773 K. *Journal of synchrotron radiation*, 10, 332-336.

1437 Berry, A. J., Stewart, G. A., O'Neill, H. S. C., Mallmann, G., & Mosselmans, J. F. W. (2018). A
 1438 re-assessment of the oxidation state of iron in MORB glasses. *Earth and Planetary Science Letters*,
 1439 483, 114-123.

1440 Borisov, A., Lahaye, Y., & Palme, H. (2004). The effect of TiO₂ on Pd, Ni, and Fe solubilities
 1441 in silicate melts. *American Mineralogist*, 89, 564-571.

1442 Borisov, A., Lahaye, Y., & Palme, H. (2006). The effect of sodium on the solubilities of metals
 1443 in silicate melts. *American Mineralogist*, 91, 762-771.

1444 Borisov, A. A. (2007). Experimental study of the influence of SiO₂ on the solubility of cobalt
 1445 and iron in silicate melts. *Petrology*, 15, 523-529.

1446 Botcharnikov, R. E., Linnen, R. L., Wilke, M., Holtz, F., Jugo, P. J., & Berndt, J. (2011) High
 1447 gold concentrations in sulphide-bearing magma under oxidizing conditions. *Nature Geoscience*, 4,
 1448 112-115.

1449 Buchanan, D. L., Nolan, J., Wilkinson, N. & de Villiers, J. P. R. (1983). An experimental
 1450 investigation of sulphur solubility as a function of temperature in synthetic silicate melts.
 1451 Geological Society of South Africa Special Publication 7, 383-391.

1452 Chan, A. H., & Fruehan, R. J. (1986). The sulfur partition ratio and the sulfide capacity of
 1453 Na₂O-SiO₂ slags at 1200° C. *Metallurgical Transactions B*, 17(3), 491-496.

1454 Chan, A. H., & Fruehan, R. J. (1988). The sulfur partition ratio and the sulfide capacity of
 1455 Na₂O-SiO₂ Slags at 1400° C. *Metallurgical Transactions B*, 19(2), 334-336.

1456 Chase Jr, M. W. (1998). NIST-JANAF thermochemical tables. National Institute of Standards
 1457 and Technology.

1458 Clémente, B., Scaillet, B., & Pichavant, M. (2004). The solubility of sulphur in hydrous
 1459 rhyolitic melts. *Journal of Petrology*, 45(11), 2171-2196.

1460 Coogan, L. A. (2014) The lower oceanic crust. In: Holland, HD, Turekian, KK (Eds.) *Treatise*
 1461 *on Geochemistry*. Second Edition, Elsevier, Oxford. Vol. 4. The crust (ed. Rudnick, R. L.) pp. 497-
 1462 541.

1463 Cottrell, E., & Kelley, K. A. (2011). The oxidation state of Fe in MORB glasses and the oxygen
 1464 fugacity of the upper mantle. *Earth and Planetary Science Letters*, 305, 270-282.

1465 Czamanske, G. K., & Moore, J. G. (1977). Composition and phase chemistry of sulfide globules
 1466 in basalt from the Mid-Atlantic Ridge rift valley near 37 N lat. *Geological Society of America*
 1467 *Bulletin*, 88, 587-599.

1468 Danckwerth, P. A., Hess, P. C. & Rutherford, M. J. (1979). The solubility of sulfur in high-TiO₂
 1469 mare basalts. *Proceedings of the 10th Lunar Planetary Science Conference*, pp. 517-530.

1470 Davis, A. S., D. A. Clague, B. L. Cousens, R. Keaten, and J. B. Paduan. (2008) Geochemistry of
 1471 basalt from the North Gorda segment of the Gorda Ridge: Evolution toward ultraslow spreading
 1472 ridge lavas due to decreasing magma supply." *Geochemistry, Geophysics, Geosystems* 9, no. 4.

1473 De Hoog, J. C. M., Mason, P. R. D. & Van Bergen, M. J. (2001). Sulfur and chalcophile
 1474 elements in subduction zones: Constraints from a laser ablation ICP-MS study of melt inclusions
 1475 from Galunggung Volcano, Indonesia. *Geochimica et Cosmochimica Acta* 65, 3147-3164.

1476 De Hoog, J. C. M., Hattori, K. H., & Hoblitt, R. P. (2004). Oxidized sulfur-rich mafic magma at
 1477 Mount Pinatubo, Philippines. *Contributions to Mineralogy and Petrology*, 146(6), 750-761.

1478 Ding, S., Dasgupta, R., & Tsuno, K. (2014). Sulfur concentration of martian basalts at sulfide
 1479 saturation at high pressures and temperatures—implications for deep sulfur cycle on Mars.
 1480 *Geochimica et Cosmochimica Acta*, 131, 227-246.

1481 Dixon, J. E., Clague, D. A. & Stolper, E. M. (1991). Degassing history of water, sulfur, and
 1482 carbon in submarine lavas from Kilauea Volcano, Hawaii. *Journal of Geology* 99, 371-394.

1483 Dixon, J. E., & Stolper, E. M. (1995). An experimental study of water and carbon dioxide
 1484 solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. *Journal of*
 1485 *Petrology*, 36(6), 1633-1646.

1486 Doyle, C. D. (1988). Prediction of the activity of FeO in multicomponent magma from known
 1487 values in [SiO₂-KAlO₂-CaAl₂Si₂O₈] - FeO liquids. *Geochimica et Cosmochimica Acta* 52, 1827-
 1488 1834.

1489 Doyle, C. D. (1989). The effect of substitution of TiO₂ for SiO₂ on a_{FeO} in magma. *Geochimica*
 1490 *et Cosmochimica Acta* 53, 2631-2638.

1491 Doyle, C. D. & Naldrett, A. J. (1986). Ideal mixing of divalent cations in mafic magma and its
 1492 effect on the solution of ferrous oxide. *Geochimica et Cosmochimica Acta* 5 435-443.

1493 D'Souza, R. J., & Canil, D. (2018). Effect of alkalinity on sulfur concentration at sulfide
 1494 saturation in hydrous basaltic andesite to shoshonite melts at 1270 C and 1 GPa. *American*
 1495 *Mineralogist: Journal of Earth and Planetary Materials*, 103, 1030-1043.

1496 Evans, K. A., O'Neill, H. S. C., & Mavrogenes, J. A. (2008). Sulphur solubility and sulphide
1497 immiscibility in silicate melts as a function of the concentration of manganese, nickel, tungsten and
1498 copper at 1 atm and 1400 °C. *Chemical Geology*, 255, 236-249.

1499 Evans, K. A., O'Neill, H. S. C., Mavrogenes, J. A., Keller, N. S., Jang, L. Y., & Lee, J. F.
1500 (2009). XANES evidence for sulphur speciation in Mn-, Ni- and W-bearing silicate melts.
1501 *Geochimica et Cosmochimica Acta*, 73, 6847-6867.

1502 Fincham, C. J. B. & Richardson, F. D. (1954). The behaviour of sulphur in silicate and
1503 aluminate melts. *Proceedings of the Royal Society of London, Ser. A* 223, 40-62.

1504 Flood, H., Forland, T. & Gzothheim, K. (1954). Ueber den Zusammenhang zwischen
1505 Konzentration und Aktivitäten in geschmolzenen Salzmischungen. *Zeitschrift für Anorganische*
1506 *Allgemeine Chemie* 276, 290-315.

1507 Fonseca, R. O., Campbell, I. H., O'Neill, H. StC., & Fitzgerald, J. D. (2008). Oxygen solubility
1508 and speciation in sulphide-rich mattes. *Geochimica et Cosmochimica Acta*, 72, 2619-2635.

1509 Fortin, M. A., Riddle, J., Desjardins-Langlais, Y., & Baker, D. R. (2015). The effect of water on
1510 the sulfur concentration at sulfide saturation (SCSS) in natural melts. *Geochimica et Cosmochimica*
1511 *Acta*, 160, 100-116.

1512 Fougereux, T. (2014) Influence du contexte géodynamique sur l'état d'oxydoréduction du fer
1513 dans les magmas. Thèse de doctorat. Nantes.

1514 Frost, D. J., & Wood, B. J. (1997). Experimental measurements of the fugacity of CO₂ and
1515 graphite/diamond stability from 35 to 77 kbar at 925 to 1650 C. *Geochimica et Cosmochimica Acta*,
1516 61(8), 1565-1574.

1517 Gaetani, G. A., & Grove, T. L. (1997). Partitioning of moderately siderophile elements among
1518 olivine, silicate melt, and sulfide melt: constraints on core formation in the Earth and Mars.
1519 *Geochimica et Cosmochimica Acta*, 61, 1829-1846.

1520 Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y., & Schilling, J. G. (2013). The mean
1521 composition of ocean ridge basalts. *Geochemistry, Geophysics, Geosystems*, 14, 489-518.

1522 Grant, N. J., & Chipman, J. (1946). Sulphur equilibria between liquid iron and slags. Trans.
 1523 AIME, 167, 134-154.

1524 Gurenko, A. A., Belousov, A. B., Trumbull, R. B., & Sobolev, A. V. (2005). Explosive basaltic
 1525 volcanism of the Chikurachki Volcano (Kurile arc, Russia): Insights on pre-eruptive magmatic
 1526 conditions and volatile budget revealed from phenocryst-hosted melt inclusions and groundmass
 1527 glasses. *Journal of Volcanology and Geothermal Research*, 147, 203-232.

1528 Haughton, D. R., Roeder, P. L. & Skinner, B. J. (1974). Solubility of sulfur in mafic magmas.
 1529 *Economic Geology* 69, 451-467.

1530 Hauri, E., Wang, J., Dixon, J. E., King, P. L., Mandeville, C., & Newman, S. (2002). SIMS
 1531 analysis of volatiles in silicate glasses: 1. Calibration, matrix effects and comparisons with FTIR.
 1532 *Chemical Geology*, 183, 99-114.

1533 Hillert, M. (1998) Phase equilibria, phase diagrams and phase transformations. Subtitled “Their
 1534 thermodynamic basis”. Cambridge University Press.

1535 Hillert, M. (2001). The compound energy formalism. *Journal of Alloys and Compounds*, 320(2),
 1536 161-176.

1537 Holmquist, S. (1966). Oxygen ion activity and the solubility of sulfur trioxide in sodium silicate
 1538 melts. *Journal of the American Ceramic Society*, 49(9), 467-473.

1539 Holzheid, A., Palme, H., & Chakraborty, S. (1997). The activities of NiO, CoO and FeO in
 1540 silicate melts. *Chemical Geology*, 139(1-4), 21-38.

1541 Holzheid, A., & Grove, T. L. (2002). Sulfur saturation limits in silicate melts and their
 1542 implications for core formation scenarios for terrestrial planets. *American Mineralogist*, 87(2-3),
 1543 227-237.

1544 Jarosewich, E., Nelen, J. A. & Norberg, J. A. (1979). Electron microprobe reference samples for
 1545 mineral analyses. *Smithsonian Contributions to Earth Sciences* 20, 68-72.

1546 Jégo, S., & Dasgupta, R. (2014). The fate of sulfur during fluid-present melting of subducting
 1547 basaltic crust at variable oxygen fugacity. *Journal of Petrology*, 55, 1019-1050.

1548 Jenner, F. E. & O'Neill, H. StC. (2012). Analysis of 60 Elements in 616 Ocean Floor Basaltic
 1549 Glasses. *Geochemistry geophysics geosystems* **13**, DOI: 10.1029/2011GC004009.

1550 Jenner, F. E., O'Neill, H. St.C., Arculus, R. J. & Mavrogenes, J. A. (2010). The Magnetite Crisis
 1551 in the Evolution of Arc-related Magmas and the Initial Concentration of Au, Ag, and Cu. *Journal of*
 1552 *Petrology* **51**, 2445-2464.

1553 Jugo, P. J., Wilke, M., & Botcharnikov, R. E. (2010). Sulfur K-edge XANES analysis of natural
 1554 and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen
 1555 fugacity. *Geochimica et Cosmochimica Acta*, 74, 5926-5938.

1556 Kamenetsky V. S., Everard J. L., Crawford A. J., Varne R., Eggins S. M. and Lanyon R. (2000)
 1557 Enriched end-member of primitive MORB melts: petrology and geochemistry of glasses from
 1558 Macquarie Island (SW Pacific). *J. Petrol.* 41, 411–430.

1559 Kamenetsky, V. S. & Eggins, S. M. (2012). Systematics of metals, metalloids, and volatiles in
 1560 MORB melts: Effects of partial melting, crystal fractionation and degassing (a case study of
 1561 Macquarie Island glasses). *Chemical Geology* 302-303, 76-86.

1562 Kamenetsky, V. S., Gurenko, A. A., & Kerr, A. C. (2010). Composition and temperature of
 1563 komatiite melts from Gorgona Island, Colombia, constrained from olivine-hosted melt inclusions.
 1564 *Geology*, 38(11), 1003-1006.

1565 Kang, Y. B., & Pelton, A. D. (2009). Thermodynamic model and database for sulfides dissolved
 1566 in molten oxide slags. *Metallurgical and Materials Transactions B*, 40(6), 979-994.

1567 Katsura, T. & Nagashima, S. (1974). Solubility of sulfur in some magmas at 1 atmosphere.
 1568 *Geochimica et Cosmochimica Acta* 38, 517-531.

1569 Kendrick, M. A., Jackson, M. G., Kent, A. J., Hauri, E. H., Wallace, P. J., & Woodhead, J.
 1570 (2014). Contrasting behaviours of CO₂, S, H₂O and halogens (F, Cl, Br, and I) in enriched-mantle
 1571 melts from Pitcairn and Society seamounts. *Chemical Geology*, 370, 69-81.

1572 Kiseeva, E. S., & Wood, B. J. (2013). A simple model for chalcophile element partitioning
 1573 between sulphide and silicate liquids with geochemical applications. *Earth and Planetary Science*
 1574 *Letters*, 383, 68-81.

1575 Kiseeva, E. S., & Wood, B. J. (2015). The effects of composition and temperature on
 1576 chalcophile and lithophile element partitioning into magmatic sulphides. *Earth and Planetary*
 1577 *Science Letters*, 424, 280-294.

1578 Kress, V. (1997). Thermochemistry of sulfide liquids. I. the system O-S Fe at 1 bar.
 1579 *Contributions to Mineralogy and Petrology* 127, 176-186.

1580 Kress, V., Greene, L.E., Ortiz, M.D., and Mioduszewski, L (2008) Thermochemistry of sulfide
 1581 liquids IV: density measurements and the thermodynamics of O–S–Fe–Ni–Cu liquids at low to
 1582 moderate pressures. *Contributions to Mineralogy and Petrology* 156, 785-797.

1583 Lange RA, Carmichael ISE (1990) Thermodynamic properties of silicate liquids with an
 1584 emphasis on density, thermal expansion and compressibility. In: J Nicholls, JK Russell (eds)
 1585 *Modern Methods of Igneous Petrology: Understanding Magmatic Processes*. (Reviews in
 1586 *Mineralogy* 24) Mineral Soc Am, Washington, D.C., pp 25-64.

1587 Laurenz, V., Fonseca, R. O., Ballhaus, C., Jochum, K. P., Heuser, A., & Sylvester, P. J. (2013).
 1588 The solubility of palladium and ruthenium in picritic melts: 2. The effect of sulfur. *Geochimica et*
 1589 *Cosmochimica Acta*, 108, 172-183.

1590 Le Voyer, M., Cottrell, E., Kelley, K. A., Brounce, M. & Hauri, E. H. (2015). The effect of
 1591 primary versus secondary processes on the volatile content of MORB glasses: An example from the
 1592 equatorial Mid-Atlantic Ridge (5°N–3°S). *Journal of Geophysical Research: Solid Earth* 120, 125-
 1593 144.

1594 Le Voyer, M., Kelley, K. A., Cottrell, E., & Hauri, E. H. (2017). Heterogeneity in mantle carbon
 1595 content from CO₂-undersaturated basalts. *Nature Communications*, 8, 14062.

1596 Li, J., Agee, C. B. (2001) The effect of pressure, temperature, oxygen fugacity and composition
 1597 on partitioning of nickel and cobalt between liquid Fe–Ni–S alloy and liquid silicate: implications
 1598 for the Earth's core formation. *Geochimica Cosmochimica Acta* 65,1821–1832.

1599 Li, C. & Naldrett, A. J. (1993). Sulfide capacity of magma: a quantitative model and its
 1600 application to the formation of sulfide ores at Sudbury, Ontario. *Economic Geology* 88, 1253-1260.

1601 Liu, X., O'Neill, H. St.C., & Berry, A. J. (2005). The effects of small amounts of H₂O, CO₂ and
 1602 Na₂O on the partial melting of spinel lherzolite in the system CaO–MgO–Al₂O₃–
 1603 SiO₂±H₂O±CO₂±Na₂O at 1.1 GPa. *Journal of Petrology*, 47, 409-434.

1604 Liu, Y., Samaha, N. T., & Baker, D. R. (2007). Sulfur concentration at sulfide saturation (SCSS)
 1605 in magmatic silicate melts. *Geochimica et Cosmochimica Acta*, 71, 1783-1799.

1606 Luhr, J. F. (1990). Experimental phase relations of water-and sulfur-saturated arc magmas and
 1607 the 1982 eruptions of El Chichón volcano. *Journal of Petrology*, 31, 1071-1114.

1608 Luhr, J. F. (2008). Primary igneous anhydrite: Progress since its recognition in the 1982 El
 1609 Chichón trachyandesite. *Journal of Volcanology and Geothermal Research*, 175(4), 394-407.

1610 Martin, M. (2001) Life and achievements of Carl Wagner, 100th birthday. *Solid State Ionics*.
 1611 152-153: 15–17.

1612 Mathez, E. A. (1976). Sulfur solubility and magmatic sulfides in submarine basalt glass. *Journal*
 1613 *of Geophysical Research* 81, 4269-4276.

1614 Matjuschkin, V., Blundy, J. D., & Brooker, R. A. (2016). The effect of pressure on sulphur
 1615 speciation in mid-to deep-crustal arc magmas and implications for the formation of porphyry copper
 1616 deposits. *Contributions to Mineralogy and Petrology*, 171, 66.

1617 Mavrogenes, J. A. & O'Neill, H. S. C. (1999). The relative effects of pressure, temperature and
 1618 oxygen fugacity on the solubility of sulfide in mafic magmas. *Geochim. Cosmochim. Acta* 63,
 1619 1173-1180.

1620 Métrich, N., Joron, J.-L. and Berthier B. (1998) Occurrence of boron-rich potassic melts in the
1621 Vulsini Volcanic District, Italy: Evidence from melt inclusions. *Geochim. Cosmochim. Acta*, 62,
1622 507-514.

1623 Métrich, N., Berry, A. J., O'Neill, H. St.C., & Susini, J. (2009). The oxidation state of sulfur in
1624 synthetic and natural glasses determined by X-ray absorption spectroscopy. *Geochimica et*
1625 *Cosmochimica Acta*, 73, 2382-2399.

1626 Michael, P. (1995). Regionally distinctive sources of depleted MORB: Evidence from trace
1627 elements and H₂O. *Earth and Planetary Science Letters*, 131, 301-320.

1628 Moussallam, Y., Edmonds, M., Scaillet, B., Peters, N., Gennaro, E., Sides, I., & Oppenheimer,
1629 C. (2016). The impact of degassing on the oxidation state of basaltic magmas: a case study of
1630 Kīlauea volcano. *Earth and Planetary Science Letters*, 450, 317-325.

1631 Mungall, J. E., & Brenan, J. M. (2014). Partitioning of platinum-group elements and Au
1632 between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile
1633 elements. *Geochimica et Cosmochimica Acta*, 125, 265-289.

1634 Mysen, B. O. (1983). The structure of silicate melts. *Annual Review of Earth and Planetary*
1635 *Sciences*, 11, 75-97.

1636 Mysen, B. O., and Richet, P. (2005). *Silicate glasses and melts: properties and structure* (Vol.
1637 10). Elsevier.

1638 Naldrett, A. J., & Richardson, S. W. (1967). Effect of water on the melting of pyrrhotite-
1639 magnetite assemblages. *Carnegie Institute of Washington, Year Book*, 66, 429-431.

1640 Nash, W. M., Smythe, D. J., & Wood, B. J. (2019). Compositional and temperature effects on
1641 sulfur speciation and solubility in silicate melts. *Earth and Planetary Science Letters*, 507, 187-198.

1642 Nilsson, K., & Peach, C. L. (1993). Sulfur speciation, oxidation state, and sulfur concentration
1643 in backarc magmas. *Geochimica et Cosmochimica Acta*, 57, 3807-3813.

1644 O'Neill, H. St.C., & Berry, A. J. (2006). Activity coefficients at low dilution of CrO, NiO and
1645 CoO in melts in the system CaO–MgO–Al₂O₃–SiO₂ at 1400 C: using the thermodynamic behaviour

1646 of transition metal oxides in silicate melts to probe their structure. *Chemical Geology*, 231(1-2), 77-
 1647 89.

1648 O'Neill, H. St.C., Berry, A. J. and Mallmann G. (2018). The oxidation state of iron in Mid-
 1649 Ocean Ridge basaltic (MORB) glasses: implications for their petrogenesis and oxygen fugacities.
 1650 *Earth and Planetary Science Letters*, 504, 152-162.

1651 O'Neill, H. St.C. and Eggins, S. M. (2002). The effect of melt composition on trace element
 1652 partitioning: an experimental investigation of the activity coefficients of FeO, NiO, CoO, MoO₂
 1653 and MoO₃ in silicate melts. *Chemical Geology* 186, 151-181.

1654 O'Neill, H. St.C., & Mavrogenes, J. A. (2002). The sulfide capacity and the sulfur content at
 1655 sulfide saturation of silicate melts at 1400 C and 1 bar. *Journal of Petrology*, 43, 1049-1087.

1656 O'Neill, H. St.C., & Mavrogenes, J. A. (2019). The sulfate capacity of silicate melts at
 1657 atmospheric pressure. *Goldschmidt Abstracts*, 2019.

1658 O'Neill, H. S. C., & Pownceby, M. I. (1993). Thermodynamic data from redox reactions at high
 1659 temperatures. I. An experimental and theoretical assessment of the electrochemical method using
 1660 stabilized zirconia electrolytes, with revised values for the Fe-“FeO”, Co-CoO, Ni-NiO and Cu-
 1661 Cu₂O oxygen buffers, and new data for the W-WO₂ buffer. *Contributions to Mineralogy and*
 1662 *Petrology*, 114, 296-314.

1663 Patten, C., Barnes, S. J., & Mathez, E. A. (2012). Textural variations in MORB sulfide droplets
 1664 due to differences in crystallization history. *The Canadian Mineralogist*, 50(3), 675-692.

1665 Patten, C., Barnes, S. J., Mathez, E. A., & Jenner, F. E. (2013). Partition coefficients of
 1666 chalcophile elements between sulfide and silicate melts and the early crystallization history of
 1667 sulfide liquid: LA-ICP-MS analysis of MORB sulfide droplets. *Chemical Geology*, 358, 170-188.

1668 Peach, C. L., & Mathez, E. A. (1993). Sulfide melt-silicate melt distribution coefficients for
 1669 nickel and iron and implications for the distribution of other chalcophile elements. *Geochimica et*
 1670 *Cosmochimica Acta*, 57(13), 3013-3021.

1671 Peach, C. L., Mathez, E. A., Keays, R. R., & Reeves, S. J. (1994). Experimentally determined
 1672 sulfide melt-silicate melt partition coefficients for iridium and palladium. *Chemical Geology*, 117,
 1673 361-377.

1674 Pelton, A. D., Eriksson, G. & Romero-Serrano, A. (1993). Calculation of sulfide capacities of
 1675 multicomponent slags. *Metallurgical Transactions B* 24B, 817-825.

1676 Poulson, S. R. & Ohmoto, H. (1990). An evaluation of the solubility of sulfide sulfur in silicate
 1677 melts from experimental data and natural samples. *Chemical Geology* 85, 57-75.

1678 Putirka, K. D. (2008). Thermometers and Barometers for Volcanic Systems. *Reviews in*
 1679 *Mineralogy and Geochemistry* 69, 61-120.

1680 Reddy, R. G., & Blander, M. (1987). Modeling of sulfide capacities of silicate melts.
 1681 *Metallurgical Transactions B*, 18B, 591-596.

1682 Richter, K., Pando, K., & Danielson, L. R. (2009). Experimental evidence for sulfur-rich
 1683 martian magmas: Implications for volcanism and surficial sulfur sources. *Earth and Planetary*
 1684 *Science Letters*, 288, 235-243.

1685 Ripley, E. M., Brophy, J. G., & Li, C. (2002). Copper solubility in a basaltic melt and sulfide
 1686 liquid/silicate melt partition coefficients of Cu and Fe. *Geochimica et Cosmochimica Acta*, 66(15),
 1687 2791-2800.

1688 Roberge, J., White, R. V., & Wallace, P. J. (2004). Volatiles in submarine basaltic glasses from
 1689 the Ontong Java Plateau (ODP Leg 192): implications for magmatic processes and source region
 1690 compositions. *Geological Society, London, Special Publications*, 229, 239-257.

1691 Robie, R.A., Hemingway, B.S. (1995) Thermodynamic properties of minerals and related
 1692 substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *US Geological*
 1693 *Survey Bulletin* 2131, 1-461.

1694 Roeder, P. L. (1974). Activity of iron and olivine solubility in basaltic liquids. *Earth and*
 1695 *Planetary Science Letters* 23, 397-410.

1696 Sattari, P., Brenan, J. M., Horn, I., & McDonough, W. F. (2002). Experimental constraints on
 1697 the sulfide-and chromite-silicate melt partitioning behavior of rhenium and platinum-group
 1698 elements. *Economic Geology*, 97, 385-398.

1699 Schrama, F. N. H., Beunder E. M., Van den Berg, B., Yang, Y.-X. and Boom, R. (2017)
 1700 Sulphur removal in ironmaking and oxygen steelmaking, *Ironmaking & Steelmaking*, 44:5, 333-
 1701 343.

1702 Schmalzried, H. (1995) *Chemical Kinetics of Solids*, VCH, Weinheim

1703 Self, S., Blake, S., Sharma, K., Widdowson, M., & Sephton, S. (2008). Sulfur and chlorine in
 1704 Late Cretaceous Deccan magmas and eruptive gas release. *Science*, 319(5870), 1654-1657.

1705 Shima, H. & Naldrett, A. J. (1975). Solubility of sulfur in ultramafic melt and the relevance of
 1706 the system Fe-S-O. *Economic Geology* 70, 960-967.

1707 Shimizu, K., Saal, A. E., Myers, C. E., Nagle, A. N., Hauri, E. H., Forsyth, D. W., Kamenetsky,
 1708 V.S., & Niu, Y. (2016). Two-component mantle melting-mixing model for the generation of mid-
 1709 ocean ridge basalts: implications for the volatile content of the Pacific upper mantle. *Geochimica et*
 1710 *Cosmochimica Acta*, 176, 44-80.

1711 Stolper, E., Sherman, S., Garcia, M., Baker, M., & Seaman, C. (2004). Glass in the submarine
 1712 section of the HSDP2 drill core, Hilo, Hawaii. *Geochemistry, Geophysics, Geosystems*, 5(7)
 1713 Q07G15.

1714 Smythe, D. J., Wood, B. J., & Kiseeva, E. S. (2017). The S content of silicate melts at sulfide
 1715 saturation: new experiments and a model incorporating the effects of sulfide composition. *American*
 1716 *Mineralogist*, 102, 795-803.

1717 Thordarson, T., Self, S., Óskarsson, N. & Hulsebosch, T. (1996). Sulfur, chlorine, and fluorine
 1718 degassing and atmospheric loading by the 1783-1784 AD Laki (Skaftár Fires) eruption in Iceland.
 1719 *Bulletin of Volcanology* 58, 205-225.

1720 Thornber, C. R., Sherrod, D. R., Siems, D. F., Heliker, C. C., Meeker, G. P., Oscarson, R. L.,
 1721 Kauahikaua, J. P., 2002, Whole-rock and glass major-element geochemistry of Kilauea Volcano,

1722 Hawaii, near-vent eruptive products: September 1994 through September 2001: U.S. Geological
 1723 Survey Open-File Report 2002-17, <https://pubs.usgs.gov/of/2002/0017/>.
 1724 Tuff, J., & O'Neill, H. S. C. (2010). The effect of sulfur on the partitioning of Ni and other first-
 1725 row transition elements between olivine and silicate melt. *Geochimica et Cosmochimica Acta*, 74,
 1726 6180-6205.
 1727 Vidal, C. M., Métrich, N., Komorowski, J. C., Prato, I., Michel, A., Kartadinata, N., Robert,
 1728 V. & Lavigne, F. (2016). The 1257 Samalas eruption (Lombok, Indonesia): the single greatest
 1729 stratospheric gas release of the Common Era. *Scientific Reports*, 6, 34868.
 1730 Wallace, P. & Carmichael, I. S. E. (1992). Sulfur in basaltic magmas. *Geochimica et*
 1731 *Cosmochimica Acta* 56, 1683-1874.
 1732 Waldner, P., & Pelton, A. D. (2005). Thermodynamic modeling of the Fe-S system. *Journal of*
 1733 *phase equilibria and diffusion*, 26(1), 23-38.
 1734 Wilke, M., Jugo, P. J., Klimm, K., Susini, J., Botcharnikov, R., Kohn, S. C., & Janousch, M.
 1735 (2008). The origin of S⁴⁺ detected in silicate glasses by XANES. *American Mineralogist*, 93, 235-
 1736 240.
 1737 Wilke, M., Klimm, K., & Kohn, S. C. (2011). Spectroscopic studies on sulfur speciation in
 1738 synthetic and natural glasses. *Reviews in Mineralogy and Geochemistry*, 73, 41-78.
 1739 Wood, B. J. & Nicholls, J. (1978). The thermodynamic properties of reciprocal solid solutions.
 1740 *Contributions to Mineralogy and Petrology* 66, 389-400.
 1741 Wood, B. J., & Wade, J. (2013). Activities and volatilities of trace components in silicate melts:
 1742 a novel use of metal–silicate partitioning data. *Contributions to Mineralogy and Petrology*, 166(3),
 1743 911-921.
 1744

1745 Table 1. Experimental studies used in parameterizing the sulfide content at sulfide saturation
1746 (SCSS) in silicate melts.
1747

Reference	T range (°C)	P range (GPa)	No. data used	Chalcophile elements
<i>Anhydrous</i>				
Haughton et al. (1974)	1200	10 ⁻⁴	C _S ²⁻ only	-
Danckwerth et al. (1979)	1200 -1260	10 ⁻⁴	14	-
Peach and Mathez (1993)	1450	0.8	10	Ni
Peach et al. (1994)	1450	0.8	24	-
Gaetani and Grove (1997)	1350	10 ⁻⁴	22	Ni & Cu
Mavrogenes and O'Neill (1999)	1400-1800	0.5 – 5.5	16	-
Baker et al. (2001)	1225-1450	1.0	6	-
O'Neill and Mavrogenes (2002)	1400	10 ⁻⁴	34	-
Holzheid and Grove (2002)	1350 - 1600	0.9 – 2.7	4	Ni
Ripley et al. (2002)	1245	10 ⁻⁴	22	Cu
Sattari et al. (2002)	1330	1.0	5	-
Jugo et al. (2005)	1355	1.6	7	-
Liu et al. (2007)	1150 - 1450	0.5 - 1.0	41	-
Brenan (2008)	1200 - 1300	10 ⁻⁴ , 0.9 - 1.6	21	Ni & Cu
Righter et al. (2009)	1200 - 1500	10 ⁻⁴ , 0.8	16	-
Tuff and O'Neill (2010)	1370	10 ⁻⁴	15	minor Ni
Kiseeva and Wood (2013)	1400	1.5	14	Ni & Cu
Ding et al. (2014)	1500 - 1700	1 - 4	25	-
Kiseeva and Wood (2015)	1300 - 1700	1.5	29	Ni & Cu
Wood and Kiseeva (2015)	1400 - 1460	1 – 1.5	9	minor Ni
Wykes et al. (2015)	1400	1.5	12	-
Fortin et al. (2015)	1250	1.0	3	-
Smythe et al. (2017)	1400 - 1800	1.5 – 5.5	36	Ni & Cu
O'Neill and Mavrogenes (in prep.)	1300	10 ⁻⁴	22	-
<i>Hydrous</i>				
Moune et al. (2009)	1045	0.2 – 0.3	16	-
Fortin et al. (2015)	1250	1.0	10	-
D'Souza and Canil (2018)	1270	1.0	13	-
This study (Table 3)	1400	1.5	6	-

1748
1749

1750 Table 2. Sulfur analyses in natural OFB glass VG2 (USNM 111240/52) by electron microprobe,
 1751 unless identified otherwise (*italics*). Also listed are analyses of JD2 (USNM 117354/46), which
 1752 has often been presumed to be the same sample. The identification of JD2 as a different glass
 1753 (VG7432) is based on the information in Cottrell and Kelley (2011).
 1754

S (ppm)	s(S) (ppm)	No. analyses	Reference
1340	80	19	Dixon et al. (1991)
1420	40	6	Wallace and Carmichael (1991) ^a
<i>1320</i>	<i>50</i>	<i>2</i>	<i>Wallace and Carmichael (1991)</i> ^{a,b}
1400	40	?	Nilsson and Peach (1993) ^a
1348	62	135	Thordarson et al. (1996) ^c
1365	29	139	Thordarson et al. (1996) ^c
1450	30	?	Métrich et al. (1999)
1416	36	10	De Hoog et al. (2001)
1403	31	?	O'Neill and Mavrogenes (2002)
1305	35	203	Thornber et al. (2002)
1310	130	57	Stolper et al. (2004)
1380	60	?	De Hoog et al. (2004)
1549	166	?	Roberge et al. (2004)
1490	60	38	Gurenko et al. (2005)
1414	30	38	Liu et al. (2007)
1405	39	?	Baker (2008)
1362	160	48	Davis et al. (2008)
1410	60	23	Self et al. (2008)
1300	44	?	Bell et al. (2009)
1400	115	37	Kamenetsky et al. (2010)
1415	68	247 ^d	Jenner and O'Neill (2012)
1440	30	?	Laurenz et al. (2013)
1610	30	?	Jégo and Dasgupta (2014)
1422	11	17 x 5	Fougeroux (2014) ^a
1392	61	21	Wykes et al. (2015)
1402	28	4	Fortin et al. (2015)
1435	40	43	Vidal et al. (2016)
<i>1486</i>	<i>27</i>	<i>77</i>	<i>LeVoyer et al. (2017)^e</i>
1521	41	18	D'Souza and Canil (2018)

1755 ^a glass identified as JD2 rather than VG2; ^b wet chemistry; ^c Two different EMPA routines;
 1756 ^d in 19 sessions, spanning two years; ^e SIMS
 1757
 1758

1759 Table 3. SCSS experiments in Re capsules at 1400°C, 1.5 GPa using the starting composition and
 1760 experimental methods described in Wykes et al. (2015).
 1761

run number	G60*	G61	G70	G76*	G93	G94*
added H ₂ O	1.4	1.8	4	0.2	0.2	5
Na ₂ O	2.64	2.61	2.46	2.59	2.48	2.41
MgO	9.5	9.5	9.4	9.7	9.3	9.4
Al ₂ O ₃	19.6	19.5	19.3	19.5	19.1	19.2
SiO ₂	50.4	50.5	49.8	50.2	49.1	50.1
CaO	10.7	10.7	10.1	10.5	10.3	10.2
TiO ₂	1.27	1.28	1.21	1.19	1.23	1.14
FeO(t)	5.2	5.3	7.3	5.6	8.2	7.3
H ₂ O	0.44	0.43	0.21	0.60	0.17	0.15
S	1176	1193	1332	1434	1268	1256
s(S)	82	90	69	79	169	24

1762 * Sulfur K-edge XANES spectra for these samples were obtained by Métrich et al. (2009)
 1763

1764 Table 4. SCSS model sensitivities (anhydrous model)
1765

Variable (X)	Unit (n _X)	$\partial[S]_{\text{SCSS}}/\partial n_X$ (ppm n _X ⁻¹)
Na ₂ O	1 wt%	7
MgO	1 wt%	60
Al ₂ O ₃	1 wt%	-37
SiO ₂	1 wt%	-19
CaO	1 wt%	45
TiO ₂	1 wt%	31
MnO	0.1 wt%	17.9
FeO _t	1 wt%	106
Ni	1 ppm	-1.1
Cu	1 ppm	-1.9
Fe ³⁺ /ΣFe	0.01	-12
T	1 K	2.25
P	0.01 GPa	1.5

1766
1767

1768 **FIGURE CAPTIONS**

1769 Figure 1. Comparison between values of $A_M^{S^{2-}}$ from O'Neill and Mavrogenes (2002) and Evans et
1770 al. (2008) with thermodynamic data for the difference in the free energies of the orthosilicate and
1771 sulfide solid phases, $(\frac{1}{2}\mu_{M_4SiO_4}^o - \mu_{M_2S}^o)/1400R$. The correlation suggests how approximate values
1772 of $A_{Ni}^{S^{2-}}$ and $A_{Cu}^{S^{2-}}$, which are difficult to measure experimentally (Evans et al. 2008), may be
1773 estimated.

1774

1775 Figure 2. The relationship between $S^{6+}/\sum S$ and $Fe^{3+}/\sum Fe$, estimated by combining the results of
1776 Jugo et al. (2010) on hydrated basalt at 1050°C and 0.2 GPa, with those of Berry et al. (2018) on
1777 MORB glasses (dashed curve), compared to the model of Nash et al. (2019) calculated at 1190°C
1778 (solid curve). The $\pm 2s$ range of measured $Fe^{3+}/\sum Fe$ in MORB glasses from Berry et al. (2018),
1779 taken here to correspond to 95% of the population by assuming a normal distribution of $Fe^{3+}/\sum Fe$,
1780 is indicated by the shaded region. The model of Nash et al. (2019) predicts only a few percent
1781 $S^{6+}/\sum S$ even in the more oxidized MORB glasses.

1782

1783 Figure 3. a) Observed values of the sulfide capacity, $C_{S^{2-}}$, at 1400°C of silicate melts at with
1784 NBO/T from 0.05 to 2, compared to the parameterization of this work (Eqn. 33). The experimental
1785 data are from O'Neill and Mavrogenes (2002) and Tuff and O'Neill (2010). Only the data with \ln
1786 $C_{S^{2-}} > -4$ are plotted, as the few data at lower $C_{S^{2-}}$ have NBO/T ~ 0 , and furthermore are imprecise
1787 due to low S. b) Calculated values of $C_{S^{2-}}$ from Eqn. (34) versus the measured values of Haughton
1788 et al. (1974) at 1200°C.

1789

1790 Figure 4. Comparison between measured values of the activity coefficient of FeO in silicate melts
1791 ($\gamma_{FeO}^{sil\ melt}$) with the parameterization of Equation (46).

1792 a) Data of Doyle and Naldrett (1986), and Doyle (1987, 1988), all at 1327°C. b) Data of Roeder
1793 (1974), O'Neill and Eggins (2002), Borisov et al. (2004, 2006), and Borisov (2007), temperatures

1794 between 1150 and 1500°C. All experiments equilibrated silicate melt with Fe metal at imposed
 1795 oxygen fugacity. The grey areas on either side of the 1:1 lines indicates $\pm 10\%$ relative error.
 1796
 1797 Figure 5. The oxygen contents as the component FeO in sulfide mattes coexisting with silicate melt.
 1798 Data from Brenan (2008), Kiseeva and Wood (2013, 2015), Wood and Kiseeva (2015) and Smythe
 1799 et al. (2017). The dashed line is the least-squares best fit, $[\text{FeO}]_{\text{sulf}} = 1.20 (\pm 0.04) [\text{FeO}]_{\text{sil melt}}$, with
 1800 $R^2 = 0.81$. The solid line is $[\text{FeO}]_{\text{sulf}} = [\text{FeO}]_{\text{sil melt}}$, which was used in the SCSS modeling for
 1801 simplicity.
 1802
 1803 Figure 6. The effect of pressure on the SCSS, comparing Eqn. (43) of this study, calculated starting
 1804 from $[\text{S}]_{\text{SCSS}} = 1400$ ppm at ambient pressure, with the equations for SCSS from Mavrogenes and
 1805 O'Neill (1999), Holzheid and Grove (2002) and Smythe et al. (2017), all at 1400°C. The different
 1806 calculated values of $[\text{S}]_{\text{SCSS}}$ at $P = 0$ are due in part to the different compositions studied. The effect
 1807 of pressure found by Wendlandt (1982) is similar to that of Mavrogenes and O'Neill (1999) and
 1808 Holzheid and Grove (2002), and is not shown for clarity. The effect of pressure from Smythe et al.
 1809 (2017) is smaller than those from Mavrogenes and O'Neill (1997) or Holzheid and Grove (2002),
 1810 but is similar to the hypothetical parameterization postulated in this study at > 1 GPa. This
 1811 comparison shows the desirability of integrating experiments at high pressure with those at 1 bar, to
 1812 constrain the effect of pressure more precisely in the range 1 bar to 1.5 GPa.
 1813
 1814 Figure 7. SCSS for a binary compositional join between FeO-free “matrix” and FeO. Experimental
 1815 data from Wykes et al. (2015) and this study (Table 3) compared to the SCSS model. The model
 1816 gives a good fit to the data at < 1 wt% FeO, which were not used as input, and also to the data at
 1817 high FeO, which have not been well fitted by previous models, see Fig. 9 of Wykes et al. (2015).
 1818

1819 Figure 8. The effect of H₂O on SCSS. Data from Moune et al. (2009) at 1045°C, ~ 0.3 GPa, in
1820 equilibrium with pyrrhotite; Fortin et al. (2015), 1250°C, 1 GPa; D’Souza and Canil (2018),
1821 1270°C, 1 GPa; and this work, Table 3, 1400°C, 1.5 GPa. a) The difference $\ln [S]_{\text{obs}} - \ln [S]_{\text{SCSS}}(\text{dil})$,
1822 which is equivalent to $\ln C_{S2-}^H$, see text for further explanation. b) $[S]_{\text{SCSS}}$ calculated from the model
1823 vs. $[S]_{\text{obs}}$. The shaded area around the 1:1 line indicates $\pm 10\%$.

1824

1825 Figure 9. Sulfur saturation in Ocean Floor Basaltic (OFB) glasses from Jenner and O’Neill (2012).
1826 a) Calculated SCSS versus S contents analysed by electron microprobe. Of the 329 glasses, only 11
1827 (3%) were identified as probably having lost S. (Two samples with very low S plot off the
1828 diagram). b) This S loss is correlated with decreasing S/Se. The vector for this loss is calculated
1829 assuming 1000 ppm S and 0.33 ppm Se, with Se contents of the melt assumed to be conserved
1830 (Jenner et al. 2010).

1831

1832 Figure 10. The difference between $[S]_{\text{obs}}$ and the calculated SCSS from the model for 35 OFB
1833 glasses from Jenner and O’Neill (2012) compared against their $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined from XANES
1834 by Berry et al. (2018). There is almost no correlation ($R^2 = 0.16$). One glass, VG6822, not used in
1835 the regression, has low S due to loss by volatility, but retains typical $\text{Fe}^{3+}/\Sigma\text{Fe}$.

1836

1837 Figure 11. Calculated atomic Ni/Fe (a) and Cu/Fe (b) in sulfide liquid in equilibrium with the OFB
1838 glasses analysed by Jenner and O’Neill (2012), compared to observed Ni/Fe and Cu/Fe in sulfide
1839 globules from basalts analysed by electron microprobe, by Czamanske and Moore (1977) and
1840 Patten et al. (2012). Also plotted are calculated Ni/Fe and Cu/Fe for the same OFB glasses from the
1841 model of Smythe et al. (2017).

1842

1843 Figure 12. Comparison with the SCSS model of Smythe et al. (2017). a) Calculated $[S]_{\text{SCSS}}$ for the
1844 OFB glasses of Jenner and O’Neill (2012) from the model of Smythe et al. (2017) vs. $[S]_{\text{obs}}$,

1845 compared to the model of this work. b) The difference between the models is a function of the FeO
1846 content of the glasses.

1847

1848 Figure 13. a) Reproducibility of S analyses in basaltic glasses: a comparison of SIMS vs. EMPA.
1849 SIMS analyses of Macquarie Island glasses from Shimizu et al. (2016) are compared against EMPA
1850 analyses of the same glasses from Kamenetsky et al. (2000), and SIMS and EMPA analyses of
1851 some Ocean Island Basalt glasses from Kendrick et al. (2014). b) Comparison of model $[S]_{SCSS}$
1852 calculated from the analyses of Shimizu et al. (2016) with those calculated for the same glasses
1853 from the analyses of Kamenetsky et al. (2000) and Kamenetsky and Eggins (2012).

1854

1855 Figure 14. Comparison of model $[S]_{SCSS}$ with $[S]_{obs}$ for Macquarie Island basaltic glasses, using the
1856 analyses of Shimizu et al. (2016) and those of Kamenetsky et al. (2000) and Kamenetsky and
1857 Eggins (2012). The latter scatter around the 1:1 line, the former are displaced to higher model
1858 $[S]_{SCSS}$, which, if accurate could be interpreted as indicating sulfide-undersaturation. The shaded
1859 area surrounding the 1:1 line indicates $\pm 10\%$ uncertainty

1860

1861 Figure 15. Comparison between model $[S]_{SCSS}$ and $[S]_{obs}$ for two sets of glasses from Shimizu et al.
1862 (2016) analysed by SIMS. Most glasses are displaced to high $[S]_{obs}$ by 9% (dashed line) from the
1863 1:1 line, which could be a systematic analytical artifact. However, a few glasses have even higher
1864 $[S]_{obs}$, suggesting excess S as SO_4^{2-} . These glasses could be checked for $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ by
1865 XANES.

1866

1867 Figure 16. Olivine-hosted melt inclusions from Le Voyer et al. (2017). a) model $[S]_{SCSS}$ compared
1868 to $[S]_{obs}$, both uncorrected (i.e., as analysed), and with silicate melt compositions corrected for post-
1869 entrapment crystallization. The agreement for the uncorrected compositions is mostly within $\pm 10\%$
1870 (shaded area). B) shows that the larger the correction for post-entrapment crystallization, the worse

1871 the discrepancy between $[S]_{\text{obs}}$ and calculated $[S]_{\text{SCSS}}$. However, there is also a significant
1872 correlation ($R^2 = 0.43$) between $[S]_{\text{obs}}$ and calculated $[S]_{\text{SCSS}}$ for the uncorrected data, indicating that
1873 the perceived need for correction may be a sign of disequilibrium between olivine and melt at the
1874 time of entrapment.

1875

1876 Figure 17. Ni and Cu abundances in Ocean Floor Basaltic (OFB) glasses versus MgO. Data from
1877 Jenner and O'Neill (2012) and Gale et al. (2013).

1878

1879 Figure 18. Calculated $[S]_{\text{SCSS}}$ vs. $[S]_{\text{obs}}$ for olivine-hosted melt inclusions from the Siqueiros
1880 Fracture Zone (Saal et al. 2002), with Ni and Cu contents estimated using the correlations with
1881 MgO shown in Fig. 17. Both the uncorrected melt compositions and those corrected for post-
1882 entrapment crystallization plot around the 1:1 line, indicating that most inclusions are likely sulfide-
1883 saturated. Only four inclusions have significantly lower $[S]$ than expected for saturation.

1884

1885 Figure 19. a) $\log_{10} fS_2$ and b) $\log_{10} fSO_2$ calculated for 35 sulfide-saturated OFB glasses. S analyses
1886 from Jenner and O'Neill (2012), $Fe^{3+}/\Sigma Fe$ from Berry et al. (2018), calculated ΔQFM from O'Neill
1887 et al. (2018).

1888

Figure 1

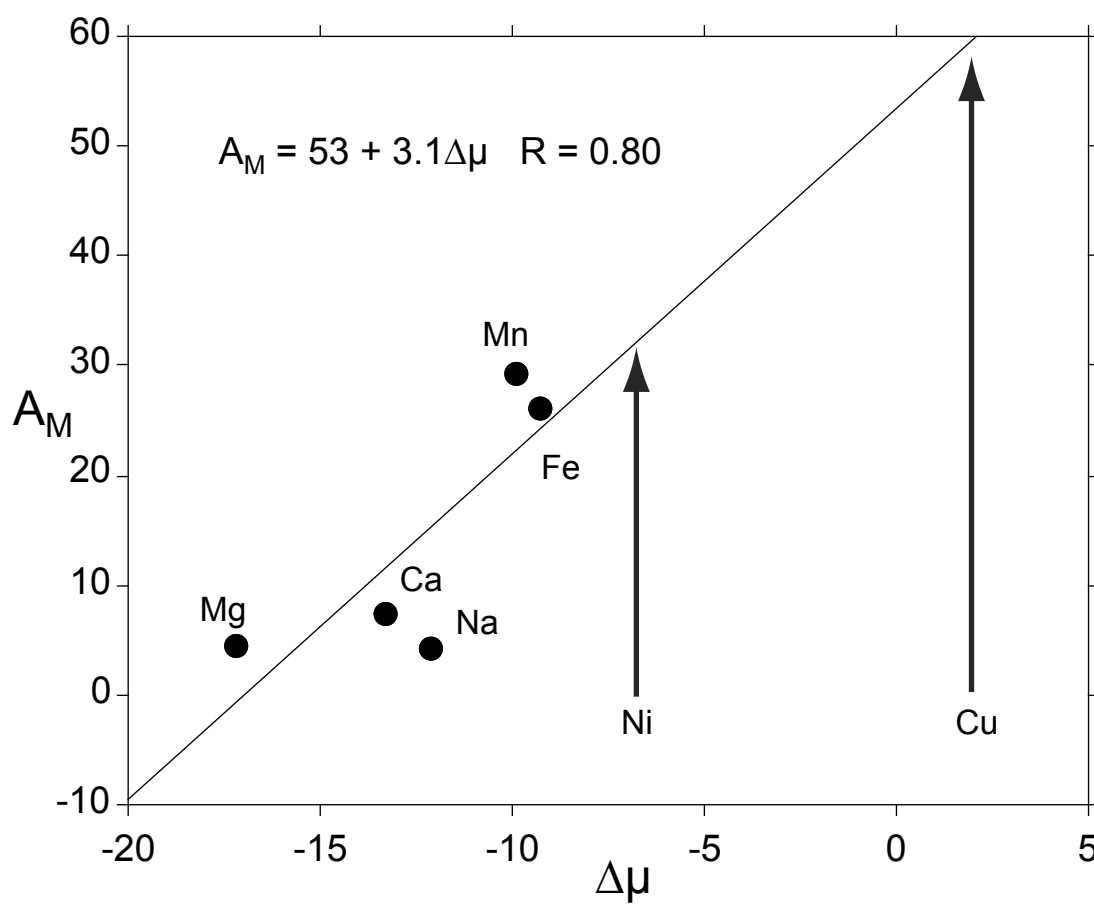


Figure 2

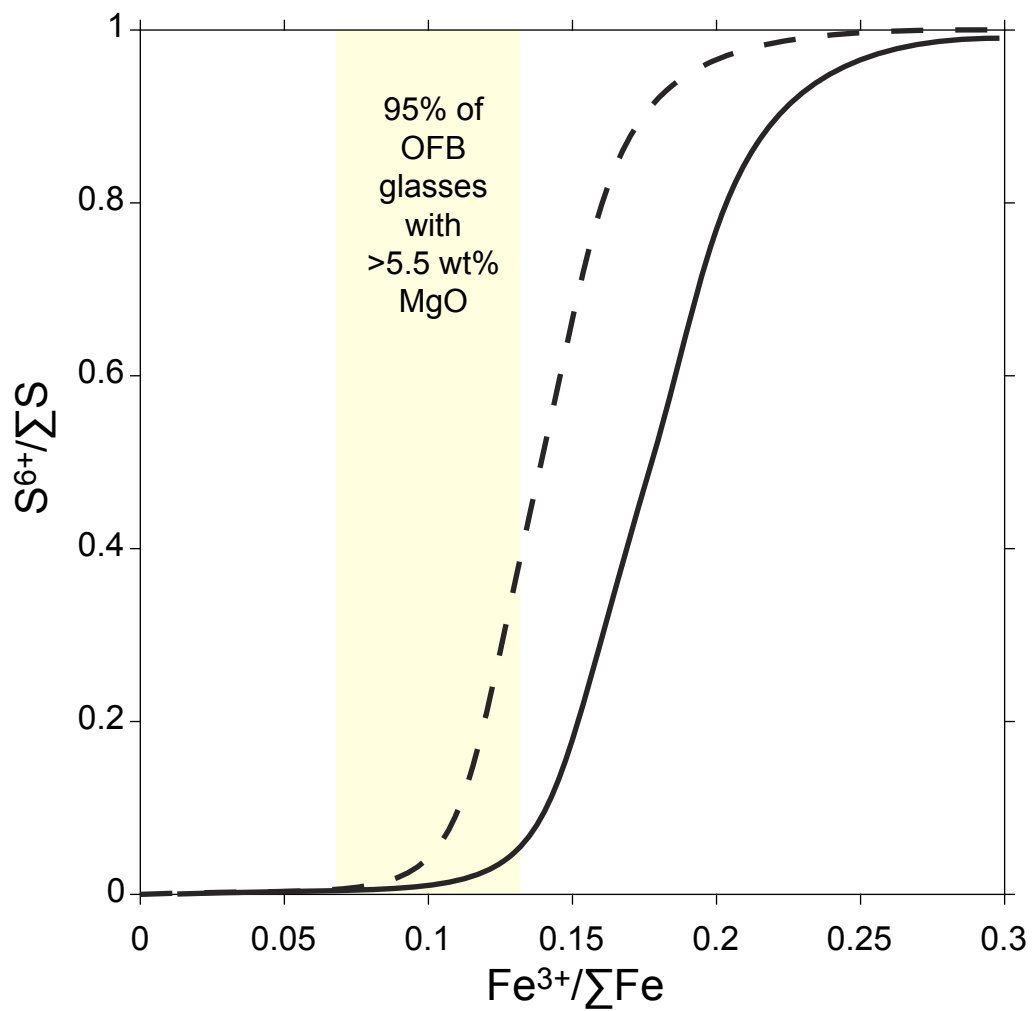


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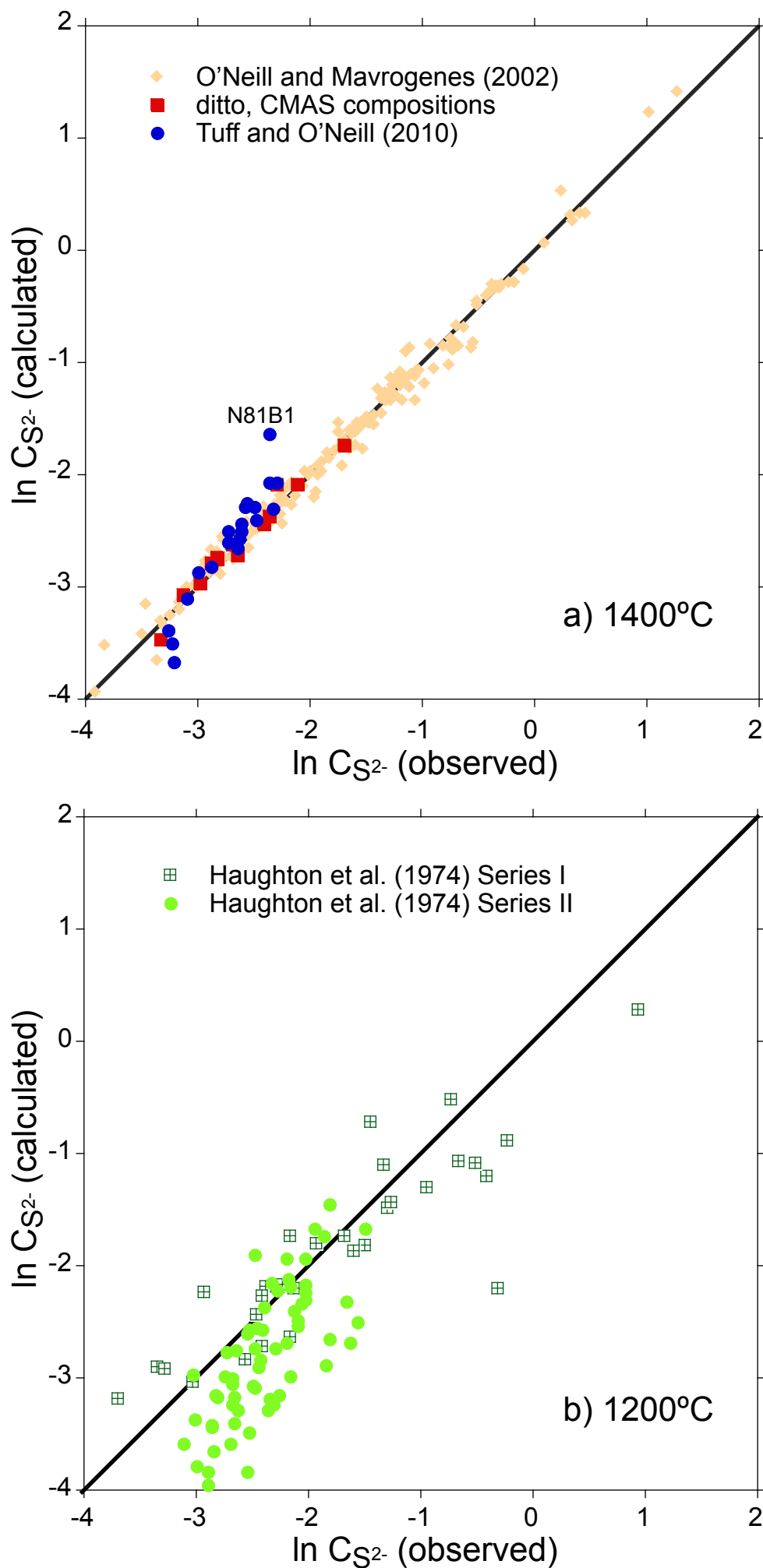


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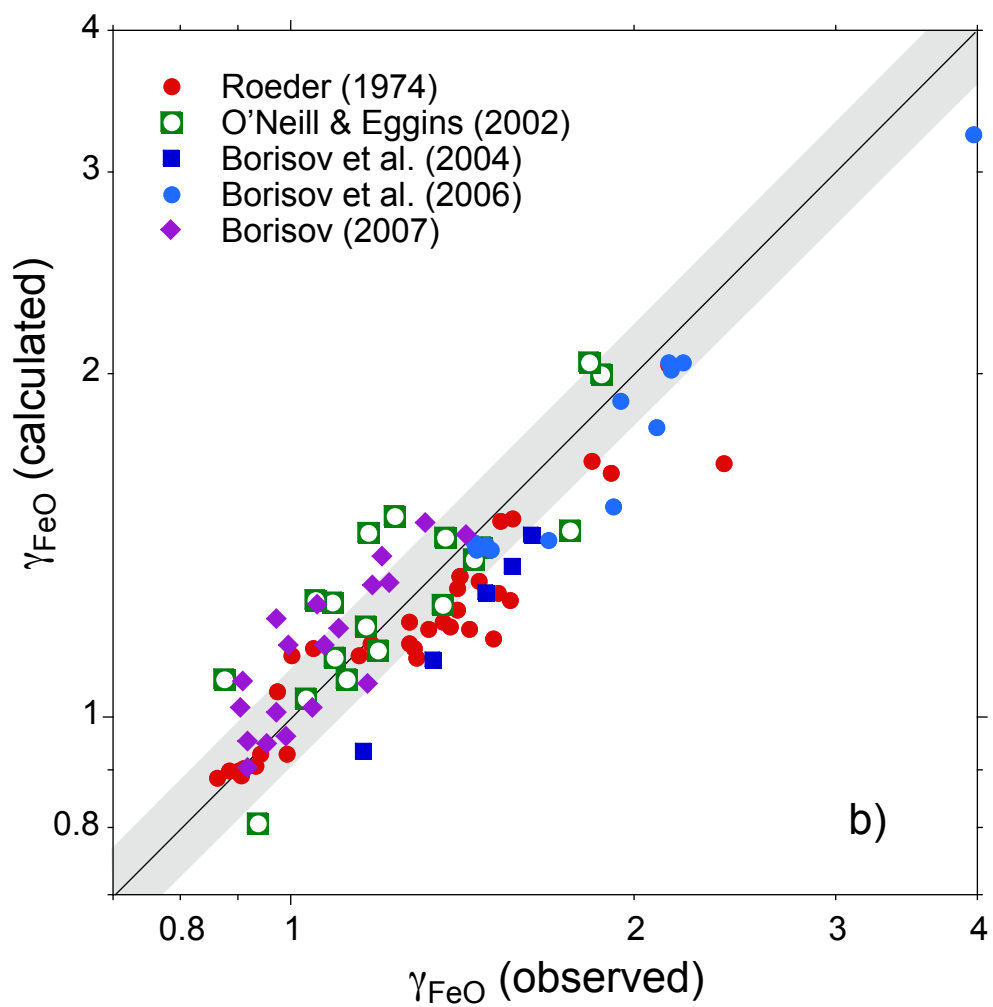
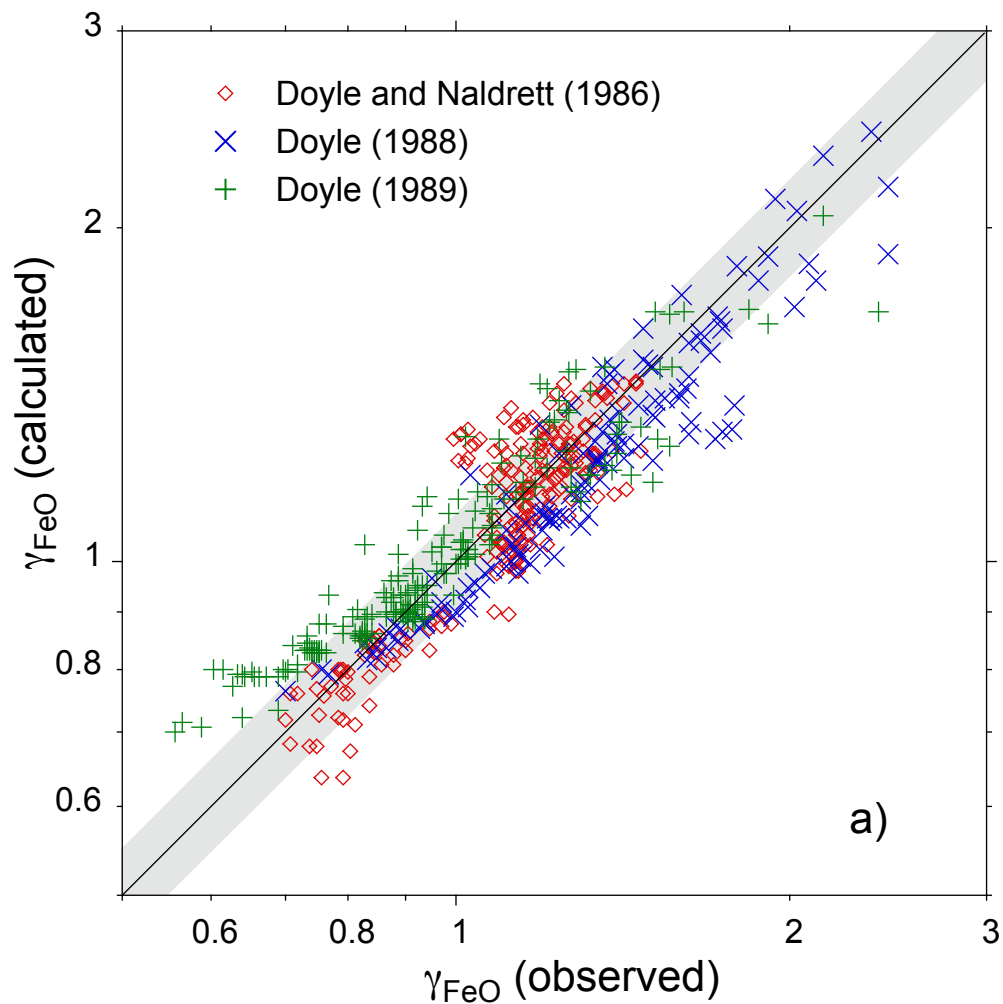


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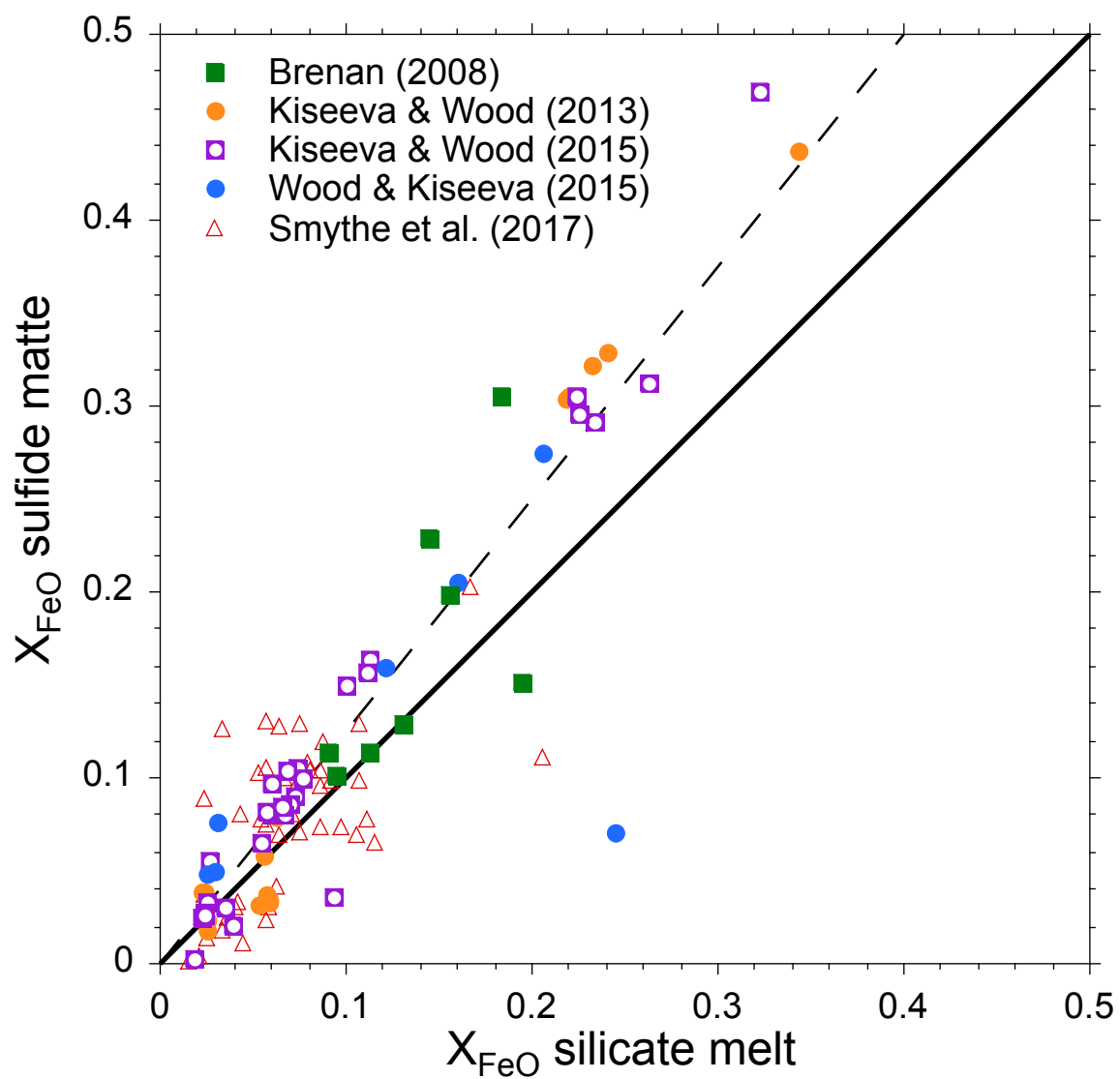


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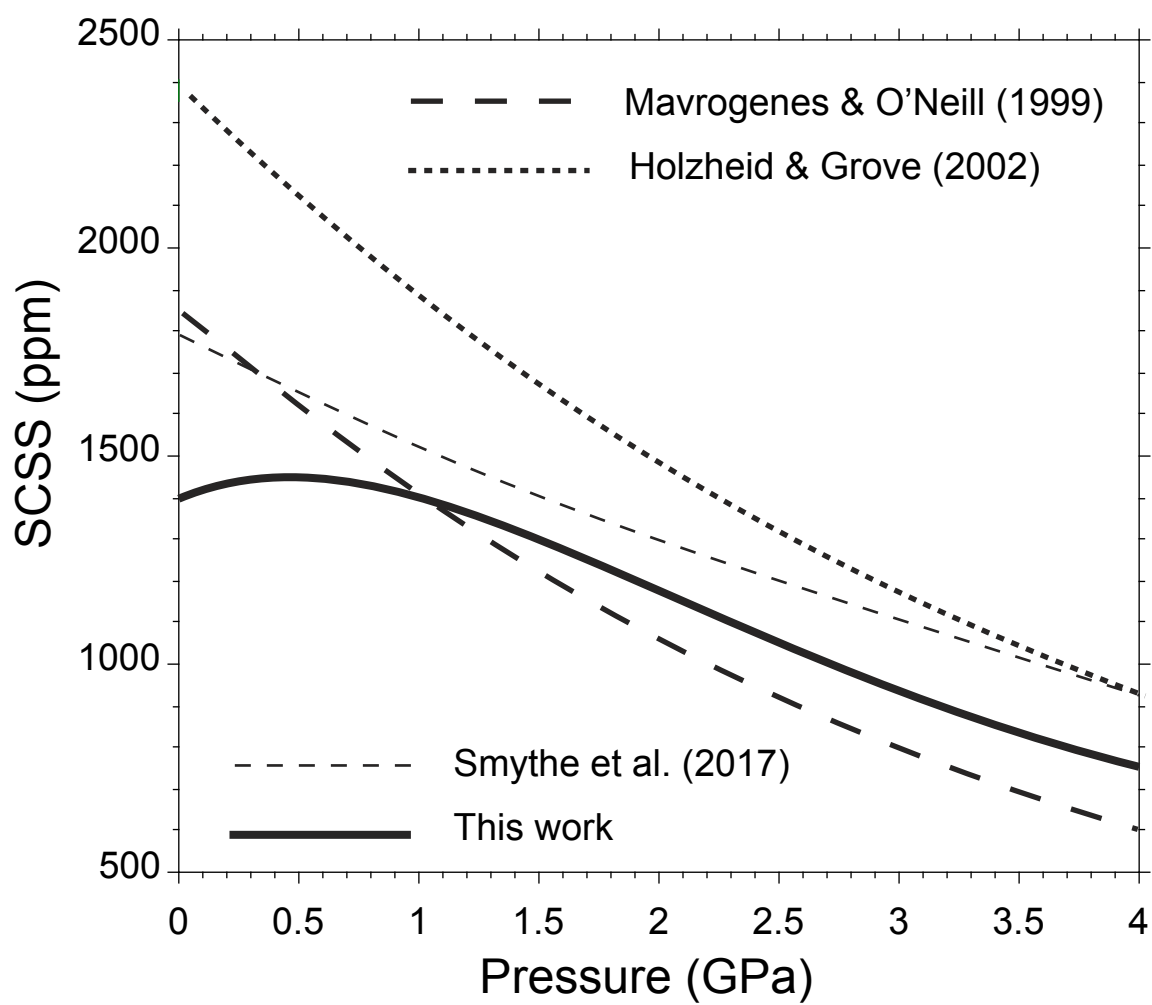


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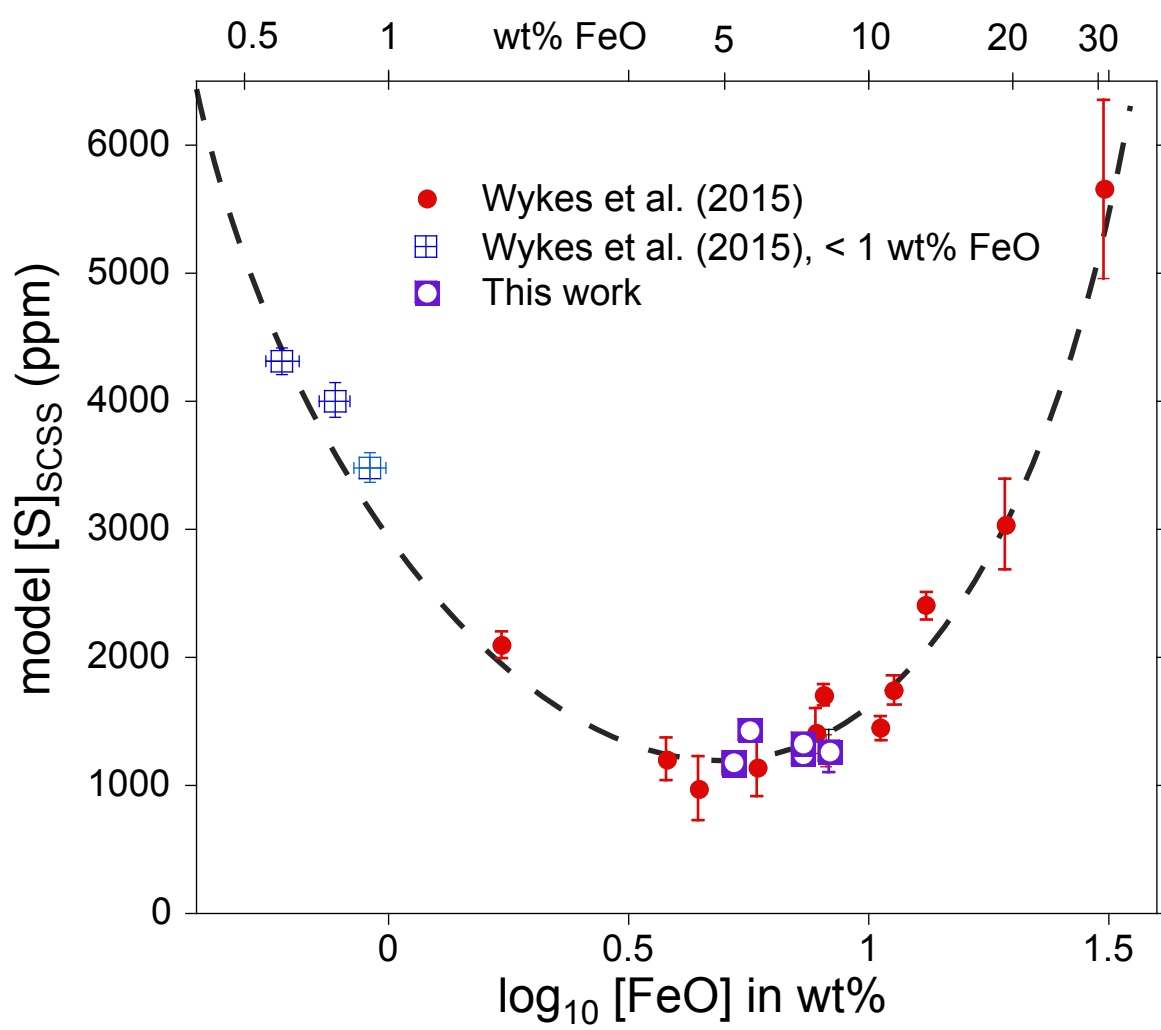


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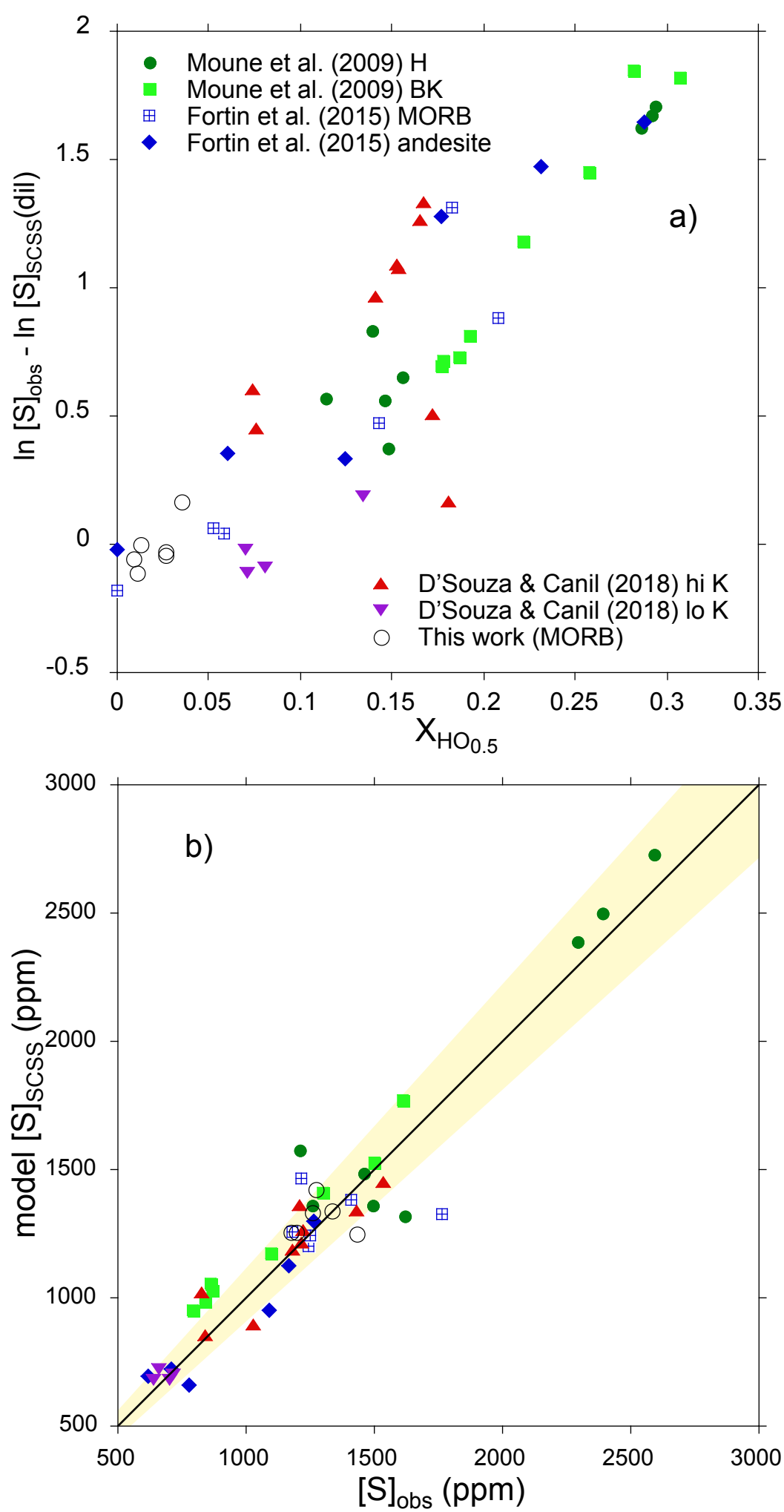


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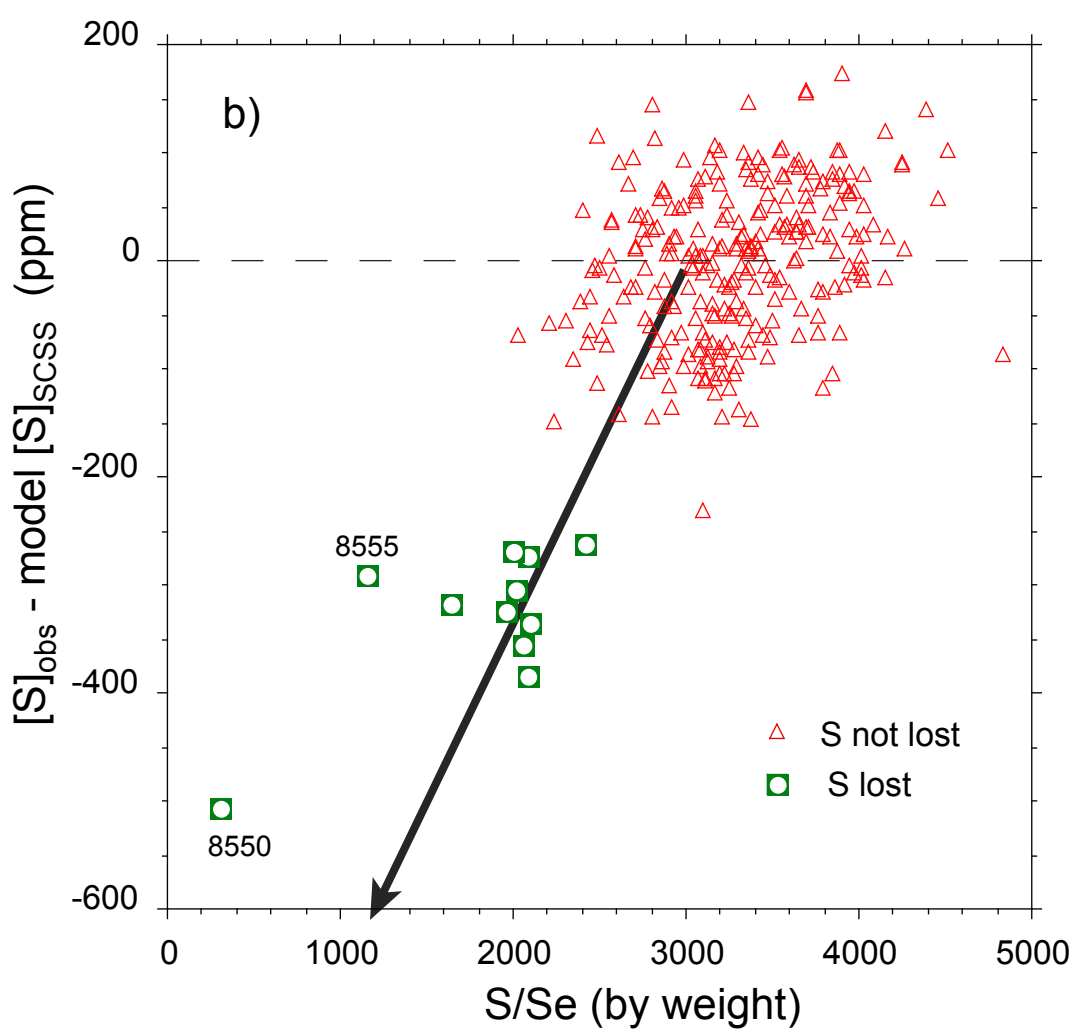
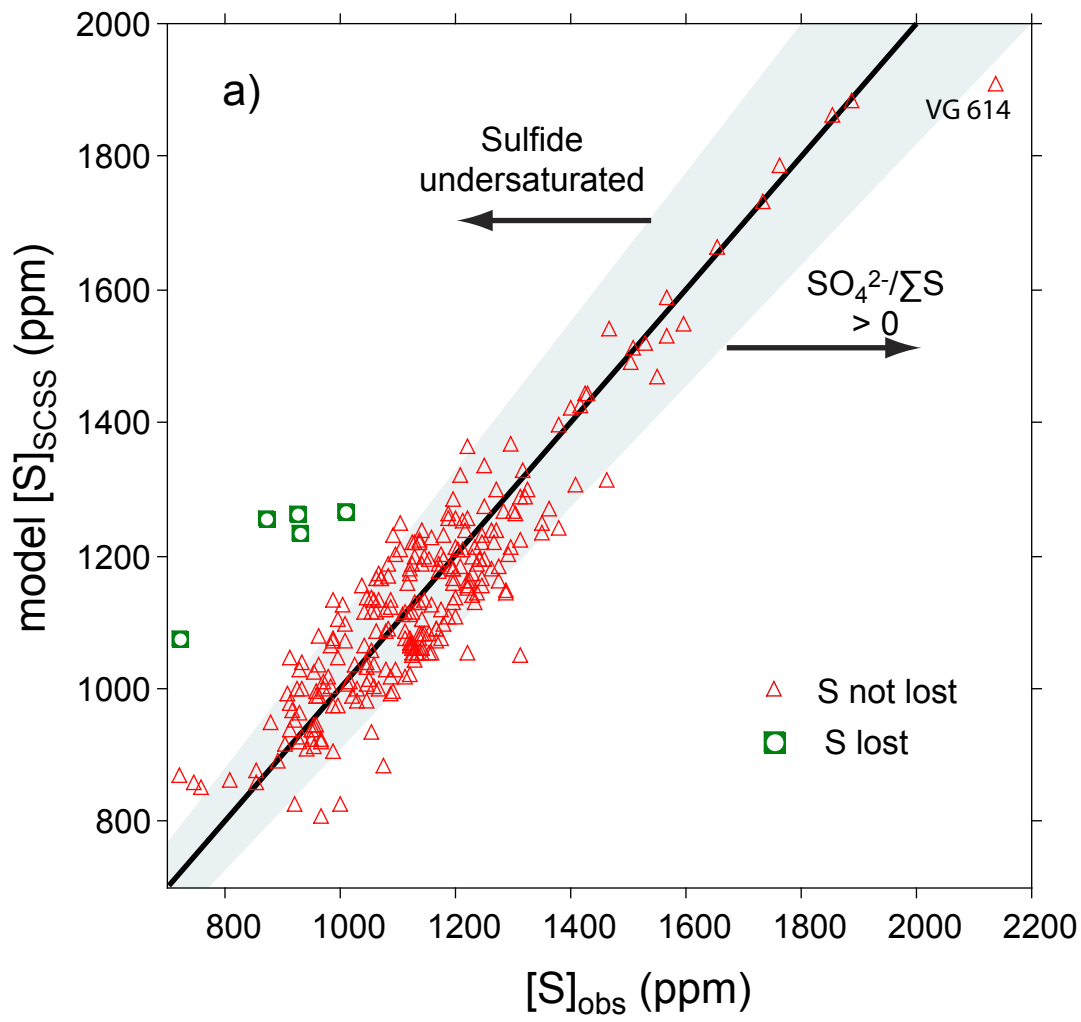


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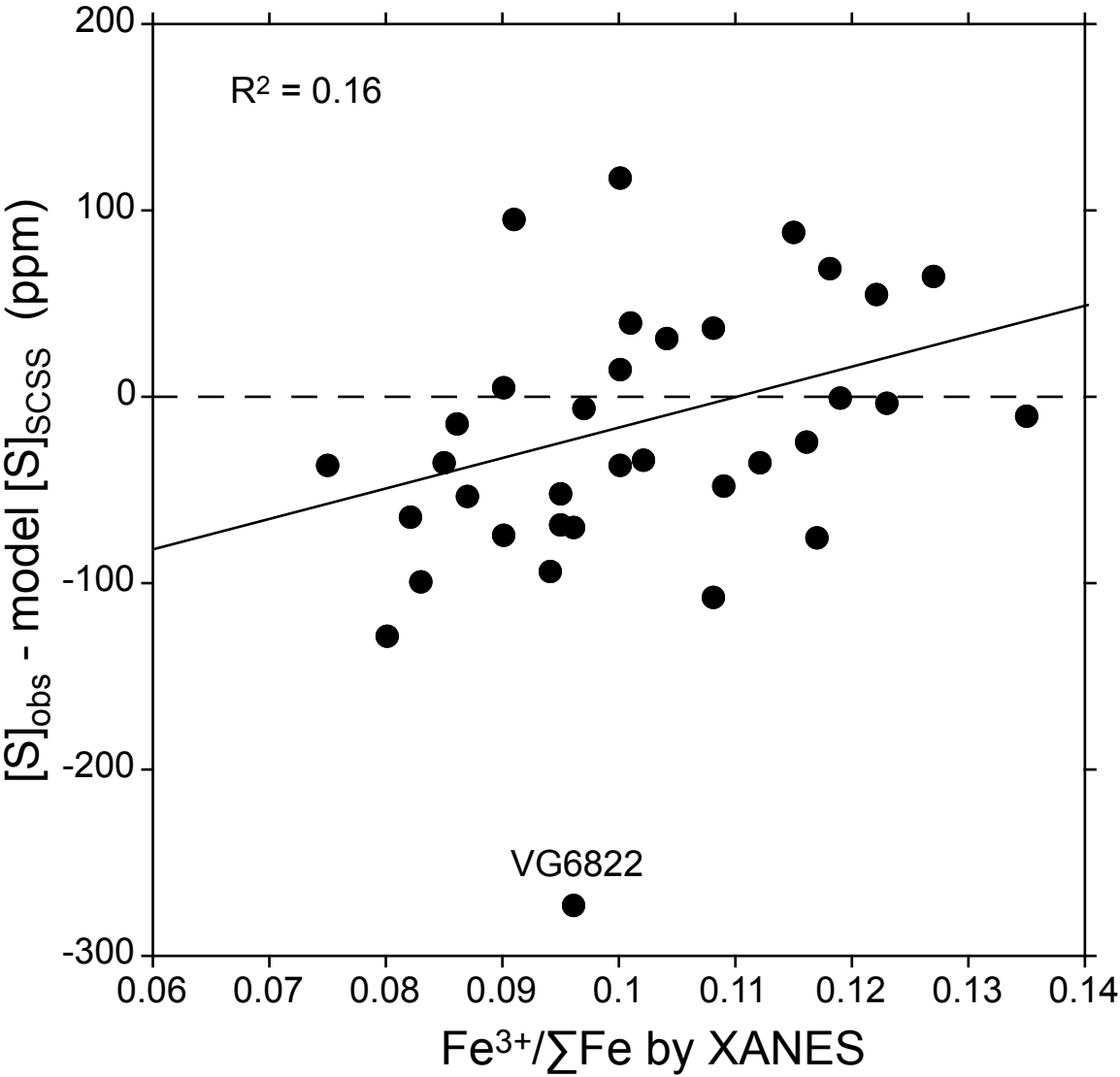


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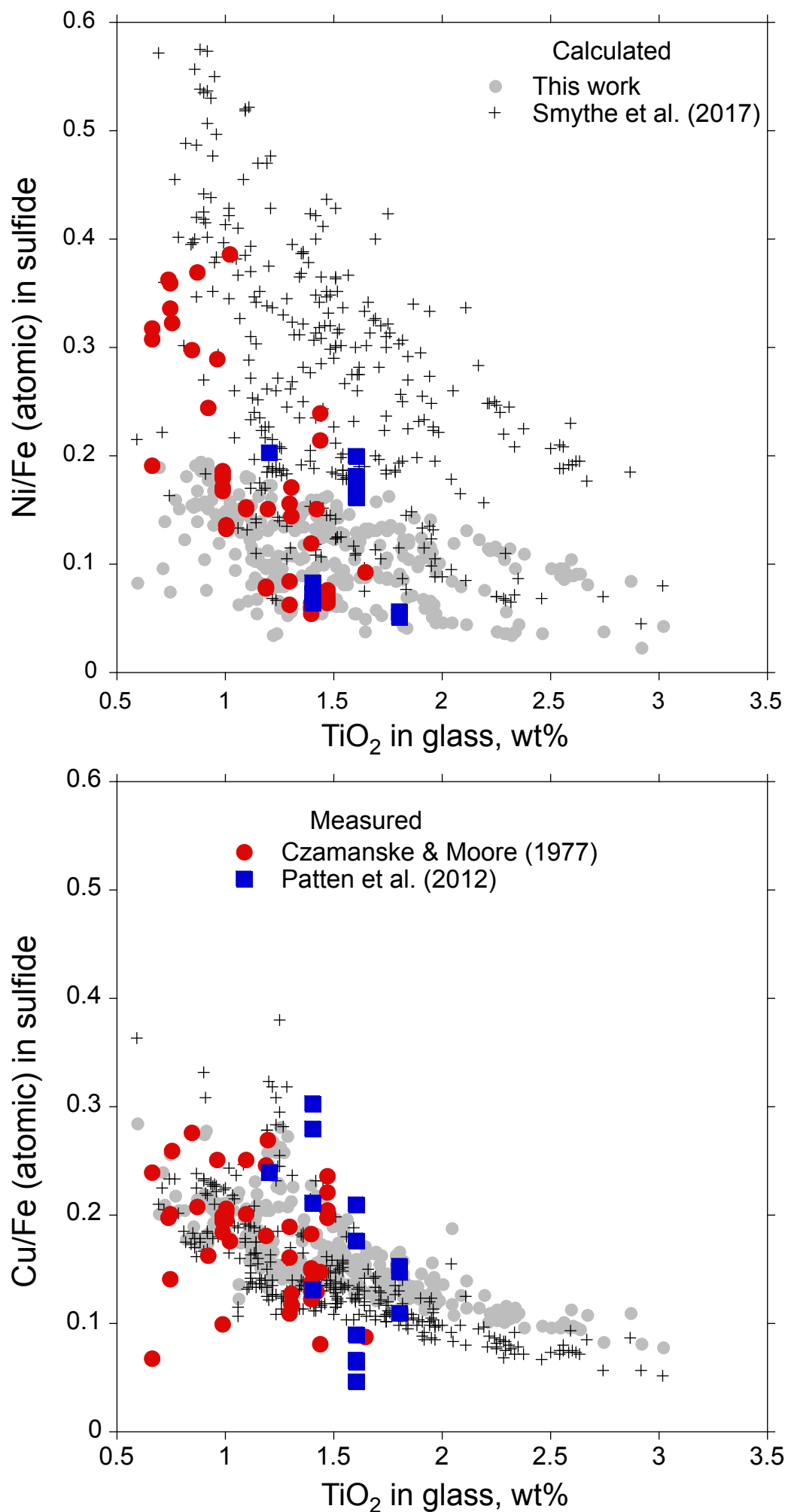


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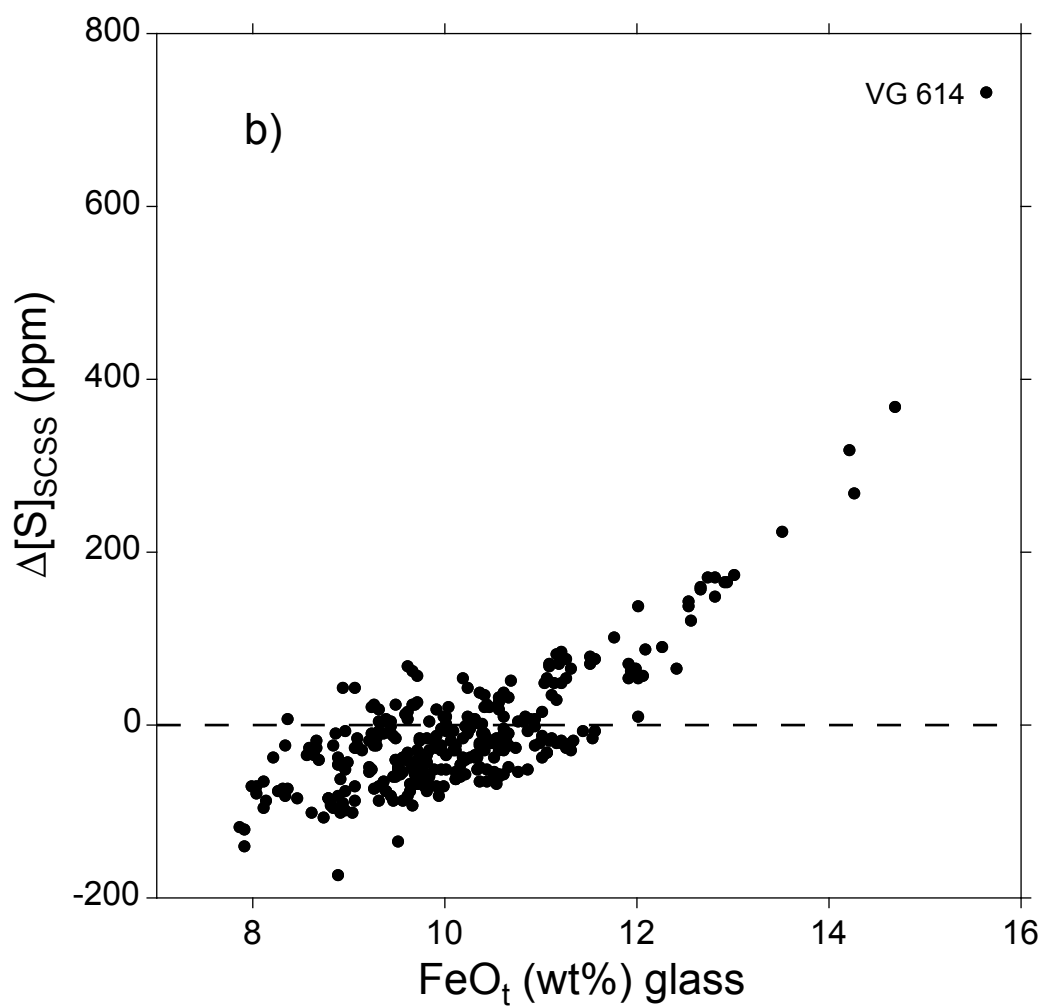
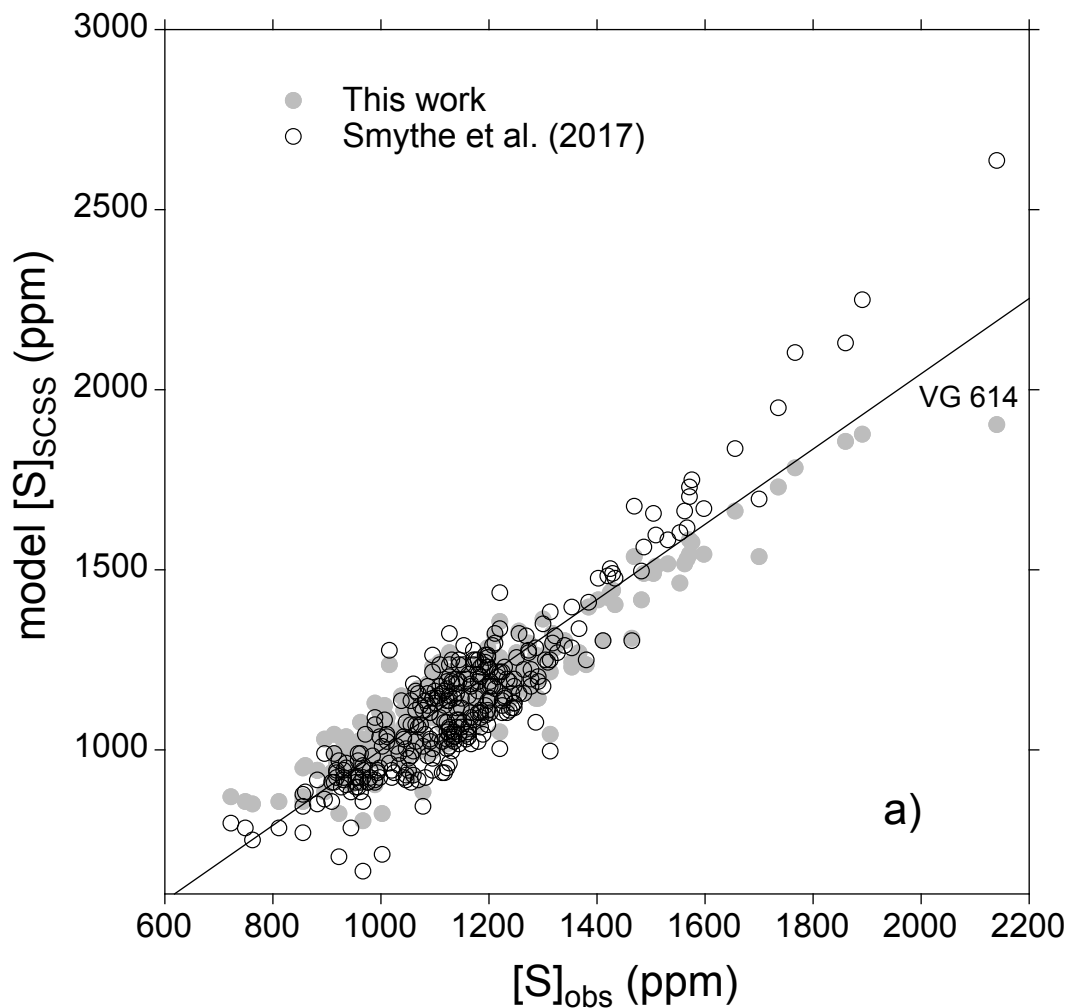


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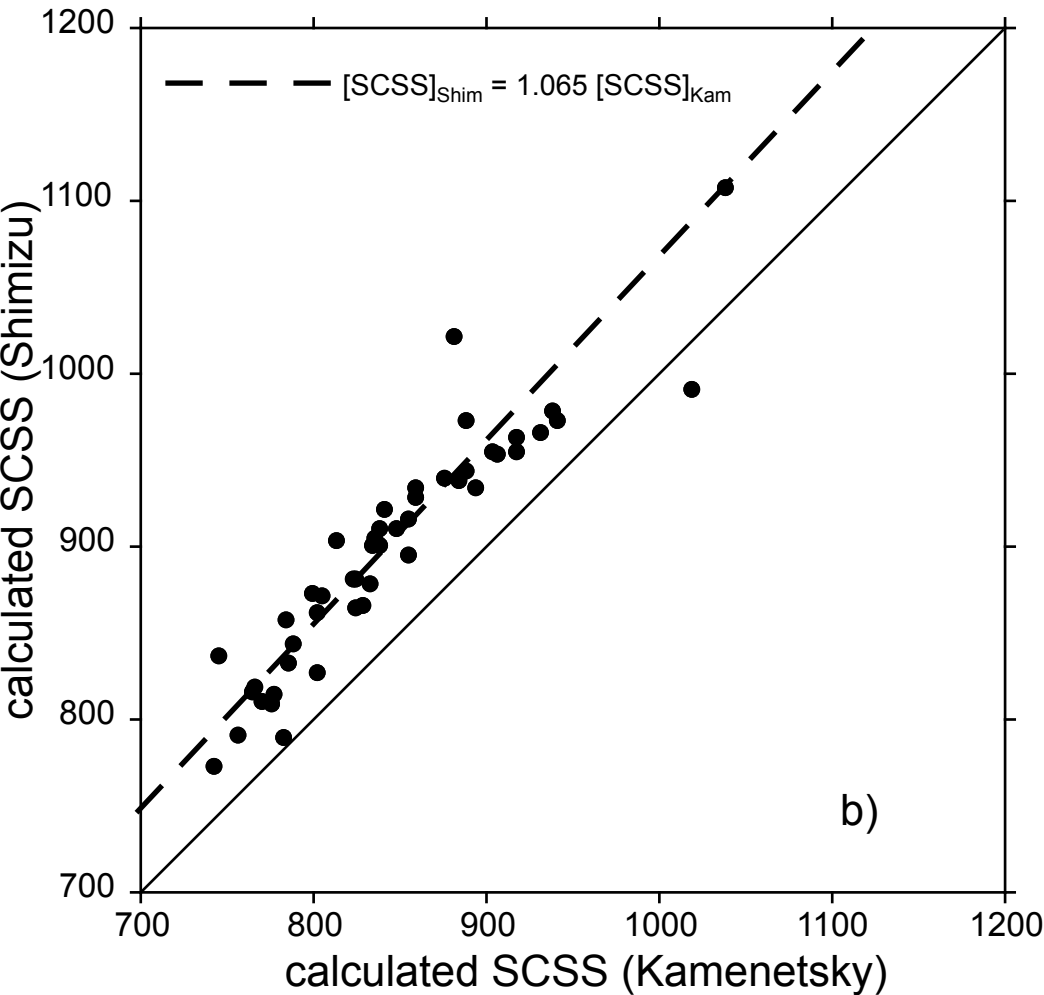
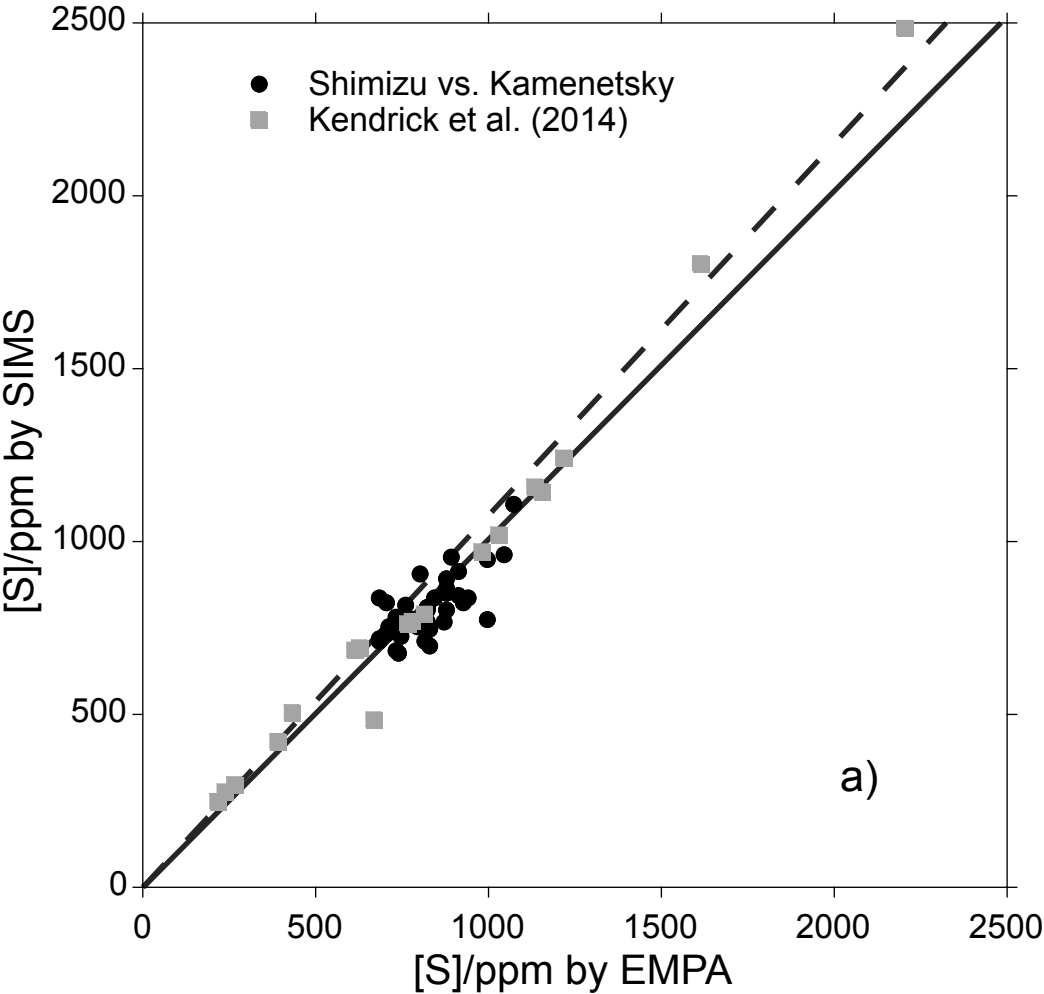


Figure 14

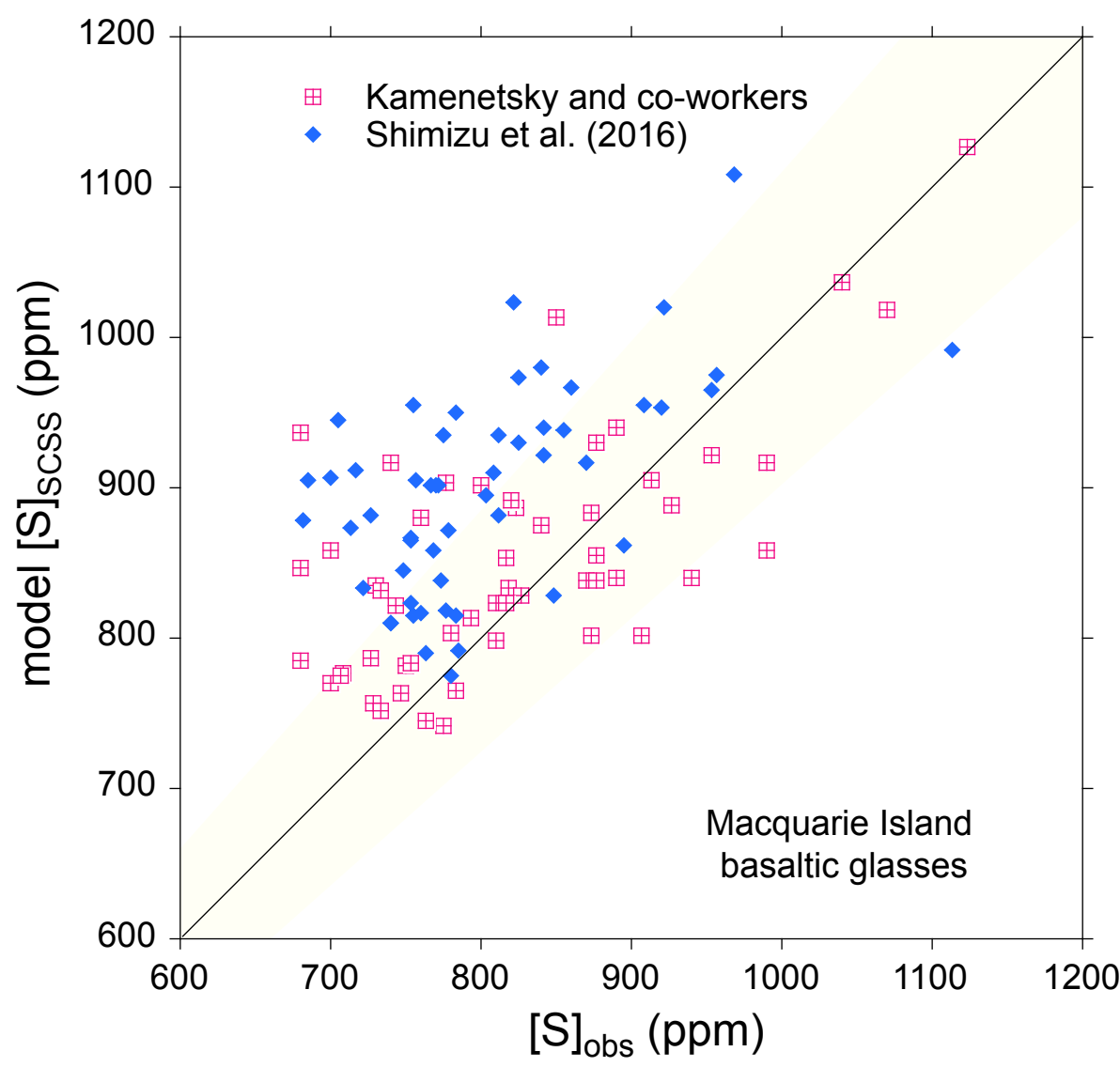


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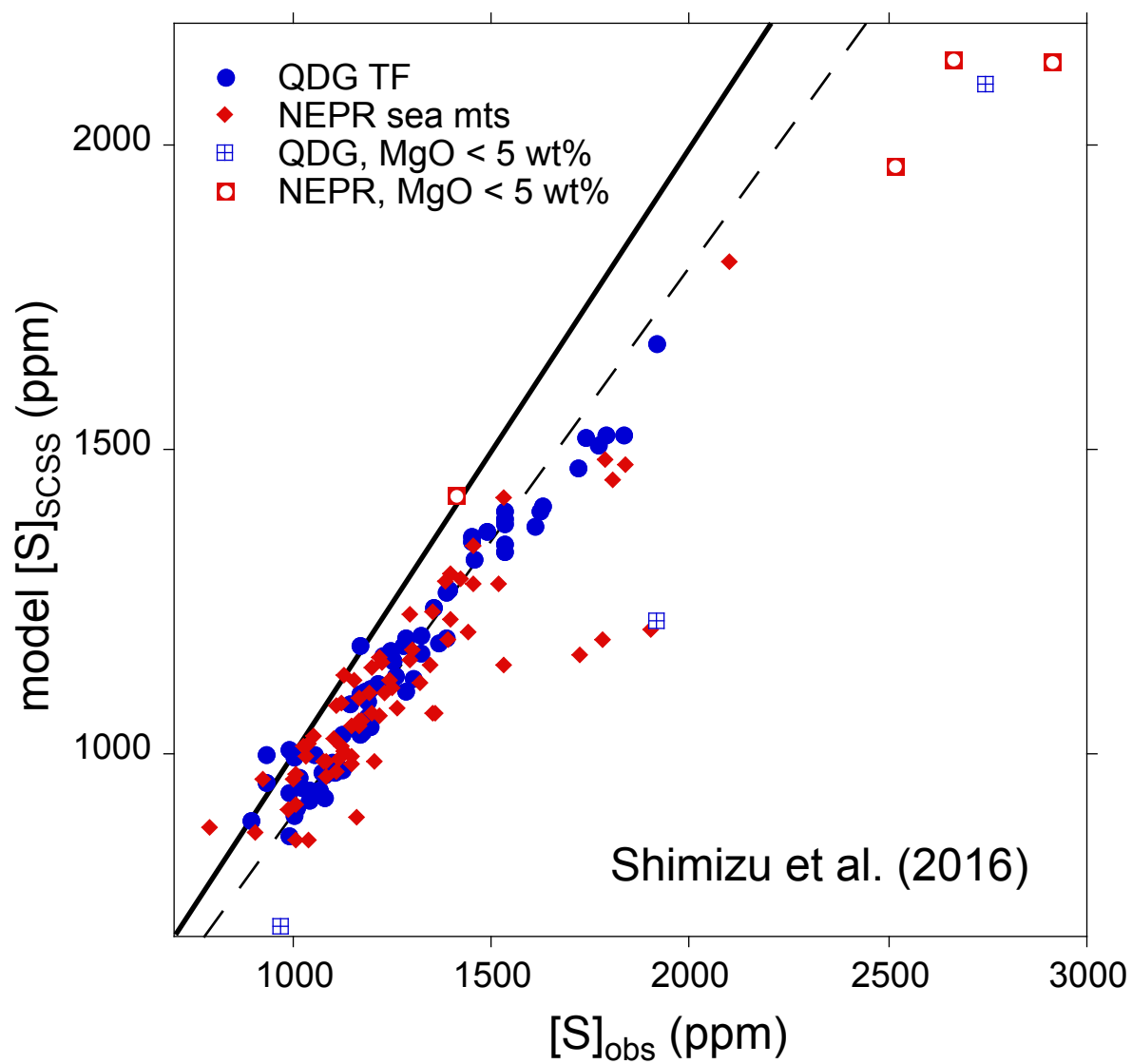


Figure 16

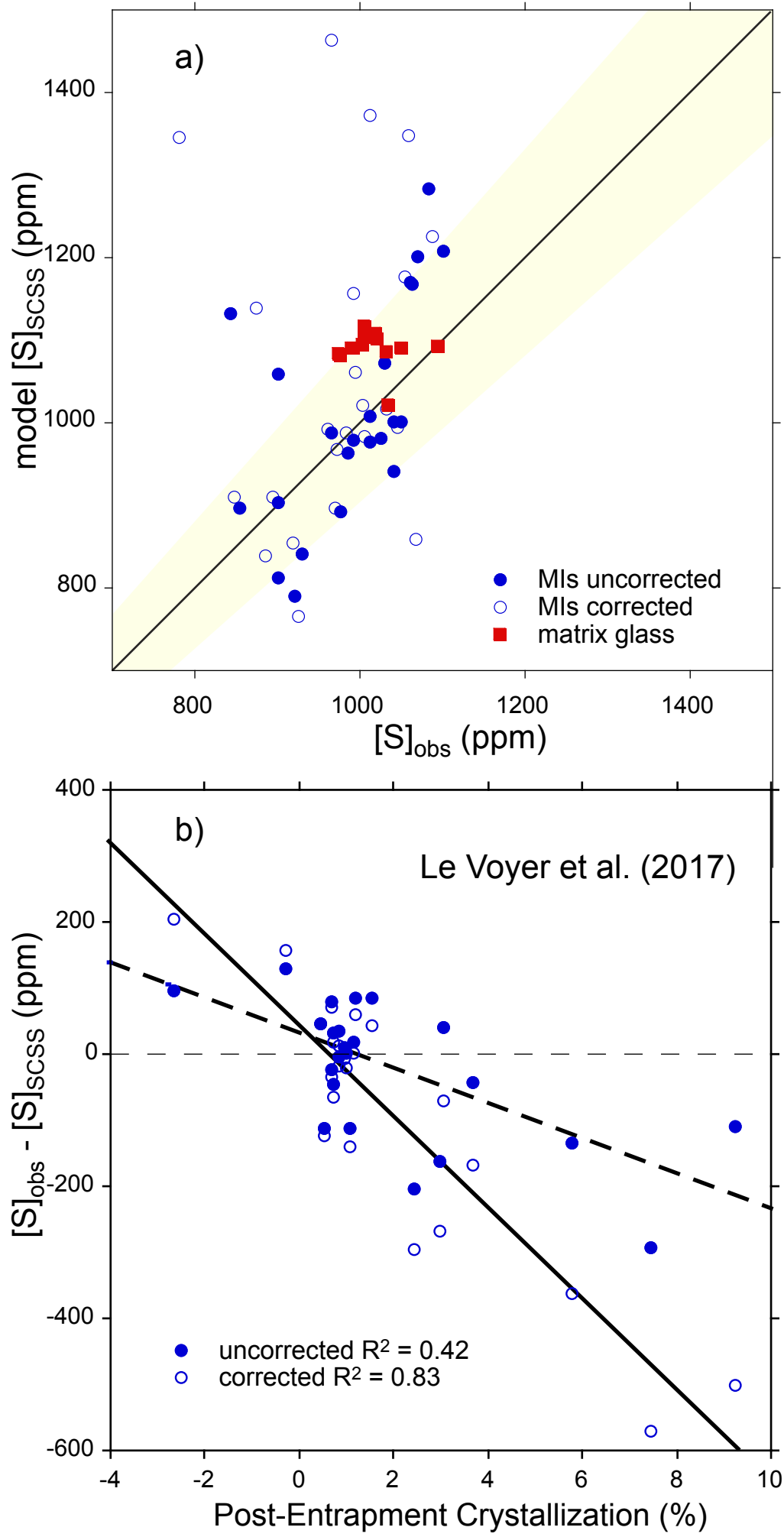


Figure 17

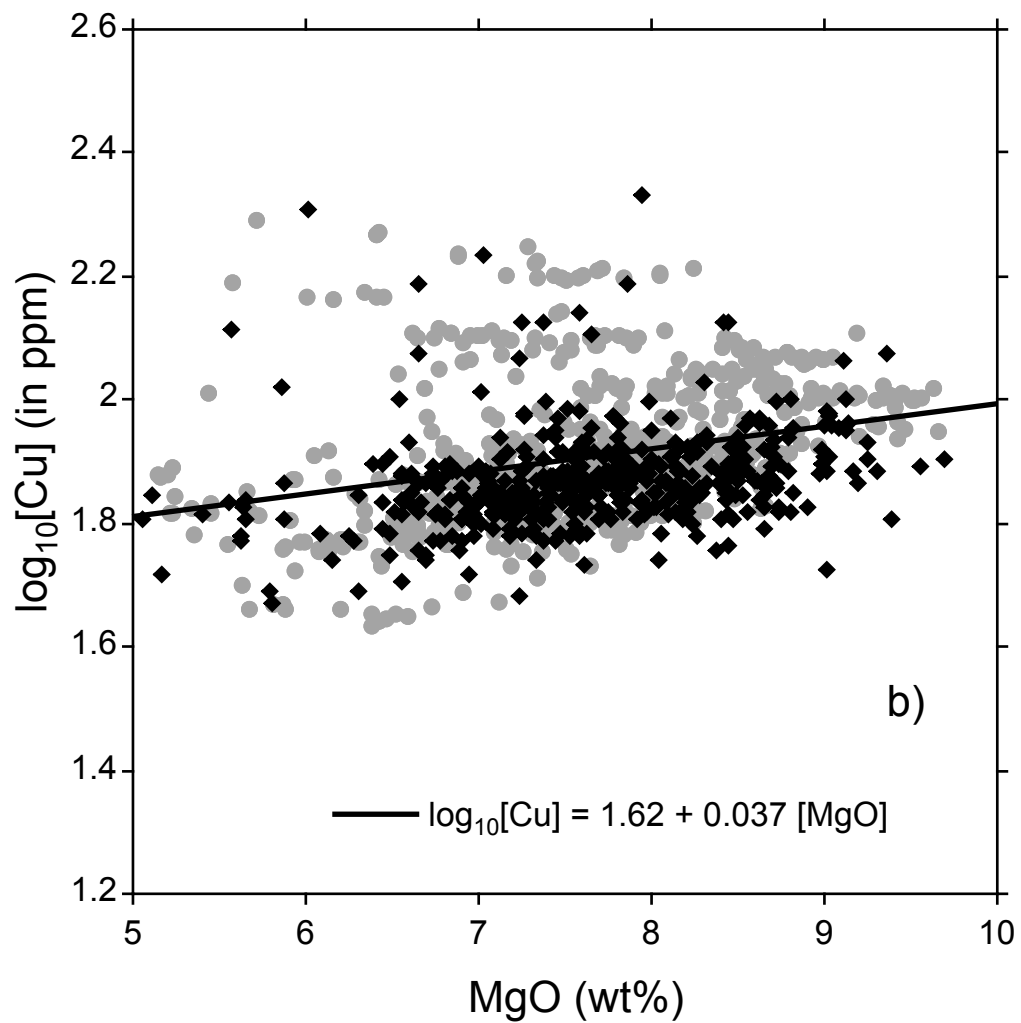
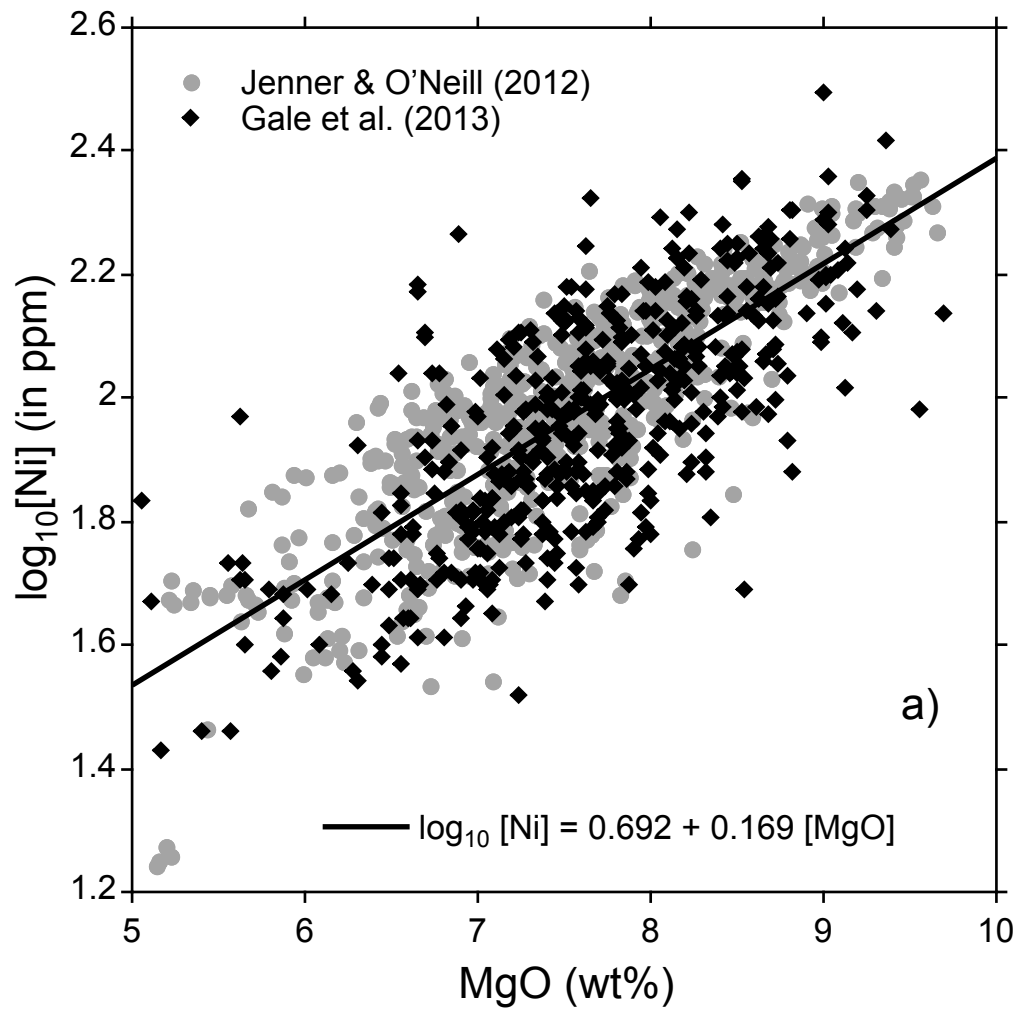


Figure 18

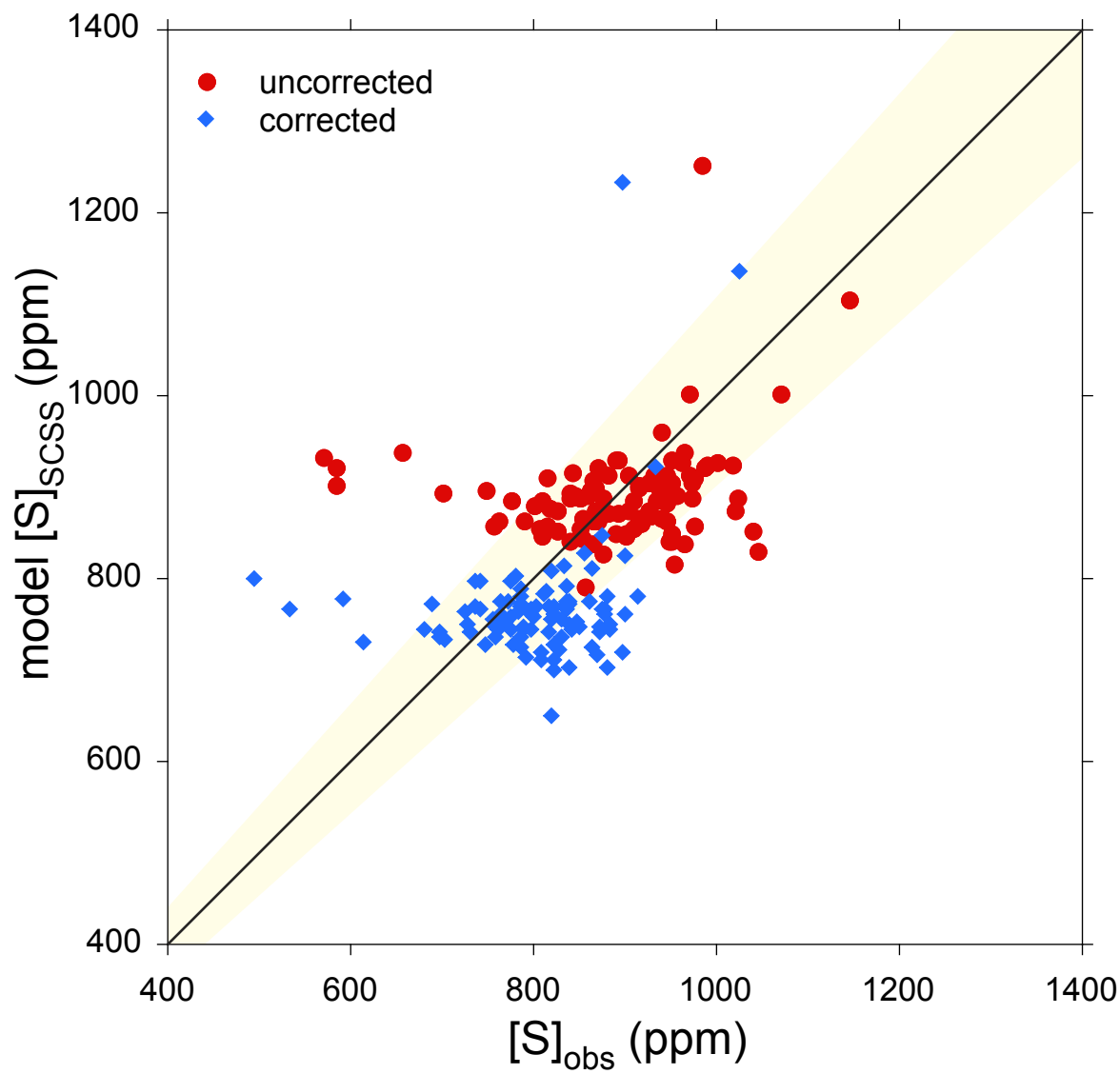


Figure 19

