

1 Reply to: O'Neill, H. S., 2020; Comment on 'Compositional and temperature effects  
2 on sulfur speciation and solubility in silicate melts" by Nash et al. (Earth and  
3 Planetary Science Letters 507, 187–198, 2019)

4  
5 | Bernard J. Wood\*, William M. Nash, Duane [JM](#). Smythe; Department of Earth  
6 Sciences, South Parks Road, Oxford OX1 3AN, UK

7  
8 \*Corresponding author: [Bernie.wood@earth.ox.ac.uk](mailto:Bernie.wood@earth.ox.ac.uk)

9  
10  
11 Keywords: sulfur speciation, sulfur-iron electron exchange, Redox

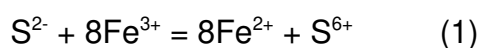
## Introduction

We begin by stating that we reject the assertion of O'Neill (2020) that, in Nash et al (2019) we made an inappropriate temperature-extrapolation of our 1300°C experimental data. Our approach to this extrapolation is, in fact, one which is commonly followed in the literature and was found, in this case, to match lower temperature data exactly. We also reject his suggestion that the exchange of electrons between S and Fe should “quench-in” at the glass transition temperature.

In Nash et al (2019) we developed a novel approach to determining the speciation of sulfur in Fe-bearing silicate melts based on measurements of sulfur concentration as a function of sulfur and oxygen fugacities. As pointed out by O'Neill (2020) “*Such measurements are not affected by the re-speciation problem, and therefore we now know the speciation of S in anhydrous melts at the temperature of their study, 1300°*”. After establishing S<sup>2-</sup> - S<sup>6+</sup> speciation in melt compositions ranging from dacite to Fe-rich martian basalt, we plotted the latter as a function of the expected Fe<sup>2+</sup>-Fe<sup>3+</sup> speciation at the oxygen fugacity of the experiment (Fig 1). We found that the compositional effects on the interdependence of these redox ratios are small (Fig 1) but that, based on 1050° data on basalt (Jugo et al., 2010) and andesite (Botcharnikov et al., 2011) there is a large apparent temperature effect on the relationship between Fe<sup>2+</sup>-Fe<sup>3+</sup> speciation and S<sup>2-</sup>-S<sup>6+</sup> speciation. Specifically, the S<sup>6+</sup>/S<sup>2-</sup> ratio at a given Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio appears to decline as temperature is lowered (Fig 1). This “temperature” effect is due either to (i) temperature itself or (ii) the effect of H<sub>2</sub>O in the 1050° experiments on the exchange of electrons between Fe<sup>3+</sup> and S<sup>2-</sup> or (iii) it is an artifact of the different quenching rates of the different experiments. We started with the simplest explanation (i) and attempted to determine whether or not the effect could indeed be due to differences in temperature of equilibration.

## Temperature effect on Fe-S electron exchange

We considered the electron exchange between S<sup>2-</sup> and Fe<sup>3+</sup> in terms of the homogeneous equilibrium:



In Nash et al (2019) we fixed the apparent equilibrium constant for this reaction at the 1300° (1573K) value obtained from our experiments:

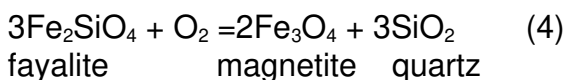
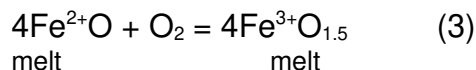
$$\log K_{1573} = \log \hat{c}$$

We derived an initial guess of the temperature dependence of reaction (1) by modelling its thermodynamic properties on those of solid analogues. We assumed that the temperature dependence of logK for reaction (1) exactly parallels that of logK for the reaction:



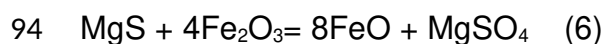
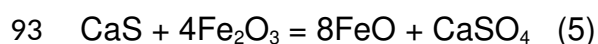
By making this assumption we found that the apparent 1050° isotherm for reaction (1) exactly reproduces the 1050°C data of Fig 1. The 1050°C isotherm shown in the figure was calculated from the 1300°C results for equilibrium (1) using the temperature dependence of equilibrium (2). It was not fit to the 1050° data. To be clear, we did not aim to develop an exact temperature-dependence of the equilibrium constant for reaction (1). We were simply using thermodynamic data to determine whether or not the difference between 1300 and 1050°C data could reasonably be attributed to temperature.

In making the assumption that the temperature dependence of homogeneous equilibrium (1) could be modelled by the heterogeneous reaction (2), we followed O'Neill et al (2018) who made exactly the same assumption for Fe<sup>2+</sup>-Fe<sup>3+</sup> equilibria in the reactions:



O'Neill et al (2018) state “*The effect of temperature on  $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$  (reaction 3) was found to run parallel to the temperature dependence of the quartz–fayalite–magnetite (QFM) buffer (reaction 4), so we replaced  $\log f\text{O}_2$  with  $\Delta\text{QFM}$ , which is the difference from the QFM buffer*”. Note that, in this case O'Neill (2018) did not fix the entropies of the 2 reactions at the same value, a path he advocates in his comment, but instead fixed the enthalpies at the same value, a path which we also followed.

90 Aware of potential criticisms and referees' comments on the use of reaction (2),  
91 particularly with respect to the bonding in FeS, we investigated other solid analogues  
92 such as:



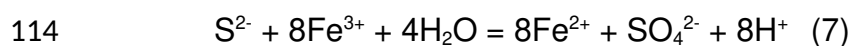
95

96 Both of these reactions have slightly smaller temperature dependences than our  
97 model reaction (2) (0.6 and 0.72 times respectively) but, importantly, all 3 indicate a  
98 significant shift to the right on Figure 1 with decreasing temperature implying that  
99 temperature is indeed the dominant effect on Fe-S electron exchange in silicate melt.

## 100 **The entropy of the exchange reaction**

101 The entropy of the solid-solid reaction (2) involving  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{S}^{2-}$  and  $\text{S}^{6+}$   
102 components is about  $141 \text{ J.K}^{-1}$  in the  $1050^\circ\text{--}1300^\circ\text{C}$  temperature interval. As pointed  
103 out by O'Neill (2020), by fixing the enthalpy change rather than the entropy change  
104 of exchange reaction (1) we have increased the estimated entropy change by  $144$   
105  $\text{J.K}^{-1}$  from  $141$  to  $285 \text{ J.K}^{-1}$ . He also states "*Entropy changes are usually small across*  
106 *reactions that do not involve gases, and may be expected to be small in this case*".  
107 This statement is central to his argument that entropy of exchange should be small  
108 and fixed at a low value rather than assuming parallel temperature-dependences of  
109 reactions. The fixing of entropy of exchange at a low value is frequently a reasonable  
110 approximation, but it does not apply for equilibria involving highly dilute solutes such  
111 as  $\text{S}^{2-}$  and  $\text{SO}_4^{2-}$  which in this case are dilute in the silicate melt. An illustration is  
112 provided by the analogous S-Fe electron exchange reaction in aqueous solution:

113



115 At  $298\text{K}$  this reaction has a standard state entropy change  $\Delta S^\circ$  of  $+1127 \text{ J.K}^{-1}$   
116 (Phillips and Phillips, 2000; Shock et al., 1997). In contrast the solid-solid reactions  
117 (2), (5) and (6) have entropy changes at  $298\text{K}$  of  $+197$ ,  $+186.5$  and  $+177.5 \text{ J. K}^{-1}$   
118 respectively, or more than  $900 \text{ J.K}^{-1}$  less than the value for the analogous reaction in  
119 solution. Clearly, fixing the entropy change of reaction (7) to that of any of the  
120 analogous solid-solid reactions, in the manner advocated by O'Neill (2020), would

have produced large errors in the calculated temperature-dependence of reaction (7). There is, therefore, no theoretical or observational reason for fixing the entropy of the S-Fe electron exchange reaction in melts at a value fixed by the entropies of solids in an analogous solid-solid reaction. Our assumption, that solid-solid and analogous homogeneous melt equilibria parallel one another with changing temperature is often reasonable (e.g. O'Neill et al 2018) and, in this case, apparently borne out by experimental data (Fig 1).

### **Quench-temperature of electron-hopping**

Electron-exchange has in common with diffusion that it has an activation energy. During cooling of a liquid both phenomena exhibit “closure temperatures” (Dodson, 1973) after which, at lower temperature, there will cease to be diffusion or electron-exchange. Closure temperature depends both on chemical composition and cooling or quench rate. From Figure 1 it can be seen that XANES spectroscopic and analytical determinations of sulfur speciation in our experiments agree with one another. This is important because the spectroscopic method is sensitive to re-equilibration during cooling while the analytical method is not. In the case of our rapidly drop-quenched samples we are therefore below the “closure temperature” because the two methods agree. The experiments performed by Jugo et al (2010) and Botcharnikov et al (2011) (Fig 1) may also, plausibly, be below the closure temperature for the rapid cooling rates they employed. In contrast, when we calculate log K values for equilibrium (1) in the basaltic glasses from Mauna Kea analysed by Brounce et al (2017) we find apparent equilibration temperatures which average 993°C. This indicates that the closure temperature for the more slowly-cooled natural glasses is well below the liquidus temperature of ~1200°C. O'Neill (2020) suggests that the closure temperature should actually correspond to the glass transition temperature which is closer to 700°C. But there is no theoretical or experimental basis for such a statement. Closure temperature does not have a fixed value in any particular glass, solid or liquid because it depends on cooling rate. The glass transition temperature itself corresponds to a change in the temperature-dependence of the diffusion coefficient, not a cessation of diffusion. Furthermore, it is

well-known that diffusion and electron hopping occur in some glasses well below the glass transition temperature (Vrentas and Duda, 1978).

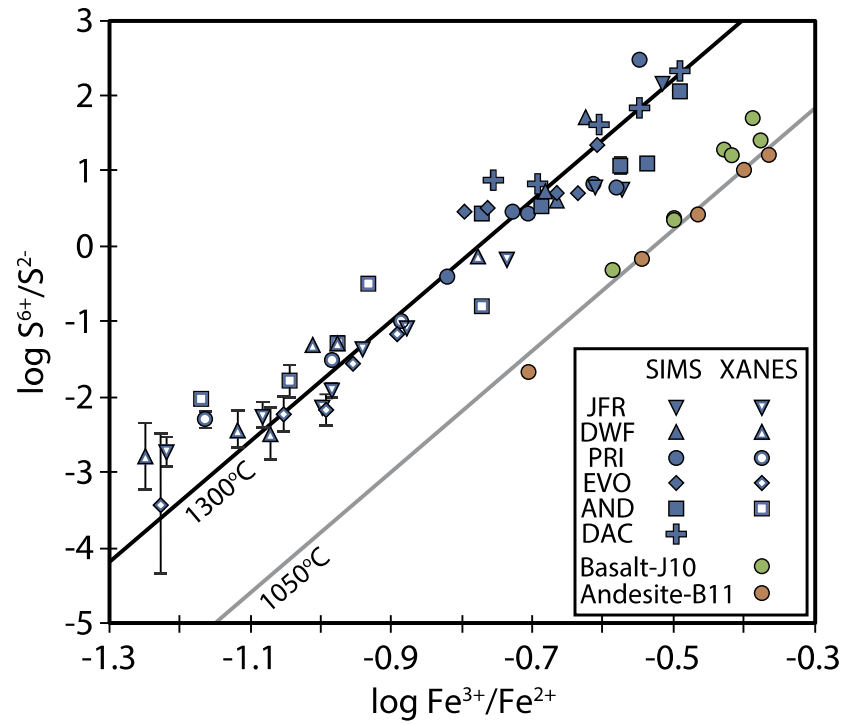
## **Conclusions**

Our conclusions are as follows:

- 1) The temperature-dependence which we imposed on logK for the S-Fe exchange equilibrium (1) connects the measured values at 1300°C with those at 1050°C in a rational way, consistent with the temperature-dependences of analogous solid-solid equilibria. Other authors (O'Neill et al 2018) have shown that the same approach can be applied to connect the temperature-dependence of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  equilibrium in melts to that of the fayalite-magnetite-quartz solid oxygen buffer.
- 2) In contrast to the observations in (1) above, there is no justification for fixing the entropy of an exchange equilibrium involving highly dilute solutes to the value for an analogous solid-solid reaction involving high concentrations of components.
- 3) Closure temperature of S-Fe electron exchange is both temperature and cooling-rate dependent and hence attempts to fix it at the glass transition temperature have no validity.

**Acknowledgements:** Our research was supported by the Science and Technology Facilities Council (UK) grant ST/R000999/1. We acknowledge discussions with Don Dingwell on the nature of the glass transition.

**Fig 1**



**Figure caption**

Figure showing  $\text{S}^{6+}/\text{S}^{2-}$  from our experiments at 1300° C and those of Jugo et al (2010) and Botcharnikov et al (2011) at 1050° plotted as a function of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  calculated at the  $f\text{O}_2$  of the experiment from (Kress and Carmichael, 1991). The 6 compositions used cover the range from Dacite (DAC) to Fe-rich martian basalt (JFR) (Nash et al 2019). The methods used to determine  $\text{S}^{6+}/\text{S}^{2-}$  were spectroscopic (XANES) and analytical (SIMS). The latter is independent of any electron-exchange during quenching (Nash et al 2019) The black line (1300°C) was fit by weighted linear regression assuming the theoretical electron-exchange relationship of

Equation (1) ( $R^2=0.931$ ). The grey line was calculated using Equation(11) of Nash et al (2019)

## References

- Botcharnikov, R.E., Linnen, R.L., Wilke, M., Holtz, F., Jugo, P.J., Berndt, J., 2011. High gold concentrations in sulphide-bearing magma under oxidizing conditions. *Nature Geoscience* 4, 112-115.
- Dodson, M.H., 1973. Closure Temperature in Cooling Geochronological and Petrological Systems. *Contributions to Mineralogy and Petrology* 40, 259-274.
- Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity. *Geochimica Et Cosmochimica Acta* 74, 5926-5938.
- Kress, V.C., Carmichael, I.S.E., 1991. The compressibility of silicate liquids containing  $Fe_2O_3$  and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contributions to Mineralogy and Petrology* 108, 82-92.
- Nash, W.M., Smythe, D.J., Wood, B.J., 2019. Compositional and temperature effects on sulfur speciation and solubility in silicate melts. *Earth and Planetary Science Letters* 507, 187-198.
- O'Neill, H.S., Berry, A.J., Mallmann, G., 2018. The oxidation state of iron in Mid-Ocean Ridge Basaltic (MORB) glasses: Implications for their petrogenesis and oxygen fugacities. *Earth and Planetary Science Letters* 504, 152-162.
- O'Neill, H. S., 2020; Comment on 'Compositional and temperature effects on sulfur speciation and solubility in silicate melts" by Nash et al. (*Earth and Planetary Science Letters* 507, 187–198, 2019) *Earth Planet Sci. Lett.* (submitted)
- Phillips, D.J., Phillips, S.L., 2000. High temperature dissociation constants of  $HS^-$  and the standard thermodynamic values for  $S^{2-}$ . *J Chem Eng Data* 45, 981-987.
- Shock, E.L., Sassani, D.C., Willis, M., Sverjensky, D.A., 1997. Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochimica Et Cosmochimica Acta* 61, 907-950.
- Vrentas, J.S., Duda, J.L., 1978. Free-Volume Interpretation of Influence of Glass-Transition on Diffusion in Amorphous Polymers. *J Appl Polym Sci* 22, 2325-2339.