The sulfur solubility minimum and maximum in silicate melt

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Abstract

The behaviour of sulfur in magmas is complex because it dissolves as both sulfide ($S^{2-}$) and sulfate ($S^{6+}$) in silicate melt. An interesting aspect in the behaviour of sulfur is the solubility minima ($SS^{\text{min}}$) and maxima ($SS^{\text{max}}$) with varying oxygen fugacity ($f_{O_2}$). We use a simple ternary model (silicate–$S_2$–$O_2$) to explore the varying $f_{O_2}$ paths where these phenomena occur. Both $SS^{\text{min}}$ and $SS^{\text{max}}$ occur when $S^{2-}$ and $S^{6+}$ are present in the silicate melt in similar quantities due to the differing solubility mechanism of these species. At constant $T$, a minimum in dissolved total S content ($w_{\text{mST}}$) in vapour-saturated silicate melt occurs along paths of increasing $f_{O_2}$ and either constant $f_{S_2}$ or $P$; for paths on which $w_{\text{mST}}$ is held constant with increasing $f_{O_2}$, the $SS^{\text{min}}$ is expressed as a maximum in $P$. However, the $SS^{\text{min}}$ is not encountered during closed-system depressurisation in the simple system we modelled. The $SS^{\text{max}}$ occurs when the silicate melt is multiply-saturated with vapour, sulfide melt, and anhydrite. The $SS^{\text{min}}$ and $SS^{\text{max}}$ influence processes throughout the magmatic system, such as mantle melting, magma mixing and degassing, and $SO_2$ emissions; and calculations of the pressures of vapour-saturation, $f_{O_2}$, and $SO_2$ emissions using melt inclusions.

Supplementary material: Additional information and data used to create the figures are included with the submission of this manuscript. The code used to generate the data is available at https://github.com/eryhughes/SSminmax.
It is widely accepted that there is a minimum in the solubility of sulfur (abbreviated to the $SS_{\text{min}}$, for the “sulfur solubility minimum”) in silicate melts (i.e., in the concentration of dissolved S in a silicate melt coexisting with an S-bearing vapour) as a function of oxygen fugacity ($f_{O2}$) when the speciation of S in the silicate melt changes from being sulfide ($S^2$) to sulfate ($SO_4^{2-}$ or abbreviated as $S^{6+}$) dominated. This is based on experimental studies of the concentration of S in vapour-saturated silicate melts spanning a range in $f_{O2}$ (e.g., Fincham and Richardson 1954; Katsura and Nagashima 1974; Carroll and Rutherford 1985; Backnaes and Deubener 2011; Lesne et al. 2015; Matjuschkin et al. 2016; Nash et al. 2019). Such a minimum in S solubility has implications for magmatic and volcanic processes. For example, any process where $f_{O2}$ progressively changes and becomes closer to the $f_{O2}$ of $SS_{\text{min}}$ (e.g., mixing, progressive reduction or oxidation, degassing etc.) will result in a decrease in the S-solubility. This minimum has been used as evidence of the presence of additional, low solubility, potentially unquenchable, S-bearing species in silicate melts that could be important for metal transport in arc systems (Matjuschkin et al. 2016). Also, understanding the thermodynamic basis for this feature is critical for calculating the pressure of vapour-saturation of S-bearing magmas using the volatile concentrations of quenched glasses (e.g., Lesne et al., 2015).

Despite its potential importance, the existence of an $SS_{\text{min}}$ with varying $f_{O2}$ has been somewhat mischaracterised in the literature. As emphasized by O’Neill (2020), this is at least in part due to a lack of clarity regarding the independent variables and the path followed by sulfur fugacity ($f_{S2}$) with increasing $f_{O2}$ for specific natural or experimental processes (e.g., Moretti et al., 2003) and the number and identity of additional S-bearing phase(s) with which the silicate melt is saturated (e.g., Jugo et al., 2005). In this paper, we explore the conditions and paths for which an $SS_{\text{min}}$ occurs and some of the implications for magmatic and volcanic processes. We also expand upon the work of Jugo (2009) regarding a S solubility maximum (referred to as an $SS_{\text{max}}$) for silicate melts that are multiply saturated with sulfide melt + anhydrite ± vapour. We note that although silicate melt and vapour in most natural systems contain H, C, halogens, metals, etc., in addition to S and O; here, we limit ourselves to a simple system in which S and O are the only volatile components in the silicate melt (although such a system may be appropriate of Jupiter’s moon Io: e.g., Zolotov and Fegley, 2000). By limiting our treatment to this simple end-member system, the factors leading to an $SS_{\text{min}}$ or an $SS_{\text{max}}$ can be more easily isolated and understood.

## Thermodynamic modelling

Equilibria between silicate melt, vapour, sulfide melt, and anhydrite

Sulfur occurs in several phases in magmatic systems, including dissolved S-bearing species in silicate melt, gaseous species in vapour, immiscible sulfide melts, and various sulfate phases (e.g., reviews by Parat et al., 2011; Wallace and Edmonds, 2011). In addition to silicate melt and vapour, we consider pure Fe-sulfide melt (FeS) and anhydrite (CaSO$_4$) (Figure 1a and b). The silicate melt end member can be compositionally simple (e.g., SiO$_2$, CaMgSi$_2$O$_6$, NaAlSi$_3$O$_8$) or complex (e.g., a natural basalt), provided it is fixed in composition. In our calculations, the silicate component is taken to be a S-free Hawaiian basaltic melt in which all the Fe is present as Fe$^{2+}$ (composition given in the Supplementary Material). We assume that the silicate melt is insoluble in the vapour.

The vapour is assumed to be constrained to the S–O binary subsystem and to contain only three species (S$_2$, O$_2$, and SO$_2$; Figure 1b), hence
\[ x'_{S_2} + x'_{O_2} + x'_{SO_2} = 1, \]  
(1)

where \( x'_i \) is the mole fraction of species \( i \) in the vapour. Other species are present in an S–O vapour (e.g., SO\(_3\), SO, S polymers, etc.) and could be added to our treatment. However, the three species in equation (1) are the most significant (e.g., Oppenheimer et al. 2011; Renggli et al. 2017; Henley and Seward 2018; Henley and Fischer 2021) and are sufficient to illustrate the salient points.

Sulfide (S\(^2\)) and sulfate (S\(^{6+}\)) are assumed to be the only significant S-bearing species dissolved in natural silicate melts based on XANES measurements and solubility experiments (e.g., Fincham and Richardson 1954; Paris et al. 2001; Métrich et al. 2009; Wilke et al. 2011). Intermediate S-bearing species have been observed or inferred (e.g., S\(^{4+}\), S\(^{-}\), S\(^0\), molecular SO\(_2\); Clemente et al. 2004; Métrich and Wallace 2009; Burgisser et al. 2015; Lesne et al. 2015; Matjuschkin et al. 2016; Colin et al. 2020), but these species are not thought to be significant in natural (especially in Fe-bearing) silicate melts. Hence, the silicate melt is assumed to contain only two S-bearing species (S\(^2\) and S\(^{6+}\); Figure 1b), such that

\[ w^m_{S_2} + w^m_{S^{6+}} = w^m_{ST}, \]  
(2)

where \( w^m_i \) is the weight fraction of species \( i \) in the silicate melt, and \( S_T \) refers to total dissolved S content.

Three independent reactions control the coexisting compositions of silicate melt and vapour in this system. The first reaction describes a homogeneous equilibrium that governs the speciation of the vapour (v):

\[ 0.5S_2(v) + O_2(v) = SO_2(v), \]  
(3a)

which is governed at equilibrium by

\[ K_3(T) = \frac{f_{SO_2}}{(f_{S_2})^{a_S} f_{O_2}^{a_O}}, \]  
(3b)

where \( K_3 \) is the equilibrium constant for reaction (3a) and \( f_i \) is the fugacity of species \( i \) in the vapour. If the treatment were to include other S ± O-bearing vapour species (such as SO\(_3\), SO, etc.; see above), a statement of homogeneous equilibrium would have to be added for each additional vapour species.

The second reaction describes a heterogeneous equilibrium between silicate melt (m) and vapour that governs the dissolution of sulfur from the vapour as S\(^2-\) in the silicate melt (e.g., Fincham and Richardson 1954; Moretti and Ottonello 2005, 2003; Moretti and Papale 2004; Gaillard and Scaillet 2009, 2014; Baker and Moretti 2011; Gaillard et al. 2011, 2013, 2015; Baumgartner et al. 2017; Moretti 2021), described by the following three relations:

\[ 0.5S_2(v) + O^2(m) = 0.5O_2(v) + S^{2-}(m), \]  
(4a)

\[ K_4(P, T) = \frac{a^m_{SO_2}}{a^m_{S^{2-}} (f_{S_2})^{0.5} \approx \frac{x^m_{S^{2-}}}{x^m_{O_2}} (f_{S_2})^{0.5}}, \]  
(4b)
\[ C_{S2^-} = w_{S2^-} \left( \frac{f_{O2}}{f_{S2}} \right)^{0.5}; \quad (4c) \]

where \( a^m_i, x^m_i, \) and \( w^m_i \) are the activity, mole fraction, and weight fraction, respectively, in the silicate melt of the \( i \)th ion (either S\(^2^-\) or oxide [O\(^2-\)], in this case); and Cs\(_{S2^-}\) is referred to as the sulfide capacity (e.g., Fincham and Richardson 1954; O’Neill 2020). The final term of equation (4b) makes the approximation that \( a^m_i \) can be replaced by \( x^m_i \), and this approximation is adopted throughout. Given this approximation, Cs\(_{S2^-}\) is simply related to \( K_4 \), the equilibrium constant for reaction (4a), but by convention it is defined in terms of \( w^m_i \) rather than \( x^m_i \). Finally, we assume throughout that \( x^{mO2-} \) (i.e., the O\(^2-\) that is part of the silicate melt that can be replaced by S\(^2-\)) can be approximated as constant (i.e., \( x^{mS2^-} \approx x^{mO2-} \)).

A third reaction describes an additional heterogeneous equilibrium between silicate melt and vapour that governs the dissolution of sulfur from the vapour as SO\(_4^{2-}\) in the silicate melt (e.g., Fincham and Richardson 1954; Moretti and Ottonello 2003, 2005; Moretti and Papale 2004; Baker and Moretti 2011; Moretti 2021):

\[ 0.5S_2(v) + 1.5O_2(v) + O_2^-(m) = SO_4^{2-}(m), \quad (5a) \]

\[ K_5(P, T) = \frac{a^m_{S6+}}{a^m_{O2-}(f_{S2}/f_{O2})^{3/2}} \approx \frac{x^m_{S6+}}{x^m_{O2-}(f_{S2}/f_{O2})^{3/2}} \text{, and} \]

\[ C_{S6+} = w^m_{S6+}\left(f_{S2}/f_{O2}\right)^{-0.5}; \quad (5c) \]

where \( a^{mS6+} \) and \( x^{mS6+} \) are the activity and mole fraction, respectively, of sulfate dissolved in the silicate melt; and Cs\(_{S6+}\) is referred to as the sulfate capacity (Fincham and Richardson 1954). Again, Cs\(_{S6+}\) is simply related to \( K_5 \), the equilibrium constant for reaction (5a), but using weight fraction instead of mole fraction, and assuming \( x^{mO2-} \) is constant.

An alternative heterogeneous equilibrium between silicate melt and vapour can be used instead of either reaction (4a) or (5a) to describe the conversion of S\(^2-\) to S\(^{6+}\) in the silicate melt (e.g., Wallace and Carmichael 1994; Matthews et al. 1999; Métrich et al. 2009; Jugo et al. 2010; Baumgartner et al. 2017):

\[ S^2-(m) + 2O_2(v) = SO_4^{2-}(m), \quad (6a) \]

\[ K_6(P, T) = \frac{a^m_{S6+}}{a^m_{S2^-}(f_{O2})^2} \approx \frac{x^m_{S6+}}{x^m_{S2^-}(f_{O2})^2}, \text{ and} \]

\[ \frac{x^m_{S6+}}{x^m_{S2^-}} = \left[ \frac{S^{6+}}{S^{2-}} \right]^m = \frac{w^m_{S6+}}{w^m_{S2^-}} = \frac{C_{S6+}}{C_{S2^-}} f_{O2}^2. \quad (6c) \]

Reaction (6a) can be obtained by subtracting reaction (4a) from reaction (5a) and rearranging. Reaction (6a) is useful as it emphasizes that the oxidation state of S dissolved in the silicate melt (i.e., [S\(^{6+}/S^{2-}\)]\(^m\) or [S\(^{6+}/S^{4-}\)]\(^m\)) at a given \( T \) and \( P \) is controlled only by \( f_{O2} \), Cs\(_{S2^-}\), and Cs\(_{S6+}\). However, Cs\(_{S2^-}\) and Cs\(_{S6+}\) are highly dependent on the composition of the silicate melt (e.g., O’Neill and Mavrogenes 2002, 2019; Moretti and Ottonello 2005; Nash et al. 2019; O’Neill 2020; Boullion and Wood 2021; Moretti 2021). Additionally, they will depend on \( T \) and \( P \) (because \( K_4 \) and \( K_5 \)
must depend on $T$ and $P$ unless the standard state enthalpy and volume changes of the reactions are zero) and are likely to depend on the speciation of other multivalent elements in the silicate melt (e.g., $[\text{Fe}^{3+}/\text{Fe}^{2+}]^m$). Although such factors could lead indirectly to variations in $[\text{S}^{6+}/\text{S}^{2-}]^m$ at constant $f_{O2}$, these are expected to be minor effects for most for the examples considered here. Therefore, we assume $C_{S2-}$ and $C_{S6+}$ depend only on $T$ and the composition of the silicate component (and depend only on total Fe not $[\text{Fe}^{3+}/\text{Fe}^{2+}]^m$), all of which are constant in all our calculations.

Given equation (1), if an S–O vapour is present in the system (i.e., if the silicate melt is vapour-saturated), the sum of the partial pressures ($p_i$) of the species in the vapour equals the total pressure of the system ($P$):

$$P = p_{O2} + p_{S2} + p_{SO2}. \quad (7)$$

where the partial pressures are related to fugacity and mole fraction in the vapour through fugacity coefficients ($\gamma_i$):

$$f_i = \gamma_i p_i = \gamma_i x^v_i P. \quad (8)$$

When the silicate melt is saturated with sulfide melt, the chemical potential of FeS in the silicate melt ($\mu^\text{mFeS}$) and the sulfide melt are equal. The “sulfide content at sulfide-saturation” ($S^2-$ CSS) is the dissolved S$^2-$ concentration in the silicate melt in equilibrium with sulfide melt (e.g., Shima and Naldrett 1975; O’Neill and Mavrogenes 2002; Smythe et al. 2017; O’Neill 2020):

$$w^m_{S2-} = w^m_{S2-CSS}. \quad (9)$$

The total S content of a silicate melt that is saturated with sulfide melt ($S^T$ CSS) is then given by equation (9) in combination with equations (2) and (6c):

$$w^m_{ST} = w^m_{STCSS} = (1 + (C_{S6+/C_{S2-}})(f_{O2})^2)w^m_{S2-CSS}. \quad (10)$$

Alternatively, when the silicate melt is saturated with anhydrite, the chemical potential of CaSO$_4$ in the silicate melt ($\mu^\text{mCaSO4}$) and anhydrite are equal. The “sulfate content at anhydrite-saturation” ($S^{6+}$ CAS) is the dissolved S$^{6+}$ concentration in the silicate melt in equilibrium with anhydrite (e.g., Baker and Moretti 2011; Chowdhury and Dasgupta 2019; Zajacz and Tsay 2019):

$$w^m_{S6+} = w^m_{S6+CAS}. \quad (11)$$

The total S content of a silicate melt that is saturated with anhydrite ($S^T$ CAS) is then given by equation (11) in combination with equations (2) and (6c):

$$w^m_{ST} = w^m_{STCAS} = (1 + (C_{S2-}/C_{S6+})(f_{O2})^2)w^m_{S6+CAS}. \quad (12)$$

The importance of the phase rule in our treatment of S-solubility in silicate melt

In its simplest form, the phase rule relates the number of components ($c$) and phases ($\varphi$) in a system to the variance (or the degrees of freedom, $F$) of the assemblage:
For most of the calculations presented here, our system has three components (silicate, S\textsubscript{2}, and O\textsubscript{2};
\(c = 3\)) and two phases (silicate melt + vapour; \(\varphi = 2\)) (Figure 1a). This silicate melt + vapour
assemblage is thus trivariant (\(\varphi = 2, F = 3\)); if only silicate melt were present, the system would
be quadrivariant (\(\varphi = 1, F = 4\)). Therefore, for the silicate melt + vapour assemblage, if any three
linearly independent intensive variables are chosen as independent variables, the state of the
system is fully defined, and all other intensive variables are dependent. Consequently, the values
of three independent variables \textit{must} be given to completely specify the state of the system. The
values of the other intensive variables can be calculated given the values chosen for the
independent variables and knowledge of the thermochemistry of the silicate melt and vapour
phases. Again, for vapour-undersaturated silicate melt, only one phase is present and four
independent intensive variables are needed to define fully the state of the system.

The important point here is a restatement of the cautionary note in O’Neill (2020) about the
S\textsubscript{S\textsubscript{min}} when \(f\textsubscript{O2}\) is an independent variable: i.e., assuming temperature \((T)\) is constant, the variation
of \(w\textsubscript{ST}\) is \textit{not} uniquely defined if only \(f\textsubscript{O2}\) is independently varied. The behaviour of a third variable
must also be specified for the state of the silicate melt + vapour assemblage to be defined at each
point on a path of varying \(f\textsubscript{O2}\). Only then can the variation in \(w\textsubscript{ST}\) (including the nature of any
minimum or maximum) as a function of \(f\textsubscript{O2}\) be uniquely characterized.

There are a variety of intensive variables that could be chosen as independent or dependent
variables in our model system. For example, temperature \((T)\); pressure \((P)\); the dissolved S\textsuperscript{2+}, S\textsuperscript{6+},
and S\textsubscript{T} content of the silicate melt, specified as \(x\textsuperscript{i}\), or \(w\textsuperscript{i}\) (given equation (2), only two of these
three quantities can be chosen as independent variables); the bulk composition of the silicate melt,
vapour, or the system as a whole, given as the mole or weight fractions of S, O, and/or silicate in
the silicate melt, vapour, or system; or O\textsubscript{2}, S\textsubscript{2}, or SO\textsubscript{2} in the vapour (in either case these three
variables must add up to one, so only two can be specified independently); the chemical potentials
of all but one of the vapour species (\(\mu\textsuperscript{i}, \textit{or equivalently fugacities, } f\textit{, where } i = O_2, S_2, \textit{or SO}_2\));
the chemical potential of FeS and/or CaSO\textsubscript{4} in the silicate melt (\(\mu\textsuperscript{i}\)) or in the coexisting sulphide
melt and/or anhydrite if they are present; or the oxidation state of Fe and/or S in the silicate melt,
(either [Fe\textsuperscript{3+}/Fe\textsuperscript{2+}]\textsuperscript{m} or [Fe\textsuperscript{3+}/Fe\textsubscript{t}]\textsuperscript{m} and/or [S\textsuperscript{6+}/S\textsuperscript{2-}]\textsuperscript{m} or [S\textsuperscript{6+}/S\textsubscript{T}]\textsuperscript{m}), which is equivalent to specifying
\(f\textsubscript{O2}\).

The composition of the silicate melt and vapour phases are described by our idealised three-
component system. Although the compositions of the sulphide melt and anhydrite phases could be
incorporated into our treatment, their compositions fall outside of the plane of our chosen three-
component system. This means the composition of the silicate melt does not vary if sulphide melt
and/or anhydrite phases are saturated in our calculations (i.e., Fe and Ca concentrations in the
silicate melt are constant). Despite this, we can still model the effects of sulphide melt- and
anhydrite-saturation on the properties of the silicate melt and vapour phases using \(\mu\textsuperscript{m}\textsubscript{FeS} \textit{or } \mu\textsuperscript{m}\textsubscript{CaSO}_4
\) as described in “Silicate melt + (vapour and/or sulphide melt and/or anhydrite)Silicate melt + vapour
+ (sulphide melt and/or anhydrite)”.

We use this conceptual background to explore trends in, and interrelationships among, various
choices of independent and dependent variables, focussing on the implications for the SS\textsubscript{min} and
the SS\textsubscript{max}. We model the silicate melt as a Hawaiian basalt; its composition and details of our
choices of thermodynamic parameters for vapour and silicate melt can be found in the
Supplementary Material. For all of our calculations, $T$ and the composition of the silicate component are held constant. Since we assume that $C_{S2}^-$ and $C_{S6+}$ depend only on $T$ and the composition of the silicate component, both of these parameters are the same in all calculations presented here. In particular, $C_{S2}^-$ and $C_{S6+}$ are independent of $P$ and $[\text{Fe}^{3+}/\text{Fe}^0]^\gamma$, and therefore $f_{O2}$.

It is important to emphasize that the results based on our chosen parameters only describe the representative behaviour of the particular Hawaiian melt composition given in the Supplementary Material. Although we are confident that the trends and insights derived from this choice are robust, the exact behaviour depends strongly on the chosen values of $C_{S2}^-$ and $C_{S6+}$. Therefore, the specific values of various variables – including the precise values of $f_{O2}$ where shifts in behaviour are predicted to occur – will likely vary strongly with $T$, composition of the silicate component, and the $C_{S2}^-$ and $C_{S6+}$ parameterisation used (e.g., O’Neill and Mavrogenes 2002, 2019; Moretti and Ottonello 2005; Nash et al. 2019; O’Neill 2020; Boulliu and Wood 2021; Moretti 2021).

**Independent variables of $T$, $f_{O2}$, $f_{S2}$, $w^{\text{m}_{ST}}$, $P$, $\mu_{FeS}$, and $\mu_{CaSO4}$**

In this section we calculate the state of the system by choosing $T$ (1200°C) and a value of $f_{O2}$ (-5 < AFMQ < +5, where AFMQ is the Fayalite-Magnetite-Quartz buffer; FMβQ in Frost, 1991) as two of the independent variables. The other independent variables considered are $f_{S2}$, $w^{\text{m}_{ST}}$, $P$, $\mu_{FeS}$, and $\mu_{CaSO4}$. For any given state of the system (i.e., where the values of all intensive variables are defined), the results will be the same if any three variables are chosen as independent. Therefore, the following figures convey the same results, but with different variables as the axes and contours. For most of the $P$ range shown in the following figures, $y_i \sim 1$, hence $f_i \sim p_i$ using equation (8) (e.g., for $\log_{10}[P, \text{bar}] < 3$, $y_i < 1.25$ for all species). “Silicate melt + vapour” describes the two-phase silicate melt + vapour assemblages, whilst “Silicate melt + vapour + (sulfide melt and/or anhydrite)” and “Silicate melt + (vapour and/or sulfide melt and/or anhydrite)” describe the silicate melt + (vapour and/or sulfide melt and/or anhydrite) assemblages. If the $S$ content of the silicate melt is less than $w^{\text{m}_{ST}}$ at vapour- and/or sulfide melt- and/or anhydrite-saturation, silicate melt is the only stable phase present.

**Silicate melt + vapour**

For silicate melt + vapour assemblages, $\varphi = 2$ and $F = 3$; therefore, in addition to $T$ and $f_{O2}$, only one other independent variable is needed to specify fully the state of the system. This third independent variable will be referred to as the “$Y$” variable: we first choose $Y = f_{S2}$, then $Y = w^{\text{m}_{ST}}$, and finally $Y = P$. For each of these choices of the independent variables, we solve the system of equations (3b), (7), (8), and two out of (4c), (5c), and (6c).

**$S$ speciation in the silicate melt and vapour**

Figure 2 shows how the compositions of the silicate melt and vapour change with varying $f_{O2}$ at constant $T$ and either constant $f_{S2}$ (Figure 2a–b), constant $w^{\text{m}_{ST}}$ (Figure 2c–d), or constant $P$ (Figure 2e–f) given that the silicate melt is vapour-saturated. As $f_{O2}$ changes, the speciation of sulfur in the silicate melt ($[S^{6+/7+}]^\gamma$) and in the vapour ($x^{sSO2}$) change. This leads to changes with $f_{O2}$ in the dominant species (or multiple species) in the silicate melt and vapour, which is indicated by the vertical background colour bands in Figure 2. For the vapour, $S_2$ is the dominant species at low $f_{O2}$ ($x^{sSO2} < 0.1$, purple); $SO_2$ is the dominant species at high $f_{O2}$ ($x^{sSO2} > 0.9$, turquoise-green-yellow);
and in between there is a transition from dominantly $S_2$ to SO$_2$ ($0.1 \leq x'SO_2 \leq 0.9$, blue). At sufficiently high $fO_2$, O$_2$ becomes more abundant than $S_2$ in the vapour (i.e., to the right of the point labelled $a$ in the yellow band in Figure 2b, d, and f), but both are much less abundant than SO$_2$ in the range shown. For the silicate melt, $S^2$ is the dominant S-bearing species at low $fO_2$ ($[S^{6+}/S_S]^m < 0.1$, purple-blue-turquoise); $S^{6+}$ is dominant at high $fO_2$ ($[S^{6+}/S_S]^m > 0.9$, yellow); and in between it transitions from dominantly $S^2$ to $S^{6+}$ ($0.1 \leq [S^{6+}/S_S]^m \leq 0.9$, green).

At constant $T$, the effects of varying the third independent variable ($Y = fS_2$, $w^{m}_{ST}$, or $P$) in addition to $fO_2$ on the dependent variables (which are referred to as “Z” variables) are shown using contour plots in Figure 3–Figure 5. The coloured regions from Figure 2 showing the dominant silicate melt and vapour species and their changes are also shown in Figure 3–Figure 5 using the same colour scheme. These regions in Figure 3–Figure 5 are separated by black curves, where dashed curves indicate isopleths of vapour speciation ($x'SO_2 = 0.1$ and 0.9) and solid curves indicate isopleths of silicate melt speciation ($[S^{6+}/S_S]^m = 0.1$ and 0.9). Comparison of panels (d) in Figure 3–Figure 5 shows that the topology of the silicate melt and vapour speciation (indicated by the coloured fields) is similar for all three of these choices of $Y$.

A key point of Figure 3–Figure 5d is that regardless of the choice of the $Y$ variable, at low $fO_2$ ($\Delta FMQ \lesssim +0.7$) nearly all dissolved S is present as $S^2$ (purple-blue-turquoise). Under these conditions $w^{m}_{ST} \equiv w^{m}_{S2}$, and $w^{m}_{ST}$ is controlled by equation (4c), giving $w^{m}_{S2}$ as a simple function of $fO_2$ and $fS_2$. Likewise, at sufficiently high $fO_2$ ($\Delta FMQ \gtrsim +1.7$), nearly all S is dissolved as $S^{6+}$ (yellow). Here $w^{m}_{ST} \equiv w^{m}_{S6+}$, and $w^{m}_{ST}$ is instead controlled by equation (5c), which gives $w^{m}_{S6+}$ as a simple function of $fO_2$ and $fS_2$. At intermediate $fO_2$ ($+0.7 \lesssim \Delta FMQ \lesssim +1.7$), the silicate melt transitions from being dominated by $S^2$ to $S^{6+}$ (green). This region is narrow because the S speciation in the silicate melt is defined by equation (6c), which depends on ($fO_2$)$^2$ (i.e., the difference in log$_{10}$[$fO_2$] between $[S^{6+}/S_S]^m = 0.1$ and 0.9 is log$_{10}$[9] ~ 0.95). The silicate melt isopleths (the black dashed curves defining the edges of the green region) are sub-vertical (i.e., not precisely vertical) due to the $P$-dependence of $fO_2$ on the FMQ buffer. When the value of $Y$ is large, $P$ is large, which leads to $p_i$ deviating from $f_i$, causing the silicate melt isopleths to deviate from vertical (i.e., to curve to lower $fO_2$). They would, however, be vertical if plotted against log$_{10}$[$fO_2$] without normalisation to a buffer, given that $C_{S2}$- and $C_{S6+}$ are assumed to be $P$-independent.

Unlike the speciation of S dissolved in the silicate melt, which depends only on $fO_2$ via equation (6c), vapour speciation (i.e., $x'SO_2$) depends on $fS_2$ in addition to $fO_2$ from equations (3b) and (8). Therefore, the boundaries separating where the vapour phase is dominated by $S_2$ (purple), both $S_2$+SO$_2$ (blue), and SO$_2$ (turquoise-green-yellow) depend on $fS_2$ (see the vapour isopleths in Figure 3–Figure 5). However, the slopes of the boundaries depend on the choice of the $Y$ variable and its value, as well as the silicate melt speciation (e.g., see the change in slope of $x'SO_2 = 0.9$ in Figure 4 where it enters the green region with increasing $fO_2$). The change in vapour speciation from dominantly $S_2$ to SO$_2$ occurs over a wider range of $fO_2$ than the silicate melt speciation (compare the widths of the blue and green bands in Figure 2 and Figure 3–Figure 5d) because $fS_2$ (and $x'SO_2$ via equation (8)) depends on ($fO_2$)$^1$ from equation (3b), in contrast to $[S^{6+}/S^{2-}]^m$, which depends on ($fO_2$)$^2$ from equation (6c).

Combining changes in silicate melt and vapour speciation, there are three main regions plus three transitional regions in log$_{10}$[$fO_2$]-log$_{10}$[$Y$] space (Figure 3–Figure 5): at low $fO_2$ and high $Y$, the vapour is $S_2$-dominated and the silicate melt is $S^2$-dominated (purple); at higher $fO_2$ and lower $Y$, the vapour contains both $S_2$ and SO$_2$ in similar concentrations, whereas the silicate melt is still
S²-dominated (blue); at higher \( f_{O2} \) and lower \( Y \), the vapour is now SO₂-dominated and the silicate melt is still S²-dominated (turquoise); at higher \( f_{O2} \) and most \( Y \) values shown, the vapour remains SO₂-dominated but the silicate melt contains both S² and S⁶⁺ in similar concentrations (green); at high \( f_{O2} \) and all \( Y \) values shown, the vapour is still SO₂-dominated but the silicate melt is S⁶⁺-dominated (yellow); and there is also a small region where the vapour contains both S₂ and SO₂, and the silicate melt both S² and S⁶⁺, in similar concentrations (light-turquoise region labelled [S²⁺ +S⁶⁺]⁺+[S₂+SO₂]⁻ in Figure 3–Figure 5: it is not intersected in Figure 2). At higher \( Y \) values than shown in Figure 3–Figure 5, there are three additional regions: at intermediate \( f_{O2} \), the vapour is S²-dominated and the silicate melt contains both S² and S⁶⁺ in similar concentrations; at high \( f_{O2} \) but intermediate \( Y \), the vapour contains S₂ and SO₂ in similar concentrations and the silicate melt is S⁶⁺-dominated; and at higher \( Y \), the vapour is S₂-dominated and the silicate melt is still S⁶⁺-dominated (a sketch of this topology is shown in the Supplementary Material).

**Regions with a single dominant species in the silicate melt and vapour**

For all three of our choices of a constant independent \( Y \) variable, curves (Figure 2) and contours (Figure 3–Figure 5) of the dependent variables (\( Z \)) shown in the figures have constant slopes when there is a single dominant species in the silicate melt *and* a single dominant species in the vapour. For example, when the silicate melt is S²-dominated (purple-blue-turquoise),

\[
w_{ST}^{m} \cong w_{S2}^{m},
\]  

and when S⁶⁺-dominated (yellow):

\[
w_{ST}^{m} \cong w_{S6+}^{m}.
\]  

Similarly, when the vapour is S₂-dominated (purple),

\[
P \cong p_{S2} \cong f_{s2},
\]  

and when SO₂-dominated (turquoise-green-yellow):

\[
P \cong p_{SO2} \cong f_{so2}.
\]

When \( T \) is constant and there is only one dominant species in the silicate melt and one dominant species in the vapour

\[
Z \propto (f_{O2})^{m}(Y)^{b},
\]

for all choices of \( Z \) and \( Y \) given here (see Table 1). Therefore, contours of constant \( Z \) in \( \log_{10}(Y) \)-\( \log_{10}(f_{O2}) \) plots have slopes \( (\sigma) \sim -a/b \) (Figure 3–Figure 5) and, when \( Y \) is constant, curves of different \( Z \) have slopes \( (\zeta) \sim a \) (Figure 2). Hence, the values of the slopes of the curves and contours of \( Z \) depend on the specific choice of the \( Y \) variable. Note that \( \zeta \) and \( \sigma \) are approximately, rather than exactly, equal to these values because: (1) the x-axis is \( \log_{10}(f_{O2}) \) relative to FMQ rather than strictly \( \log_{10}(f_{O2}) \); (2) partial pressure rather than fugacity is sometimes plotted, which are related through equation (8); and (3) although one species is dominant, the concentrations of the other species are not zero. At constant \( T \), the relationships between \( f_{O2}, Y \left(f_{s2}, w_{ST}^{m}, \text{and} P \right) \), and \( Z \left(f_{s2}, \)
Regions with mixed speciation in the silicate melt or vapour

Changes in the slopes of curves (ζ, Figure 2) and contours (σ, Figure 3–Figure 5) occur for dependent variables (Z) when their slopes in \( \log_{10}(Y) - \log_{10}(f_{O2}) \) space differ in regions dominated by different species (i.e., \( S_2 \) (purple) vs. \( SO_2 \) (turquoise) in the vapour and/or \( S^{2-} \) (turquoise) vs. \( S^{6+} \) (yellow) in the silicate melt). The regions in which the slopes transition from one essentially constant value to another are where there is mixed speciation in the vapour (i.e., both \( S_2 \) and \( SO_2 \) in similar concentrations: blue) or in the silicate melt (i.e., both \( S^{2-} \) and \( S^{6+} \) in similar concentrations: green).

If the log-log slope of a Z variable with respect to \( f_{O2} \) has the same sign in the low- and high-
\( f_{O2} \) regions on either side of one of the mixed species regions, the slope simply gets steeper or shallower along a constant Y path (Figure 2–Figure 5). For example, with increasing \( f_{O2} \) and \( Y = \text{constant} \) \( w^{m}_{ST} \) = 400 ppm, the slope in Figure 2d of \( \log_{10}(P) \) vs. \( \log_{10}(f_{O2}) \) is \( \zeta \equiv +1.0 \) where the silicate melt is \( S^{2-} \)-dominated and the vapour is \( S_2 \)-dominated (in the purple region). This is less than the value of \( \zeta \equiv +1.5 \) where the vapour is \( SO_2 \)-dominated (in the turquoise region), but both slopes are positive (Table 1). For the contour plot in Figure 4c, this is shown as \( \sigma \) decreasing from -0.5 to -1.5, but both being negative. This is because when the silicate melt is \( S^{2-} \)-dominated, the log-log slope for \( Z = p_{SO2} \) is steeper than for \( Z = p_{S2} \) (\( \zeta \equiv +1.5 \) vs. +1.0 or \( \sigma \equiv -1.5 \) vs. -0.5 in the purple-blue-turquoise regions in Figure 2d and Figure 4a–c). Therefore, the curves cross when \( p_{S2} = p_{SO2} \) (at the point labelled \( \beta \) in the blue region of Figure 2d). Hence, along this path \( P \) is essentially equal to \( p_{S2} \) when \( S_2 \) dominates the vapour (\( \zeta \equiv +1.0 \) or \( \sigma \equiv -0.5 \), purple), steepens continuously in the region where the concentration of \( SO_2 \) in the vapour increases (blue), and is then well approximated by \( p_{SO2} \) when \( SO_2 \) dominates the vapour (\( \zeta \equiv +1.5 \) or \( \sigma \equiv -1.5 \), turquoise).

If the log-log slope of a Z variable with respect to \( f_{O2} \) has opposite signs on the two sides of a mixed speciation region, a maximum (positive to negative slope with increasing \( f_{O2} \)) or minimum (negative to positive slope with increasing \( f_{O2} \)) in Z occurs (Figure 2–Figure 5). For example, for \( Y = \text{constant} \ f_{S2} \), there is a minimum in \( Z = w^{m}_{ST} \) at \( \left[ S^{6+/ST} \right]^{m} = 0.5 \) (this corresponds to a maximum in \( Z = \log_{10}[w^{m}_{ST}] \) contours), where the silicate melt changes from being \( S^{2-} \)- to \( S^{6+} \)-dominated (i.e., the green region in Figure 2a and Figure 3c). This is an example of an \( SS^{\text{min}} \) on a specific path of increasing \( f_{O2} \) (i.e., \( f_{S2} \) and \( T \) are constant). However, there are paths with monotonically increasing \( f_{O2} \) and variable \( f_{S2} \) for which a minimum is not encountered (e.g., all linear paths on Figure 3c with \( \sigma \geq +1 \) or \( \sigma \leq -3 \)). There is also an \( SS^{\text{min}} \) when \( Y = \text{constant} \ P \), as shown by the white \( S_{T} \) curve in Figure 2e and by the maxima in the \( \log_{10}[w^{m}_{ST}] \) contours in Figure 5c. As for the constant \( f_{S2} \)-path, this minimum also occurs at \( \left[ S^{6+/ST} \right]^{m} = 0.5 \) (i.e., in the green region). Similarly, there are paths with monotonically increasing \( f_{O2} \) and variable \( P \) that do not encounter the minimum (e.g., all \( \log_{10}(f_{O2}) - \log_{10}(P) \) paths on Figure 5c with \( \sigma \geq +1.5 \) and \( \sigma \leq -0.5 \)).
These SS_{min} occur because curves and contours of $w^{m}_{ST}$ have opposite slopes at lower-fO_{2} where S^{2-} dominates the silicate melt compared to at higher-fO_{2} where S^{6+} dominates (Figure 2a and e, Figure 3c, and Figure 5c). This occurs because O_{2} in the vapour is on the product side of reaction (4a) when sulfur dissolves dominantly as S^{2-} in the silicate melt, but on the reactant side when sulfur dissolves dominantly as S^{6+} in the silicate melt in reaction (5a). This is true whether the reactions are written for dissolving SO_{2} or S_{2} from the vapour into the silicate melt. Thus, for any path of constant fS_{2} or P (i.e., horizontal slices in Figure 3c or Figure 5c, respectively), $w^{m}_{ST}$ reaches a minimum at $[S^{6+}/S^{4+}]^{m} = 0.5$.

When $Y = w^{m}_{ST}$ and is held constant as fO_{2} increases, the SS_{min} manifests itself as a maximum in Z = P in Figure 2d (and corresponding minima in Z = P contours in the green region in Figure 4c). This is because at the SS_{min}, a higher P is required to maintain the same S content in the vapour-saturated silicate melt. Since SO_{2} is the dominant vapour species on both sides of the maximum in P (i.e., $P \geq pSO_{2}$), there is also a maximum in pSO_{2} at essentially the same point (and corresponding minima in Z = fSO_{2} contours in Figure 4b). The change in sign of the slope of pSO_{2} at the maximum with increasing fO_{2} (e.g., from $\gamma = +1.5$ to -0.5 in Figure 2d) is due to the crossover of S^{2-} to S^{6+} as the dominant species in the silicate melt (see “Regions with a single dominant species in the silicate melt and vapour”). Note that $Z = pSO_{2}$ also has a maximum in Figure 2d (and corresponding minima in Z = fSO_{2} contours in Figure 4a) with increasing fO_{2} in the same vicinity as the maxima in P and pSO_{2}. This is also because of the change in silicate melt speciation: however, since $pSO_{2} \ll pO_{2}$, the maximum in pSO_{2} has negligible influence on the maximum in P.

The maxima (and corresponding minima in the equivalent contours) in pSO_{2}, pS_{2}, and P all occur where the silicate melt speciation is mixed. The maxima in pSO_{2} and P essentially coincide because $P \geq pSO_{2}$, but the pS_{2} maximum is at a different fO_{2}, and none (unlike the $w^{m}_{ST}$ minima) occur exactly at $[S^{6+}/S^{4+}]^{m} = 0.5$ (e.g., compare Figure 2c and d). When the silicate melt has mixed speciation, equation (2) is needed rather than the approximations of equations (14a) and (14b). Substituting equations (4c) and (5c) into equation (2), and converting to partial pressure using equation (8) gives:

$$f_{S_{2}} = \gamma_{S_{2}pS_{2}} = (w^{m}_{ST}/(C_{S_{2}}(fO_{2})^{0.5} + C_{S^{6+}}(fO_{2})^{1.5}))^{2}, \quad (17a)$$

and substituting equation (3b) gives:

$$f_{SO_{2}} = \gamma_{SO_{2}pSO_{2}} = K_{3}w^{m}_{ST}/((C_{S_{2}}(fO_{2})^{0.5} + C_{S^{6+}}(fO_{2})^{2.5})). \quad (17b)$$

The fO_{2} values at the maximum for pS_{2} and pSO_{2} are given by differentiating equations (17a) and (17b) with respect to fO_{2} and solving for fO_{2} when this equals zero. As the relationships between pS_{2} and pSO_{2} with fO_{2} are different, the fO_{2} values of the maxima are also different.

We refer to the fO_{2} where the $w^{m}_{ST}$ minimum or P maximum occurs as the SS_{min}fO_{2}, but it can only be defined for silicate melt + vapour at a given T and for a choice of Y = fS_{2}, w^{m}_{ST}, or P. The SS_{min} always occurs when both S^{2-} and S^{6+} are dissolved in the silicate melt in similar concentrations, although it only occurs at $[S^{6+}/S^{4+}]^{m} = 0.5$ when $Y = fS_{2}$ or $w^{m}_{ST}$. Moreover, the minimum is not symmetric with changing fO_{2} (see Figure 2a, d, and e; and Figure 3–Figure 5c) because the stoichiometry of the reactions for sulfur dissolution as S^{2-} and S^{6+} differ. The different manifestations of the SS_{min} are related but not identical, reflecting the different fS_{2}–fO_{2} paths for different choices of Y. For example, there is a P maximum when $Y = w^{m}_{ST}$ (Figure 2d and Figure
Silicate melt + vapour + (sulfide melt and/or anhydrite)

For $Y$ values below the curves indicating sulfide melt-saturation (the grey solid curves labelled “$\text{sulf}^m$”) or anhydrite-saturation (the grey dashed curves labelled “anh”) in Figure 3–Figure 5 (and shown as vertical grey lines in Figure 2), the two-phase silicate melt + vapour assemblage is stable. At $Y$ values above these curves, the silicate melt is vapour-undersaturated but instead saturated with sulfide melt and/or anhydrite, which will be discussed in “Silicate melt + (vapour and/or sulfide melt and/or anhydrite)”. Therefore, the calculations involving silicate melt + vapour in this region describe metastable equilibria.

This section describes the behaviour on the grey curves in Figure 3–Figure 5, where silicate melt + vapour in the model ternary system are stable and saturated with sulfide melt and/or anhydrite. In our model ternary system, there are still only two phases (silicate melt + vapour) and therefore $F = 3$. Hence, given $T$ and $f_{O_2}$, the curve for sulfide melt-saturation is defined by a particular value of $Y = \mu^{\text{FeS}}$ that is equal to that of FeS in the saturating sulfide melt. In practice we apply the formulation of O’Neill (2020) to calculate S2-CSS for the silicate melt, which is conceptually equivalent to holding $\mu^{\text{FeS}}$ equal to a constant chemical potential of sulfide melt at the relevant conditions. In our calculations, we assume the sulfide melt is pure FeS (i.e., $\mu_{\text{FeS}} = \mu_{\text{FeS}^\circ}$), although this could be modified. Similarly, the curve for anhydrite-saturation is defined by $Y = \mu^{\text{CaSO}_4}$. Again, although S2-CAS is calculated based on Chowdhury and Dasgupta (2019), this is conceptually equivalent to holding $\mu^{\text{CaSO}_4}$ equal to a constant chemical potential of pure anhydrite at the relevant conditions. The stable saturation condition (i.e., sulfide melt- or anhydrite-saturation) is the one with the lowest $w^{\text{ST}}$.

If the silicate melt + vapour assemblage is saturated with either sulfide melt or anhydrite, $P$ and $w^{\text{ST}}$ are no longer independent variables. Therefore, having chosen values of $T$, $f_{O_2}$, and $\mu^{\text{FeS}}$ or $\mu^{\text{CaSO}_4}$ (which confines the state of the system to the $\text{sulf}^m$ or $\text{anh}$ curves), both $P$ and $w^{\text{ST}}$ are fixed, as can be visualized in Figure 3–Figure 5c. Moreover, when the silicate melt + vapour assemblage is saturated with both sulfide melt and anhydrite at a fixed $T$, three independent variables are specified, so no other parameters can be chosen independently. This is demonstrated graphically in Figure 3c and Figure 5c by the grey star, which for a given $T$ has fixed values of $P$, $f_{O_2}$, and $w^{\text{ST}}$ at the unique intersection of the grey solid and dashed curves. We can thus describe quantitatively with our model a constant-$T$, increasing-$f_{O_2}$ path for an assemblage containing silicate melt + vapour + (sulfide melt and/or anhydrite). The variations in the values of the $Z$ variables along this path can be read from the contours crossed by the grey curves in Figure 3–Figure 5 and Figure 6a and b show the variation in $w^{\text{ST}}$ and $P$ on this path.

At low $f_{O_2}$ (AFMQ $\leq +0.6$), the independent variables are $T$, $f_{O_2}$, and $\mu^{\text{FeS}}$: the silicate melt is $S^2$-dominated and saturated with vapour and sulfide melt (i.e., the solid grey $\text{sulf}^m$ curves in the purple-blue-turquoise regions of Figure 3–Figure 5 and Figure 6a–b). Therefore, $w^{\text{ST}}$ is controlled by $S^2$-CSS from equations (14a) and (9), hence:
\[ w^{m_{ST}} \equiv w^{m_{S2-}} = w^{m_{S2-CSS}}. \]  \hfill (18)

S\textsuperscript{2}-CSS is sub-parallel to the \( \log_{10}[w^{m_{ST}}] \sim 3 \) contour, although there is a small increase in \( w^{m_{S2-CSS}} \) with increasing \( f_{O2} \) because: (1) there is always some S present in the silicate melt as S\textsuperscript{6+}; and (2) \( w^{m_{S2-CSS}} \) depends on \( P \) and \([\text{Fe}^{3+}/\text{Fe}^{2+}] \) (O’Neill 2020), both of which increase with increasing \( f_{O2} \). Nevertheless, \( w^{m_{ST}} \) is nearly constant and therefore for all practical purposes \( P \) (and the \( p_i \)’s) behave as for the case when \( T-f_{O2}-w^{m_{ST}} \) were independent variables (Figure 2c–d and Figure 4).

At intermediate \( f_{O2} \) (+0.6 \( \leq \Delta \text{FMQ} \leq +1.5 \)), the conditions remain the same (\( Y = \mu_{\text{FeS}} \); the silicate melt is saturated with vapour and sulfide melt, and \( w^{m_{S2-}} = w^{m_{S2-CSS}} \), but the silicate melt contains significant quantities of both S\textsuperscript{2-} and S\textsuperscript{2+} (i.e., the solid grey curves in the green region of Figure 3–Figure 5 and Figure 6a–b). As the solubility of S\textsuperscript{6+} increases, \( w^{m_{ST}} \) increases based on equation (10) (e.g., in Figure 4c where the nearly horizontal grey \( sulphur \) curve turns steeply upward as it enters the green region with increasing \( f_{O2} \)). With increasing \( f_{O2} \), \( w^{m_{ST}} \) increases until the silicate melt reaches anhydrite-saturation when \( w^{m_{S6+}} = w^{m_{S6+\text{CAS}}} \) from equation (11). At this point, the silicate melt is saturated with vapour + sulfide melt + anhydrite, and the independent variables are \( T, \mu_{\text{FeS}} \), and \( \mu_{\text{CaSO}_4} \). It is important to emphasize that for this choice of independent variables, at a given \( T \), the vapour-saturated silicate melt defines a unique point in Figure 3 and Figure 5 (the grey star at the intersection of the solid and dashed grey curves) and fixes the values of all other intensive parameters. Therefore, combining equations (2), (9), and (11):

\[ w^{m_{ST}} = w^{m_{S2-CSS}} + w^{m_{S6+\text{CAS}}}. \]  \hfill (19a)

and substituting equations (9) and (11) into (6c):

\[ w^{m_{S6+\text{CAS}}}/w^{m_{S2-CSS}} = [C_{S6+}/C_{S2-}](f_{O2})^2. \]  \hfill (19b)

This corresponds to the maximum \( w^{m_{ST}} \) at \( \Delta \text{FMQ} \equiv +1.5 \) (i.e., the star on the grey curves in Figure 3c, Figure 5c, and Figure 6a: this multiply saturated point is not shown in Figure 4 because it occurs above the \( w^{m_{ST}} \) range of the figure).

At higher \( f_{O2} \) levels than those described in the previous paragraph (i.e., \( \Delta \text{FMQ} > +1.5 \)), the vapour-saturated silicate melt is no longer saturated with sulfide melt. However, it is still saturated with anhydrite (independent variables = \( T, f_{O2}, \) and \( \mu_{\text{CaSO}_4} \)) and thus follows the dashed grey \( \text{anh} \) curves. The silicate melt is S\textsuperscript{6+}-dominated and \( w^{m_{S6+}} \) is fixed at S\textsuperscript{6+}\text{CAS} (which is taken to be a constant); hence, \( w^{m_{S2-}} \) is given by equation (6c) rather than S\textsuperscript{2-CSS}. Therefore, the amount of S\textsuperscript{2-} in the silicate melt decreases whilst \( w^{m_{S6+}} \) remains constant. Hence, \( w^{m_{ST}} \) initially decreases with increasing \( f_{O2} \) based on equation (12), resulting in the maximum at the star (this is most visible in Figure 6a). At sufficiently high \( f_{O2} \) (\( \Delta \text{FMQ} > +2.0 \)), \( w^{m_{ST}} \) is essentially constant at S\textsuperscript{6+}\text{CAS} from equations (14b) and (11)

\[ w^{m_{ST}} \equiv w^{m_{S6+}} = w^{m_{S6+\text{CAS}}}, \]  \hfill (20)

and independent of \( P \) and \( f_{O2} \) given the parameterisation we have used. Hence, \( w^{m_{S6+\text{CAS}}} \) is essentially parallel to the \( \log_{10}[w^{m_{ST}}] \sim 4 \) contour over most of the yellow regions in Figure 3c and Figure 5c, except for a small (but effectively undetectable) deviation because some S\textsuperscript{2-} is always present, which decreases with increasing \( f_{O2} \).
At low $f_{O_2}$ when $f_{O_2}$ is increased, $w^{m}_{S6+}$ increases while $w^{m}_{S2-}$ is essentially constant at $w^{m}_{S2-}$ CSS. Conversely, at high $f_{O_2}$ when $f_{O_2}$ is decreased, $w^{m}_{ST}$ increases because $w^{m}_{S2-}$ increases while $w^{m}_{S6+}$ is constant at $w^{m}_{S6+}$ CAS. Thus, there is a maximum in $w^{m}_{ST}$ when the silicate melt is saturated with vapour + sulfide melt + anhydrite (i.e., the star in Figure 3c, Figure 5c, and Figure 6c). Whilst the system is at this particular $T$-$P$-$f_{O_2}$ value, $w^{m}_{ST}$ is fixed and any excess sulfur in the system above this value would form more vapour, sulfide melt, and/or anhydrite: hence, it is a "global $SS^{max}$. A maximum in $P$ also occurs at this $f_{O_2}$ (Figure 6b) because a higher $P$ is required to keep the total $S$ content dissolved in the silicate melt as described in “Regions with mixed speciation in the silicate melt or vapour”. Although this maximum occurs in the vicinity of the $SS^{min}$ (described in “Regions with mixed speciation in the silicate melt or vapour”), it follows a different path that results in an $SS^{max}$.

Silicate melt + (vapour and/or sulfide melt and/or anhydrite)

For $Y$ values above the grey curves in Figure 3–Figure 5, the stable phase assemblage is no longer silicate melt + vapour. The contours for vapour-saturated silicate melt shown beyond these curves are metastable in these regions. Since in our treatment the silicate melt is confined to the model ternary system and it is vapour-undersaturated, the silicate melt is the only stable phase. Therefore, $\varphi = 1$ and $F = 4$, meaning four independent variables are needed to specify the state of the system. Although silicate melt is the only stable phase in the model ternary system under these conditions, the silicate melt can be saturated with sulfide melt and/or anhydrite (which are not in the ternary system) if the values of $\mu_{FeS}$ and/or $\mu_{CaSO_4}$ in the silicate melt correspond to the values of these phases. In this section, we choose $T$, $f_{O_2}$, $P$ and either $\mu_{FeS}$ if the silicate melt is sulfide melt-saturated or $\mu_{CaSO_4}$ if it is anhydrite-saturated. If the silicate melt is both sulfide melt- and anhydrite-saturated, only two of the three other variables ($T$, $f_{O_2}$, and $P$) can be independent. For given values of $T$, $f_{O_2}$, and $P$ (and parameterizations of $S^2$ CSS, $S^{6+}$CAS, $C_{S2-}$, and $C_{S6+}$), $w^{m}_{ST}$ at sulfide melt-saturation can be calculated using equation (10) and at anhydrite-saturation using equation (12). As before, the stable saturation condition (i.e., sulfide melt- or anhydrite-saturation) is the one with the lowest $w^{m}_{ST}$.

Figure 4f shows in $P$–$f_{O_2}$ space (at $T = 1200^\circ$C) the phase(s) with which the silicate melt on the model ternary plane is saturated: the dark and light grey regions are for sulfide melt- and anhydrite-saturation, respectively, and the coloured regions are for vapour-saturation as described in “Silicate melt + vapour”. Where these regions intersect, the silicate melt is saturated with two of the three other phases and these curves define fully constrained paths in $P$–$f_{O_2}$ space at constant $T$. The behaviour of $w^{m}_{ST}$ and $P$ with increasing $f_{O_2}$ for silicate melt saturated with vapour + sulfide melt or vapour + anhydrite are described in “Silicate melt + vapour + (sulfide melt and/or anhydrite)”. With increasing $P$, for silicate melt saturated with sulfide melt + anhydrite (without vapour), $w^{m}_{ST}$ decreases and $f_{O_2}$ is almost constant. The three curves (silicate melt + vapour + sulfide melt; silicate melt + vapour + anhydrite; and silicate melt + sulfide melt + anhydrite) meet at a point (the star), where silicate melt is saturated with vapour, sulfide melt, and anhydrite, corresponding to a global maximum in $w^{m}_{ST}$ for a given $T$ (described in “Silicate melt + vapour + (sulfide melt and/or anhydrite)”).

We now explore how $w^{m}_{ST}$ changes along isobaric paths of increasing $f_{O_2}$, where $P$ is above or below $P = 1543$ bar where silicate melt is multiply-saturated with vapour, sulfide melt, and anhydrite (i.e., the grey star in Figure 5g and Figure 6c and e). At $P > 1543$ bar, the silicate melt
is vapour-undersaturated but the trend of $w_{\text{ST}}^m$ with increasing $f_{O_2}$ is similar to the case where vapour-saturation occurs in addition to sulphide melt- and/or anhydrite-saturation as described in “Silicate melt + vapour + (sulphide melt and/or anhydrite)” (e.g., compare Figure 6a and c). The maximum without vapour but sulphide melt + anhydrite saturation is lower than with vapour + sulphide melt + anhydrite, as the latter is a global maximum at a fixed $T$. The maximum S content at a given $P$ occurs at a unique $f_{O_2}$ (depending on the composition of the silicate component) at the near vertical curve defining saturation of the silicate melt with both sulphide melt and anhydrite. Both $\mu_{\text{FeS}}$ and $\mu_{\text{CaSO}_4}$ are specified in addition to $P$ at this point, and therefore $f_{O_2}$ is fixed for this set of three independent variables (in addition to $T$).

At $P < 1543$ bar, the stable isobaric path crosses into the stable vapour-saturated field at intermediate $f_{O_2}$ (e.g., at the grey solid curve in Figure 5g, described in “Silicate melt + vapour + (sulphide melt and/or anhydrite)”)). The behaviour (and calculations – equation (10)) at low $f_{O_2}$ ($\Delta F_{\text{MQ}} \lesssim +0.8$), when the silicate melt is only saturated with sulphide melt, is the same as at higher $P$ (i.e., compare the black solid curves in Figure 6c and e: these two curves are nearly identical since the dependence of $w_{\text{S}_2-\text{CSS}}^m$ on $P$ is minor; O’Neill, 2020). A local maximum ($\Delta F_{\text{MQ}} \equiv +0.8$) occurs when the silicate melt is saturated with both sulphide melt and vapour (i.e., labelled “$\delta$” at the solid grey vertical line in Figure 6e). When $f_{O_2}$ is further increased beyond this point ($+0.8 \lesssim \Delta F_{\text{MQ}} \lesssim +3.6$), the silicate melt is only vapour-saturated, and $w_{\text{ST}}^m$ displays the $\text{SS}^\text{min}$ as described in “Regions with mixed speciation in the silicate melt or vapour” (i.e., labelled “$\varepsilon$” on the dotted black curve in Figure 6e). When $w_{\text{S}_6}^m = w_{\text{S}_6+\text{CAS}}^m$ ($\Delta F_{\text{MQ}} \equiv +3.6$), the silicate melt is saturated with vapour and anhydrite (e.g., the grey dashed vertical line in Figure 6e). There is a small maximum at (anhydrite + vapour)-saturation (labelled “$\zeta$”), but it cannot be distinguished in Figure 6e because for the isobar chosen it is at sufficiently high $f_{O_2}$ that there is essentially only $\text{S}^{6+}$ (i.e., very little $\text{S}^2^-$) dissolved in the silicate melt at this point. Therefore, although $w_{\text{S}_2}^m$ decreases with increasing $f_{O_2}$ beyond this point, it is already so low that the magnitude of the decrease in $w_{\text{ST}}^m$ is insignificant. At $f_{O_2}$ values above this point ($\Delta F_{\text{MQ}} \gtrsim +3.6$), the silicate melt is only saturated with anhydrite (i.e., the dashed black curve in Figure 6e) and behaves as described previously under these conditions. For a given $P$, along all isobaric paths of increasing $f_{O_2}$ when vapour-saturation is encountered (i.e., $P < 1543$ bars), there is an $\text{SS}^\text{max}$ when the silicate melt is saturated with sulphide melt + vapour ($\delta$, which gets larger with increasing $P$); an $\text{SS}^\text{min}$ when the silicate melt is only vapour-saturated ($\varepsilon$); and another $\text{SS}^\text{max}$ when the silicate melt is saturated with anhydrite + vapour ($\zeta$).

**Isothermal, decompression-induced degassing**

The examples developed in “Independent variables of $T$, $f_{O_2}$, $f_{S_2}$, $w_{\text{ST}}^m$, $\mu_{\text{FeS}}$, and $\mu_{\text{CaSO}_4}$” and Figure 2–Figure 5 do not apply to the $f_{O_2}$–$f_{S_2}$ paths followed by magmas as they degas on decompression (or due to crystallisation) under equilibrium conditions because $f_{O_2}$ is not an independent variable in this process. We have evaluated whether the $\text{SS}^\text{min}$ has any impact on closed- and open-system degassing during isothermal decompression using our simple model ternary system. Inclusion of other volatiles (e.g., H and C) would add complexity to the system and are important for getting the details correct for simulation of degassing in nature (e.g., Moretti et al. 2003; Moretti and Papale 2004; Burgisser and Scaillet 2007; Gaillard and Scaillet 2009, 2014; Wallace and Edmonds 2011; Gaillard et al. 2011, 2015; Burgisser et al. 2015; Iacovino
2015; Liggins et al. 2020). However, their exclusion here allows us to isolate the behaviour of sulfur during degassing.

We model closed-system degassing by decreasing \( P \) at constant \( T \) and constant bulk composition for the two-phase system silicate melt + vapour; hence, the independent variables are \( T, P \), and bulk composition. A closed-system requires the bulk composition of the system (i.e., silicate melt ± vapour) to be constant at all \( P \). The bulk composition comprises the proportions of the silicate melt component, total \( S_2 \), and \( O_2 \) (the latter is the \( O_2 \) in excess of that in the model silicate component). For open-system degassing, any vapour present at each \( P \) step (1 bar increments) is removed from the system. Hence, the bulk composition of the system changes during depressurisation and the silicate melt composition becomes the bulk composition of the system for the subsequent \( P \) step. We do not allow sulfide melt or anhydrite to be present; hence, in some regions the silicate melt + vapour assemblage encountered during degassing is metastable (to the left of the solid grey curve in Figure 7a). Results of closed- and open-system degassing calculations are essentially indistinguishable (Figure 8), hence we only discuss closed-system degassing calculations.

For a particular bulk composition, when \( P > P^\text{sat}_v \) (pressure of vapour-saturation; above the solid black curve in Figure 7), the system is vapour-undersaturated and only silicate melt is present. At \( P = P^\text{sat}_v \) (on the solid black curve), the system is still 100% silicate melt, but the silicate melt is vapour-saturated (i.e., equation (7) is satisfied using equations (3b), (4c), (5c), (8), and the bulk composition of the system). When \( P < P^\text{sat}_v \) (below the solid black curve), the silicate melt is supersaturated with respect to vapour, such that vapour exsolves from the silicate melt and the two phases coexist under equilibrium conditions. The 5000 ppm contour is the locus of \( P^\text{sat}_v \) (i.e., the \( P \) at which degassing begins; Figure 7c) for a silicate melt corresponding to the bulk composition of the system, where the white diamond indicates \( S^\text{Smin}_{\text{Fe}_2} \) (i.e., \( \Delta \text{FMQ} + 1.30 \) for these parameters, at the maximum of the black curve).

If the silicate melt starts off more reduced than \( S^\text{Smin}_{\text{Fe}_2}, f_{\text{Fe}_2} \) decreases with decreasing \( P \) during closed-system degassing (e.g., the yellow curves in Figure 7d and g, and Figure 8b). This reflects that although the silicate melt is \( S^2^- \)-dominated, the vapour is \( S_2 \)-dominated and/or \( \text{SO}_2 \)-dominated (Figure 7f), so \( O_2 \) is consumed during degassing to convert \( S^2^- \) dissolved in the silicate melt into the more oxidised \( S_2 \) and \( \text{SO}_2 \) vapour species (see the reaction (4a) and the reaction generated by subtracting (3a) from (4a)). Therefore, reduction of the system (i.e., a decrease in \( f_{\text{Fe}_2} \)) must occur for degassing under these conditions, although this effect is buffered by changes in \( \left[ \text{Fe}^{3+}/\text{Fe}^\text{II} \right] \), which are included in our calculations. However, if the silicate melt starts off more oxidised than \( S^\text{Smin}_{\text{Fe}_2}, f_{\text{Fe}_2} \) increases with decreasing \( P \) during closed-system degassing (e.g., the turquoise curve in Figure 7d and g, and Figure 8b). This reflects that the silicate melt is \( S^{6+} \)-dominated but the vapour is \( \text{SO}_2 \)-dominated (Figure 7f), so \( O_2 \) is generated during degassing to convert \( \text{SO}_2^{2-} \) dissolved in the silicate melt into the more reduced \( \text{SO}_2 \) vapour species (see the reaction generated by subtracting (3a) from (5a)). Hence, oxidation of the system (i.e., an increase in \( f_{\text{Fe}_2} \)) must occur for degassing under these conditions. Close inspection of Figure 7d demonstrates that for a narrow range of bulk compositions that start degassing close to, but slightly more reducing than, \( S^\text{Smin}_{\text{Fe}_2}, f_{\text{Fe}_2} \) initially increases and then decreases at lower \( P \). In contrast to bulk compositions that are displaced in \( f_{\text{Fe}_2} \) from \( S^\text{Smin}_{\text{Fe}_2} \) by more than ~0.1 log units, there is minimal change in \( f_{\text{Fe}_2} \) during depressurisation for bulk compositions that start close to \( S^\text{Smin}_{\text{Fe}_2} \) (e.g., the green curves in Figure 7d and g, and Figure 8b).
At constant bulk composition when $P < P_{\text{sat}}^\text{w}$, $w_{\text{S}^\text{ST}}$ decreases monotonically with decreasing $P$ to 1 bar (Figure 7c and Figure 8c). Hence, the $SS_{\text{min}}$ is not encountered in our simple system during closed-system, depressurisation-induced degassing because changes in $f_{O_2}$ do not cause the silicate melt to cross the $SS_{\text{min}}$. However, the shapes of the $w_{\text{S}^\text{ST}}$ with decreasing $P$ are different at the $SS_{\text{min}}$ (roughly linear) compared to either side (concave down). With decreasing $P$, $f_{S_2}$ (Figure 7a and Figure 8a) and $f_{SO_2}$ (Figure 7b) always decrease; the rate of decrease depends on the bulk composition of the system. The rate of change is controlled by the trade-off between decreasing $w_{\text{S}^\text{ST}}$ and decreasing or increasing $f_{O_2}$ to the left and right of $SS_{\text{min}}$, respectively, through equations (17a) and (17b).

**Implications of $SS_{\text{min}}$ and $SS_{\text{max}}$ for magmatic and volcanic processes**

The $SS_{\text{min}}$ for silicate melt + vapour and the $SS_{\text{max}}$ for silicate melt ± vapour + sulfide melt + anhydrite occur in a similar $f_{O_2}$ range since both features depend on the silicate melt having mixed S speciation (“Independent variables of $T$, $f_{O_2}$, $f_{S_2}$, $w_{\text{S}^\text{ST}}$, $P$, $\mu_{FeS}$, and $\mu_{CaSO_4}$”). The $SS_{\text{min}}$ manifests when $T$ (held constant) and $f_{O_2}$ are independent variables, and $f_{S_2}$, $w_{\text{S}^\text{ST}}$, or $P$ are the third independent variable and held constant or varied in particular ways (see “Regions with mixed speciation in the silicate melt or vapour”; Figure 2–Figure 5). The $SS_{\text{min}}$ reflects the prominent “valleys” – centered where the silicate melt has mixed S speciation – in the isothermal surfaces showing $w_{\text{S}^\text{ST}}$ as a function of $f_{S_2}$ or $P$ vs. $f_{O_2}$ (Figure 3c and Figure 5c). An alternative expression of the $SS_{\text{min}}$ is the prominent “ridge” in the topography of the isothermal $P$ surface plotted as a function of $w_{\text{S}^\text{ST}}$ vs. $f_{O_2}$ (Figure 4c). However, there are simple linear paths that cross the valley (or ridge) with increasing $f_{O_2}$ in Figure 3–Figure 5c for which there is no $SS_{\text{min}}$. There are also geological important paths (including closed- or open-system depressurisation; “Isothermal, decompression-induced degassing”) that nearly parallel the valley floor (or ridge crest) and therefore do not encounter an $SS_{\text{min}}$.

Our model calculations place the $SS_{\text{min}}$ for this Hawaiian basalt composition at 1200 °C at $SS_{\text{min}f_{O_2}} = \Delta \text{FMQ} + 1.2$. For comparison, this is slightly more oxidised than Hawaiian basalts ($\Delta \text{FMQ}$-0.5 to +1.0; Moussallam et al. 2016; Brounce et al. 2017; Lerner et al. 2021) and more oxidised than mid-ocean ridge basalts (MORB), but within the range measured in arc and ocean island basalts (OIB) (e.g., Cottrell et al., 2021). The position of $SS_{\text{min}f_{O_2}}$ will depend on $T$, composition of the silicate component, and additional volatile components (e.g., $H_2O$, $CO_2$). To explore how the effects described here vary with $T$ and melt composition, a robust parameterisation of $C_{S_6^+}$ is required to model S solubility accurately and therefore to understand fully the importance of the $SS_{\text{min}}$ and $SS_{\text{max}}$ in natural magmas. However, numerous experimental and modelling studies have demonstrated the $SS_{\text{min}}$ at the $f_{O_2}$ range relevant to abundant terrestrial magma types (e.g., Fincham and Richardson 1954; Katsura and Nagashima 1974; Carroll and Rutherford 1985; Moretti et al. 2003; Clemente et al. 2004; Backnaes and Deubener 2011; Lesne et al. 2015; Matjuschkin et al. 2016; Nash et al. 2019). When these experimental results are combined with our model results, this phenomenon is likely to play a role in magmatic and volcanic processes affecting terrestrial magmas. We explore the influence of the $SS_{\text{min}}$ and $SS_{\text{max}}$ in experiments (“Solubility experiments”) and in natural processes and describe its possible application as a tool for constraining magmatic $f_{O_2}$ (“Using $w_{\text{S}^\text{ST}}$ as an oxybarometer”). These potential impacts on natural magmatic systems are summarised schematically in Figure 1c. We highlight natural processes throughout the magmatic and volcanic system, starting deep with mantle melting.
(“Mantle melting”); up through the crust where magmas undergo mixing (“Magma mixing and crustal assimilation”) and degassing (“Magma ascent and degassing”); and finally to volcanic emissions into the atmosphere (“Volcanic emissions”).

Solubility experiments

The SS\textsuperscript{min} and SS\textsuperscript{max} described in “Independent variables of T, f\textsubscript{O2}, f\textsubscript{S2}, w\textsuperscript{mST}, P, \mu\textsubscript{FeS}, and \mu\textsubscript{CaSO4}” have been observed in experiments that can externally control P, T, f\textsubscript{O2}, and f\textsubscript{S2}. For example, the SS\textsuperscript{min} has been observed using one-atmosphere gas-mixing experiments at constant T and P with varying f\textsubscript{O2} (e.g., Fincham and Richardson, 1954; Katsura and Nagashima, 1974). In these experiments, f\textsubscript{S2} was not constant as the volume percentage of SO\textsubscript{2} in the gas prior to heating in the gas mixing furnace was constant instead, which was mixed with other gas species to attain the required f\textsubscript{O2}. Despite the more complex gas speciation of such experiments, and that the systems were not simple ternaries, the geometry of w\textsuperscript{mST} vs. f\textsubscript{O2} are reproduced by our modelling (e.g., compare Figure 2a in Fincham and Richardson (1954) with our Figure 2e). Consistent with our analysis (“Regions with mixed speciation in the silicate melt or vapour”), Fincham and Richardson (1954) attributed the first change in slope in their Figure 2a to a change in vapour speciation and the second to change in silicate melt speciation. At constant T and P, a different f\textsubscript{S2}-f\textsubscript{O2} path can be followed in one-atmosphere gas-mixing experiments using the bulk composition of the input gas to control f\textsubscript{S2} as well as f\textsubscript{O2} (e.g., O’Neill and Mavrogenes 2002; Nash et al. 2019). O’Neill and Mavrogenes (2002) did not observe an SS\textsuperscript{min} because the f\textsubscript{O2} was always lower than the expected value of SS\textsuperscript{min}f\textsubscript{O2}, but Nash et al. (2019) did observe an SS\textsuperscript{min} (although not the change in slope due to changes in vapour speciation).

Piston cylinder experiments by Matjuschkin et al. (2016) produced an SS\textsuperscript{min} in (sulfide melt + vapour)-saturated silicate melts at constant P and T, in which f\textsubscript{O2} was controlled using solid-state buffers (their Figure 8b). Their experiments were always saturated with sulfide melt (except one set at very high f\textsubscript{O2} that were anhydrite-saturated), whereas the minimum described in “Silicate melt + (vapour and/or sulfide melt and/or anhydrite)” (e in Figure 6e) is only vapour-saturated (i.e., it is not sulfide melt-saturated). Matjuschkin et al. (2016) attributed their SS\textsuperscript{min} to the presence of an additional S-bearing melt species with intermediate charge between 2- and 6+ that was not quenchable. Alternatively, their minimum could be influenced by a decrease in S\textsuperscript{2}-CSS reflecting compositional changes in the silicate melt due to crystallisation as f\textsubscript{O2} varied.

A variety of studies using high-pressure, high-temperature apparatus at constant T and P and varying f\textsubscript{O2} have observed an increase in w\textsuperscript{mST} as the system transitioned from sulfide melt-to-anhydrite-saturation (e.g., Carroll and Rutherford 1985, 1987; Jugo et al. 2004; Beermann et al. 2011; Botcharnikov et al. 2011). However, these studies suggested a plateau rather than a maximum, likely due to the narrow f\textsubscript{O2} range of the SS\textsuperscript{max}. However, Jugo (2009) modelled the data from Carroll and Rutherford (1985, 1987) and Jugo et al. (2004) and produced an SS\textsuperscript{max} similar to what we have described in “Silicate melt + (vapour and/or sulfide melt and/or anhydrite)” (although they did not consider vapour-saturation as an additional constraint). It is encouraging that our calculated trends match Figure 1 from Jugo (2009), despite using different sets of equations, solubility mechanisms, and thermochemical parameters.
Mantle melting

The SS$^{\text{max}}$ we have described defines the maximum S content for silicate melts generated by partial mantle melting (i.e., in the presence of sulfide melt + anhydrite ± vapour at a given $T$). Once either sulfide melt or anhydrite is exhausted, the S content of the partial melt decreases to $w^{\text{mSTCAS}}$ or $w^{\text{mSTCSS}}$, respectively, and then decreases further by dilution when both phases are exhausted (e.g., Chowdhury and Dasgupta, 2019). Chowdhury and Dasgupta (2019) explored the S content of silicate melts generated by mantle melting when the mantle contains either sulfide or anhydrite. They found that the S content of most arc magmas could be generated by mantle melting in the presence of sulfide when $S^2$ is the dominate silicate melt species. For some arc magmas, they found this was not the case, but sulfide should still be present in the mantle source during melting. They attributed these higher S contents to the presence of sulfate in the silicate melt: this can be visualised in Figure 6c by partial mantle melting producing silicate melts between the dashed green vertical lines. For two of their arc magmas, the S concentrations were too high for even anhydrite-saturated melting, which Chowdhury and Dasgupta (2019) suggested requires an additional S source, such as crustal assimilation of sulfate. Alternatively, our modelling suggests these S-rich magmas could be generated by melting of mantle sources containing both sulfide and anhydrite (or with only one of these phases but at an $f_{O_2}$ close to SS$^{\text{max}}$), since this would result in $w^{\text{mST}}$ of the silicate partial melt higher than SS$^6$CAS. However, a thorough assessment requires knowledge of the $T$ and melt composition dependence of $C_{S_{64}}$ to model mantle melting.

Magma mixing and crustal assimilation

In nature, approximately constant $P$ paths could be important when mixing reduced and oxidised S-bearing silicate melts. For example, mixing vapour-undersaturated silicate melts from either side of $S^\text{SSmin}f_{O_2}$ would generate a vapour-saturated silicate melt if the combined S content is greater than $w^{\text{mST}}$ at the intermediate $f_{O_2}$, which can be visualised using Figure 7g. At $P = 550$ bar (black dashed horizontal line), both a relatively reduced (white circle at 3.26 wt% $O_2$) and oxidised (white square at 4.23 wt% $O_2$) silicate melt containing 5000 ppm $w^{\text{mST}}$ would be vapour-undersaturated (Figure 7c). Mixing these silicate melts isobarically results in a new bulk composition between the two end members in Figure 7 that depends on the mixing proportions. If the mixed silicate melt has a bulk composition inside the vapour-saturation curve for 5000 ppm $S_T$ (i.e., the black curve; between $+1.0 \leq \Delta F_{\text{MQ}} \leq +1.7$ for the example shown in Figure 7g), the silicate melt will become vapour-saturated (Figure 7f). The mixed magma will then degas until $w^{\text{mST}}$ decreases to the contour at that point (Figure 7c) and the amount of vapour degassed will depend on the mixing proportions (Figure 7e). This simple analysis assumes the oxidized and reduced silicate melts are the same in composition (other than in total $O_2$). If they differ in major element chemistry or $T$, there would be added complexity because $C_{S_{22}}$, $C_{S_{64}}$, and $T$ will change depending on the proportions of the two silicate melts in the mixture (and the possibility of crystallization of the mixture). These factors would also influence the solubility of S as a function of the mixing proportions of the two silicate melts. This would be particularly important if a reduced silicate melt assimilated oxidised country rock or an oxidised silicate melt assimilated reduced country rock (e.g., Tomkins et al. 2012; Iacono-Marziano et al. 2017). Nevertheless, encountering SS$^{\text{min}}$ during mixing could be relevant to eruptive dynamics and volcanic $SO_2$ contributions to the atmosphere by rapidly producing a large amount of vapour (e.g., Figure 7e), potentially driving eruption (e.g., Kress 1997; Di Muro...
Magma ascent and degassing

For vapour-saturated magma ascent to the surface, $P$ and bulk composition are two key independent variables. Our calculations for the model ternary system show that $f_{O_2}$ paths during isothermal depressurisation of a representative Hawaiian basalt are unlikely to cross $SS_{min}/f_{O_2}$ (Figure 7d and Figure 8b; “Isothermal, decompression-induced degassing”). Thus, in this system, $w''_{ST}$ decreases monotonically with decreasing $P$ for a closed- (and open-) system once vapour-saturation is reached (Figure 7c and Figure 8c). In this simple system at low $P$, this is expected because the partial molar volumes of the gaseous S-bearing species are higher than those of the dissolved silicate melt species. Hence, the progressively more degassed state is the more stable one with decreasing $P$ (i.e., a stable isothermal system requires that volume increases as $P$ decreases so that the bulk isothermal compressibility is always positive). We have not evaluated the possible effects of changes in $T$ or silicate melt composition during degassing (e.g., due to crystallization resulting from heat loss and/or from an increase in the liquidus on degassing). These changes would result in changes in $C_{S2}$ and/or $C_{S6+}$, and therefore the value of $SS_{min}/f_{O_2}$ at a particular $P$ could vary during degassing, possibly resulting in $SS_{min}$ influencing $w''_{ST}$ during degassing.

Degassing of C- and H-bearing species from a silicate melt can cause $f_{O_2}$ to increase (e.g., Sato and Wright 1966; Sato 1978; Mathez 1984; Candela 1986; Holloway 2004; Burgisser and Scaillet 2007; Brounce et al. 2017; Métrich 2021). The magnitude of this $f_{O_2}$ increase is greater when the initial $f_{O_2}$ of the magma is lower and depends on the relative solubilities of oxidised and reduced C- and H-bearing silicate melt species (e.g., Gaillard et al. 2015). Therefore, it may be possible to have a vapour-saturated silicate melt that starts $S^2$-dominated but oxidises sufficiently due to early $CO_2$ and/or $H_2O$ degassing to drive the system across $SS_{min}$ during depressurisation. If so, this could be manifested by initially decreasing, followed by increasing, $w''_{ST}$ with progressive closed-system, depressurisation-induced degassing. It is also possible that a maximum in $w''_{ST}$ could occur during degassing, although this would not be due to changes in $f_{O_2}$ or the $SS_{min}$. For example, the loss of $CO_2$ and $H_2O$ prior to significant S degassing could cause $w''_{ST}$ to initially increase (i.e., because the total mass of the silicate melt is decreasing while the mass of dissolved S is nearly constant); then, when S begins to degas, $w''_{ST}$ would decrease.

Progressive reduction or oxidation of magmas during degassing is expected based on previous modelling efforts and has been observed in natural samples (e.g., Anderson and Wright 1972; Candela 1986; Carmichael and Ghiorso 1986; Burgisser and Scaillet 2007; Métrich et al. 2009; Gaillard et al. 2011, 2015; Kelley and Cottrell 2012; Moussallam et al. 2016, 2014; Brounce et al. 2017). Our degassing calculations demonstrate that the $f_{O_2}$ after extensive S-degassing will not represent the initial silicate melt unless the silicate melt began degassing near $SS_{min}$ (Figure 7d). For example, when $f_{O_2}$ differs from that of $SS_{min}/f_{O_2}$ (i.e., at the diamond) by more than $\pm 0.1$ log unit (either positively or negatively), the $f_{O_2}$ after nearly complete degassing (i.e., $P =1$ bar) has increased or decreased by more than 0.5 log units (and up to $> 1$ log unit) relative to the initial (i.e., undegassed) $f_{O_2}$ of the silicate melt (Figure 7d). Therefore, as has been highlighted previously, using the $f_{O_2}$ of volcanic gases (or from the $Fe^{3+}/Fe^{2+}$ or $S^{6+}/S^{2-}$ of silicate glasses) as a proxy for the $f_{O_2}$ of the initial silicate melt (and potentially of the mantle), should be approached with caution (e.g., Anderson and Wright 1972; Carmichael and Ghiorso 1986; Burgisser and Scaillet 2007;
Métrich et al. 2009; Gaillard et al. 2015). We emphasize, however, that the direction of the change in \( f_{O_2} \) on degassing differs for more oxidized and reduced magmas relative to \( SS_{min}f_{O_2} \) (Figure 7d and Figure 8b).

The unlikelihood of crossing the \( SS_{min} \) during closed- or open-system degassing does not mean that \( SS_{min} \) is unimportant during degassing. Decompression paths to the left and right of \( SS_{min} \) begin to degas at lower \( P \) than one that passes right through the maximum (Figure 7c). The shapes of the contours in Figure 7c are simple expressions of the \( SS_{min} \) described in “Silicate melt + vapour” for the case \( Y = w^{ST} \) (Figure 2d and Figure 4c). The maximum in \( P \) at the \( SS_{min} \) is occurs because a higher \( P \) is required to keep a given concentration of \( S \) dissolved in the silicate melt (5000 ppm in Figure 7c) at the \( SS_{min} \) than when the \( S \) solubility is higher on either side. Based on our modelling, a Hawaiian basaltic melt with 5000 ppm \( S_T \) reaches vapour-saturation at 666 bars at \( SS_{min} \) (the green curve in Figure 8). This is 164 bars higher than when the melt is initially 0.5 log units higher in \( f_{O_2} \) (the turquoise curve) and 363 bars higher than when the melt is initially 0.6 log units lower in \( f_{O_2} \) (the yellow curve). Thus, \( SS_{min} \) can exert significant control on the \( P \) at which \( S \) degassing begins as a function of \( f_{O_2} \) (Figure 7). Therefore, even for \( S \)-rich magmas, \( S \) will degas only at shallow depths if the silicate melt has an initial \( f_{O_2} \) sufficiently lower than (e.g., MORB) or higher than \( SS_{min}f_{O_2} \). However, silicate melts with initial \( f_{O_2} \) close to \( SS_{min}f_{O_2} \) (e.g., many arc and OIB magmas) would – all other things being equal – begin to degas \( S \) deeper than more oxidized or reduced magmas. Therefore, the \( SS_{min} \) could be a contributing mechanism – in addition to \( S \) partitioning into the \( H_2O \)-rich vapour exsolved from \( H_2O \)-rich magmas (e.g., Wallace and Edmonds 2011; Zajacz et al. 2012; Edmonds and Mather 2017; Edmonds and Woods 2018) – for the deep degassing of \( S \) in arc and some ocean island settings.

The \( SS_{min} \) also has implications for calculating the \( P_{v_{sat}} \) using the volatile concentrations of glasses (e.g., in pillow rims and glassy melt inclusions) (e.g., Anderson et al. 1989; Blundy and Cashman 2008). Such calculated pressures are often used to constrain the architecture of magmatic systems and link volcanic products to eruptive vents in submarine systems. These calculations are based on generalisations of equation (7) that include other gaseous species for which partial pressures can be determined (e.g., \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)). This exercise is comparable to when \( T, f_{O_2} \), and \( Y = w^{ST} \) are taken as independent variables in a silicate melt + vapour assemblage and the dependent variable \( Z = P \) is calculated (e.g., Figure 4c). The effect of dissolved \( S \) is currently not included in such calculations, which include only \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) (e.g., Newman and Lowenstern 2002; Papale et al. 2006; Iacono-Marziano et al. 2012; Ghiorso and Guala 2015; Allison et al. 2019; Iacovino et al. 2021). Also, the effect \( f_{O_2} \) on volatile speciation in the silicate melt and vapour is mostly ignored (but see Scaillet and Pichavant 2004; Wetzel et al. 2015).

MORB magmas have \( S^{6+}/S_T < 0.05 \) (e.g., Métrich et al. 2009; Jugo et al. 2010; Labidi et al. 2012) and therefore including \( S \) for such melts would have a negligible effect on calculated \( P_{v_{sat}} \) because \( p_{\text{SO}_2} \) and \( p_{\text{O}_2} \) would be low (e.g., Figure 2d). However, OIB and arc volcanic glasses can have \( [S^{6+}/S_T]^{w} \) up to 1 (e.g., Jugo et al. 2010; de Moor et al. 2013; Labidi et al. 2015; Muth and Wallace 2021), and therefore the effects of the \( SS_{min} \) on the contribution of partial pressures from \( S \)-bearing species to the total \( P \) at vapour-saturation (e.g., \( \text{S}_2 \) and \( \text{SO}_2 \) in the \( \text{S}–\text{O} \) system, but potentially \( \text{H}_2\text{S} \) and \( \text{OCS} \) as well in \( \text{C}–\text{O}–\text{H}–\text{S} \) system) could be non-negligible (e.g., in the green band of Figure 2d). Melt inclusions from arc and OIB magmas reach \( w^{ST} \sim 5000 \text{ ppm} \) (Wallace 2005) and are \( \Delta \text{FMQ}-3 \) to +3 (Cottrell et al. 2021), which could lead to underestimating \( P_{v_{sat}} \) by up to 650 bars for melts at \( \Delta \text{FMQ} = +1 \) to +2 (Figure 9). The exact value of the underestimate would depend on the \( f_{O_2} \), \( C_{S6+} \), and \( C_{S2} \), and hence \( T \) and silicate melt composition, and including...
the H and C species (e.g., Burgisser et al. 2015; Lesne et al. 2015; Hughes et al. 2021). However, the potential magnitude of this $SS^\text{min}$-related effect implied by our calculations is robust. Therefore, in such cases neglecting S could result in calculated $P^\text{sat}$ values that significantly underestimate the $P^\text{sat}$ the glass is recording.

We note that the maximum in $P^\text{sat}$ at $SS^\text{min}$ based on our calculations contrasts with the modelling of Lesne et al. (2015), who predict a minimum in $P^\text{sat}$ when both reduced and oxidised S species are present in silicate melts. The difference could be due to: (1) different assumptions regarding the speciation of oxidised S in the silicate melt (i.e., as SO$_2$ rather than SO$_4^{2-}$; see “Equilibria between silicate melt, vapour, sulfide melt, and anhydrite” for discussion of potential S-bearing species in the silicate melt); and (2) the effect of H on the $SS^\text{min}$, which adds H$_2$S species to the silicate melt and vapour.

Volcanic emissions

The El Chichón 1982 and Pinatubo 1991 eruptions released the largest quantities of SO$_2$ during explosive events recorded by satellites, and most of this SO$_2$ was sourced from a coexisting vapour present prior to eruption (e.g., Wallace and Gerlach 1994; Krueger et al. 1995; Gerlach et al. 1996; Kepler 1999; Bluth et al. 2015). Additionally, both magmas contain anhydrite and pyrrhotite/sulfide in the erupted products (e.g., Luhr et al. 1984; Bernard et al. 1991; Luhr 2008a). We infer from this observation that both these magmas were stored at $SS^\text{max}$ prior to eruption (i.e., at the condition represented by the grey star in Figure 5g). Independent $f_O^2$ estimates from these magmas are within the range for experimental constraints for the coexistence of sulfide melt and anhydrite (e.g., Luhr et al. 1984; Rye et al. 1984; Carroll and Rutherford 1987; Evans and Scaillet 1997; Luhr 2008b). Older eruptions have released even greater quantities of SO$_2$ (e.g., Figure 5 in Vidal et al. 2016) and these magmas may have also been stored at $SS^\text{max}$. For example, eruptive products from the Samalas 1257 eruption contain sulfides and vapour, and anhydrite has been observed as microcrystals on the walls of fluid inclusions (Vidal et al. 2016) (although anhydrite dissolves in water and is therefore rarely observed in volcanic products; Luhr et al. 1984). These results from older eruptions are consistent with the $SS^\text{max}$ being connected to unusually large releases of SO$_2$ during explosive eruptions. If this is correct, it suggests a connection between the unique $f_O^2$ at which the $SS^\text{max}$ occurs and these events.

The “petrologic method” is often used to estimate the volatiles emissions from volcanic eruptions by subtracting the volatile concentration of the degassed matrix glass from that in melt inclusions (the latter is assumed to represent undegassed silicate melt) (e.g., Devine et al. 1984; Thordarson et al. 1996; Wallace 2001; Sharma et al. 2004). The total SO$_2$ emitted during eruption estimated in this way are often low relative to those measured using other techniques (e.g., satellite-based techniques; e.g., Stoiber and Jepsen 1973; Rose et al. 1982; Andres et al. 1991; Wallace 2001; Shinohara 2008). This “excess sulfur” problem reflects the large amounts of SO$_2$-rich vapour often present during magma storage (only minor amounts of SO$_2$ are thought to be released from the break-down of sulfide melt and anhydrite during degassing) (e.g., Anderson 1975; Luhr et al. 1984; Andres et al. 1991; Wallace and Gerlach 1994; Gerlach and McGee 1994; Gerlach et al. 1994, 1996; Giggenbach 1996; Kepler 1999; Wallace 2001; Scaillet and Pichavant 2003; Scaillet et al. 2003; Sharma et al. 2004; Shinohara 2008). Large amounts of S-rich vapour could be generated due to the $SS^\text{min}$ (and to some extents $SS^\text{max}$). Therefore, using glass-only melt inclusions trapped at $SS^\text{min}$ or $SS^\text{max}$ will result in the largest discrepancies with other methods due to the additional S in other phases. Melt inclusions that co-entrapping these additional phases cannot be used
because the proportions of the different phases present in the inclusion are unlikely to represent
the bulk system. Additionally, as melt inclusions evolve as a closed-system to S post-entrapment,
SS^{\text{min}} and SS^{\text{max}} may be encountered causing additional phases to form within the inclusion (e.g.,
vapour bubbles, sulfide blebs). Measuring only the silicate glass within these melt inclusion results
in a greater underestimate of SO$_2$ emissions because the S contribution from the silicate melt is
additionally underestimated (e.g., Venugopal et al. 2020).

Using $w_{\text{ST}}^{m}$ as an oxybarometer

For a silicate melt with a given value of $w_{\text{ST}}^{m}$ and $T$, it is possible to place constraints on its $f_{O_2}$
using the calculations we have presented based on the presence or absence of vapour, sulfide melt,
and/or anhydrite as saturating phases (Figure 6; e.g., the empirical approach of Beermann et al.,
2011). Suppose it is known that the silicate melt is vapour-saturated. If it is also saturated with
sulfide melt it must fall on the solid grey $sulf^{m}$ curve in Figure 6a: so for a known $w_{\text{ST}}^{m}$, the $f_{O_2}$ can
be read directly from the $sulf^{m}$ curve (e.g., $\alpha$ and $\beta$ for 3000 and 13000 ppm $w_{\text{ST}}^{m}$, respectively, in
Figure 6a). Likewise, if the silicate melt is known to be anhydrite-saturated it must fall on the
dashed grey $anh$ curve in Figure 5a: the implied $f_{O_2}$ for a given value of $w_{\text{ST}}^{m}$ can be read from the
$anh$ curve (e.g., $\gamma$ for 13000 ppm $w_{\text{ST}}^{m}$ in Figure 6a). If the silicate melt is known to be saturated
with both sulfide melt and anhydrite, the $f_{O_2}$ is constrained to the SS^{\text{max}} value at the grey star.

Suppose, however, that we do not know whether the vapour-saturated silicate melt is sulfide
melt and/or anhydrite saturated (or we know that it is not). Then the $f_{O_2}$ can be constrained to be
between the $sulf^{m}$ and $anh$ curves in Figure 6a for a given value of $w_{\text{ST}}^{m}$ (e.g., at 13000 ppm $w_{\text{ST}}^{m}$, the
$f_{O_2}$ must be between $\beta$ and $\gamma$ on Figure 6a). When nearly all of the dissolved S is S$^2$ (i.e., in the
purple-blue-turquoise region), the $sulf^{m}$ curve plateaus at $\sim w_{S2-CSS}^{m}$, so for values of $w_{\text{ST}}^{m} < w_{S2-
CSS}$, no constraint can be placed on a lower bound to $f_{O_2}$ using this approach. Likewise, the $anh$
curve plateaus at $\sim w_{S6+CSS}^{m}$, and thus no constraint on an upper bound on $f_{O_2}$ can be determined
by this approach if $w_{\text{ST}}^{m} < w_{S6+CSS}^{m}$. If the silicate melt is not thought to be vapour-saturated, but
$P$ is known independently, a figure like Figure 6c at the relevant $P$ can be used instead. Although
the presence of other volatiles (e.g., C and H) will modify the results from the simple S–O system,
the principles are the same.

The technique described using Figure 6a is most sensitive when measured S concentrations are
high and the S speciation in the silicate melt is mixed (AFMQ $\sim +1$ to $+2$); e.g., to obtain both
lower and upper bounds on $f_{O_2}$ in the example described requires $w_{\text{ST}}^{m} > w_{S6+CSS}^{m}$ $\sim 13000$ ppm
(i.e., the white dotted line in Figure 6a). Although this is much higher than the typical total
dissolved S contents of common magmas, S$^{6+}$CAS decreases significantly with increasing
dissolved H$_2$O and decreasing $T$: e.g., $S^{6+}$CAS $= 3000$ ppm at 5 wt% H$_2$O and 1200 °C for a
basaltic melt (Chowdhury and Dasgupta 2019). Melt inclusions from arcs and ocean islands can
be S-rich (up to $\sim 5000$ ppm Sr), hydrous (up to $\sim 6$ wt% H$_2$O for arcs and $\sim 3$ wt% H$_2$O for ocean
islands), and relatively oxidised (up to $+3$ ΔFMQ) (e.g., Wallace 2005; Moussallam et al. 2019;
Cottrell et al. 2021) and may therefore provide useful $f_{O_2}$ estimates based on this technique.
However, this will require accurate knowledge of $C_{S2}$, $C_{S6+}$, $S^{2-}$CSS, and $S^{6+}$CSS at the relevant
conditions (especially the effects of $T$ and silicate melt composition – including the influence of
H$_2$O), as these parameters strongly influence the $f_{O_2}$ of the transition from $S^{2-}$- to $S^{6+}$-dominated
silicate melt (e.g., O’Neill and Mavrogenes 2002, 2019; Li and Ripley 2005; Moretti and Ottonello
Conclusions

Depending on the choice of independent variables, vapour-saturated silicate melts can with increasing \( fO_2 \) encounter a “sulfur solubility minimum” (\( SS^{\text{min}} \)) when both \( S^2^- \) and \( S^{6+} \) are dissolved in the silicate melt in similar concentrations (Figure 2–Figure 5). This occurs because \( O_2 \) is on different sides of the reactions describing \( S^2^- \) and \( S^{6+} \) dissolution in the silicate melt from \( S_2^- \) and/or \( SO_2 \)-dominant vapour (e.g., reactions (4a) and (5a)). Examples of choices of independent variables and the paths they follow that exhibit a minimum in the dissolved total \( S \) content (\( w^{\text{mST}} \)) in vapour-saturated silicate melt include paths of increasing \( fO_2 \) for which \( T \) and either \( fS_2 \) or \( P \) are held constant (Figure 3c and Figure 5c). For paths on which \( w^{\text{mST}} \) is held constant with increasing \( fO_2 \) and constant \( T \), the \( SS^{\text{min}} \) is expressed a maximum in \( P \) (Figure 4c). However, not all choices of independent variables or paths defined by changes in these variables display the \( SS^{\text{min}} \). An important geological example of this is that despite changing \( fO_2 \), \( w^{\text{mST}} \) decreases monotonically (i.e., no minimum in \( w^{\text{mST}} \) is encountered) during isothermal, closed-system, decompression-induced degassing in a system in which the vapour contains only \( S^- \) and \( O_2^- \)-bearing species (Figure 7c).

There is also a maximum in \( w^{\text{mST}} \) (\( SS^{\text{max}} \)) of silicate melts that are multiply-saturated with sulfide melt and anhydrite at fixed \( T \), and a global maximum if vapour is also present. Like the \( SS^{\text{min}} \), this \( SS^{\text{max}} \) also occurs at a \( fO_2 \) value at which both \( S^2^- \) and \( S^{6+} \) are dissolved in the silicate melt in similar concentrations (Figure 5g). This maximum can be explained by the constraints of sulfide melt- and anhydrite-saturation leading to simultaneous maximization of the concentrations of both the \( S^2^- \) and \( S^{6+} \) species in the silicate melt. Additionally, \( P \) and \( fO_2 \) are dependent variables at \( SS^{\text{max}} \) once the independent conditions of constant \( T \), sulfide melt-saturation (which sets the value of \( fB_{\text{FeS}} \), and anhydrite-saturation (which sets \( fK_{\text{CaSO}_4} \)) are imposed. A maximum in \( w^{\text{mST}} \) is also encountered at constant \( T \) with increasing \( fO_2 \) when a vapour-undersaturated silicate melt is both sulfide melt- and anhydrite-saturated (Figure 6c).

These \( SS^{\text{min}} \) and \( SS^{\text{max}} \) features can play important roles over the entire magmatic and volcanic system, extending from the mantle to eruption (Figure 1c). However, their influences depends on the independent variables governing the system at each point during the process, the paths followed by these variables, and their effects on dependent parameters. For example, these features can influence the maximum \( S \) concentration in mantle melts; the volatile release from magma mixing and crustal assimilation; the depth that significant amounts of \( S \) begin to degas from silicate melt; the \( fO_2 \) of erupted magma and emissions of volcanic gases; and the amounts of \( SO_2 \) released to the atmosphere during explosive eruptions. Additionally, they may also impact some of the tools used to infer intensive and extensive variables of these systems. Excluding the effects of the \( SS^{\text{min}} \) (and \( SS^{\text{max}} \) can cause significant underestimations in calculations of \( P^{v}_{\text{sat}} \), as well as \( SO_2 \) emissions using the petrologic method. \( SS^{\text{max}} \) also provides the possibility of constraining \( fO_2 \) for \( S^- \)-bearing magmas based on limits set by the \( fO_2 \) dependence of \( w^{\text{mST}} \) of silicate melts saturated with vapour, sulfide melt, and/or anhydrite.

We emphasize that our approach has been to use a simplified ternary system (silicate–\( O_2^-–S_2^- \)) to model thermodynamically the coexistence of silicate melt + (vapour and/or sulfide melt and/or
This choice allows us to isolate and analyse the interplay of key variables in a system in which all the volatile species in the vapour are on the S-O join. Therefore, we have not included the effects of other volatile components that typically make up most of the gas phase. Although we are confident that the patterns and behaviour expressed in this simple system can be generalized to natural systems, an important next step will be to include other components and species in the silicate melt and vapour. Our approach can be readily expanded to model such complex natural systems, particularly when H and C are present. Principally, this involves including additional species and homogeneous equilibria to the vapour (e.g., H₂, H₂O, CO, CO₂, CH₄, H₂S, OCS, etc.) and solubility reactions for the species that dissolve in the silicate melt (e.g., OH⁻, H₂O, H₂, CO₃²⁻, CO₂, CO, CH₄, H₂S, SH⁻ etc.). Full generalization of our results to natural systems will require exploring the effects of variations in composition on solubility and speciation (e.g., the composition of the silicate melt, including H₂O and [Fe³⁺/Fe⁺]m) and the P and T dependence of the equilibrium constants for heterogenous silicate melt-vapour equilibria. This is currently of particular importance for the sulfate capacity (C₅⁶⁺), which controls the behaviour of dissolved sulfate and is expected to be strongly influenced by T and melt composition (e.g., Moretti and Ottonello 2005; Nash et al. 2019; O’Neill and Mavrogenes 2019; Boulliung and Wood 2021; Moretti 2021). Although such an expanded treatment will be important and useful in detailed modelling of natural systems, the complexity already present in our simple system – for a single Hawaiian basaltic melt composition in which only S ± O-bearing species are included – highlights in our view the importance of adding complexity (especially in terms of silicate melt and vapour composition) incrementally to such end member systems for understanding the behaviour of sulfur in magmatic systems.

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**Conflict of interest**

The authors declare no known conflicts of interest associated with this publication.

**Author contributions**

ECH, EMS, and LS conceived the project idea. ECH wrote the code with the help of PL. ECH ran the analyses. ECH and EMS led manuscript production, with further contribution from LS and PL.

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Tables

Table 1 Summary of the relationships $[Z \propto (f_{SO_2})^i(Y)^j]$ and slopes between independent $(Y)$ and dependent $(Z)$ variables when $T$ and $f_{O_2}$ are always independent variables for silicate melt + vapour.

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$Y$</th>
<th>$f_{SO_2}$</th>
<th>$w_{ST}$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$f_{S_2}$</td>
<td>$w_{S_2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$a$</td>
<td>$b$</td>
<td>$\zeta$</td>
</tr>
<tr>
<td>Silicate melt $\cong S^{2+}$ and vapour $\cong S^{2}$ (purple)</td>
<td></td>
<td>\textbf{0.0}</td>
<td>\textbf{+1.0}</td>
<td>\textbf{0.0}</td>
</tr>
<tr>
<td>$f_{S_2}$</td>
<td>+1.0</td>
<td>+0.5</td>
<td>+1.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>$f_{SO_2}$</td>
<td>0.0</td>
<td>+1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$P (\cong p_{S_2} \equiv f_{S_2})$</td>
<td>-0.5</td>
<td>+0.5</td>
<td>-0.5</td>
<td>+1.0</td>
</tr>
<tr>
<td>$w_{S_2}$</td>
<td>+1.5</td>
<td>+0.5</td>
<td>+1.5</td>
<td>-3.0</td>
</tr>
<tr>
<td>$w_{S_2}^{m}$</td>
<td>+1.5</td>
<td>+0.5</td>
<td>+1.5</td>
<td>-3.0</td>
</tr>
<tr>
<td>$w_{ST}^{m} (\cong w_{S_2}^{m})$</td>
<td>-0.5</td>
<td>+0.5</td>
<td>-0.5</td>
<td>+1.0</td>
</tr>
</tbody>
</table>

| Silicate melt $\cong S^{2}$ and vapour $\cong SO_2$ (turquoise) | | \textbf{0.0} | \textbf{+1.0} | \textbf{0.0} | \textbf{0.0} | \textbf{+1.0} | \textbf{+2.0} | \textbf{+1.0} | \textbf{-0.5} | \textbf{-2.0} | \textbf{+2.0} | \textbf{-2.0} | \textbf{+1.0} |
| $f_{S_2}$ | +1.0 | +0.5 | +1.0 | -2.0 | +1.5 | +1.0 | +1.5 | -1.5 | \textbf{0.0} | \textbf{+1.0} | \textbf{0.0} | \textbf{+1.0} |
| $f_{SO_2}$ | +1.0 | +0.5 | +1.0 | -2.0 | +1.5 | +1.0 | +1.5 | -1.5 | \textbf{0.0} | \textbf{+1.0} | \textbf{0.0} | \textbf{+1.0} |
| $P (\cong p_{SO_2} \equiv f_{SO_2})$ | -0.5 | +0.5 | -0.5 | +1.0 | 0.0 | +1.0 | 0.0 | 0.0 | -1.5 | +1.0 | -1.5 | +1.5 |
| $w_{S_2}$ | +1.5 | +0.5 | +1.5 | -3.0 | +2.0 | +2.0 | +2.0 | -1.0 | +1.5 | +0.5 | +1.5 | -3.0 |
| $w_{S_2}^{m}$ | +1.5 | +0.5 | +1.5 | -3.0 | +2.0 | +2.0 | +2.0 | -1.0 | +1.5 | +0.5 | +1.5 | -3.0 |
| $w_{ST}^{m} (\cong w_{S_2}^{m})$ | -0.5 | +0.5 | -0.5 | +1.0 | \textbf{0.0} | \textbf{+1.0} | \textbf{0.0} | \textbf{0.0} | -1.5 | +1.0 | -1.5 | +1.5 |

| Silicate melt $\cong S^{6+}$ and vapour $\cong SO_2$ (yellow) | | \textbf{0.0} | \textbf{+1.0} | \textbf{0.0} | \textbf{0.0} | \textbf{-3.0} | \textbf{+2.0} | \textbf{-3.0} | \textbf{+1.5} | \textbf{-2.0} | \textbf{+2.0} | \textbf{-2.0} | \textbf{+1.0} |
| $f_{S_2}$ | +1.0 | +0.5 | +1.0 | -2.0 | -0.5 | +1.0 | -0.5 | +0.5 | 0.0 | +1.0 | 0.0 | +1.0 |
| $f_{SO_2}$ | +1.0 | +0.5 | +1.0 | -2.0 | -0.5 | +1.0 | -0.5 | +0.5 | 0.0 | +1.0 | 0.0 | +1.0 |
| $P (\cong p_{SO_2} \equiv f_{SO_2})$ | -0.5 | +0.5 | -0.5 | +1.0 | 0.0 | +1.0 | 0.0 | 0.0 | -1.5 | +1.0 | -1.5 | +1.5 |
| $w_{S_2}$ | +1.5 | +0.5 | +1.5 | -3.0 | 0.0 | +1.0 | 0.0 | 0.0 | +0.5 | +1.0 | +0.5 | -0.5 |
| $w_{S_2}^{m}$ | +1.5 | +0.5 | +1.5 | -3.0 | 0.0 | +1.0 | 0.0 | 0.0 | +0.5 | +1.0 | +0.5 | -0.5 |
| $w_{ST}^{m} (\cong w_{S_2}^{m})$ | +1.5 | +0.5 | +1.5 | -3.0 | 0.0 | +1.0 | 0.0 | 0.0 | +0.5 | +1.0 | +0.5 | -0.5 |

Notes: Derivations are in the Supplementary Material. The slopes of log$_{10}(Y)$ vs. log$_{10}(Z)$ are given as $\zeta$ when $Y$ is constant (slopes of $Z$-curves in Figure 2) and $\sigma$ when $Y$ varies (slopes of $Z$-contours in Figure 3–Figure 5). $p_i \cong f_i$ because $Y_{i-1} = 1$. **Bold** indicates the independent variable ($Y$). For example, when the silicate melt is $S^{2+}$-dominated and the vapour is $S_2$-dominated in the purple region (first group of $f_{S_2}$-$f_{SO_2}$-$P$-$w_{S_2}$-$w_{S_6}$-$w_{ST}$ horizontally) and $Y = f_{S_2}$ (first group of $a$-$b$-$\zeta$-$\sigma$ vertically), the slope of $w_{ST}$ when $f_{S_2}$ is constant (\zeta) is +1.5 (Figure 2a) and the slope of the contours (\sigma) of $Z = w_{ST}$ are (-0.5)/(0.5) = +1.0 (Figure 3c).
Figure 1 Schematic figures of sulfur in magmatic and volcanic systems. In all panels, silicate melt is shown in pink, vapour in blue, sulfide melt in yellow, and anhydrite in grey. (a) Ternary diagram of the idealised silicate-S₂-O₂ system used in this study, which contains silicate melt and vapour. The vapour is constrained to the S₂-O₂ binary, which includes S₂, O₂, and SO₂ as species. An example tie-line between the composition of the silicate melt and vapour (including the composition of the bulk system) is shown by the black line. Sulfide melt and anhydrite lie outside this ternary. (b) Schematic illustration of the interplay between the different species in the silicate melt, which contains S²⁻, SO₄²⁻, FeO, and FeO₁.₅; vapour, which contains S₂, O₂, and SO₂; sulfide melt, which contains S³⁻; and anhydrite, which contains SO₄²⁻. Phases and species that dominate under reducing conditions are to the left, whilst those that dominate under oxidising conditions are to the right. Two-way arrows indicate species that can interact within, and between different, phases. (c) Illustration showing the involvement of sulfur in different magmatic and volcanic processes. In detail, the process and techniques influenced by the sulfur solubility minimum (SS^min, left) and maximum (SS^max, right) are highlighted from “Implications of SS min and SS max for magmatic and volcanic processes”. SS^min, where silicate melt + vapour are stable, effects the gas release from magma mixing and crustal assimilation (“Magma mixing and crustal assimilation”), degassing depth (“Magma ascent and degassing”), and the fO₂ of surface gas emissions (“Magma ascent and degassing”), as well as causing P^sat to be underestimated (“Magma ascent and degassing”) and affecting the reliability of the petrologic method (“Volcanic emissions”). SS^max, where silicate melt + vapour + sulfide melt + anhydrite are stable, sets the maximum S content of partial mantle melts (“Mantle melting”) and is a common feature of large SO₂ emissions from explosive eruptions (“Volcanic emissions”). It also effects the reliability of the petrologic method (“Volcanic emissions”) and can be utilised as an oxybarometer from w^mST measurements (“Using w^mST as an oxybarometer”). Abbreviations: sil⁰, silicate melt; v, vapour; sulf⁰, sulfide melt; anh, anhydrite; P^sat, pressure of vapour-saturation; fO₂, oxygen fugacity; w^mST, total dissolved S content of the silicate melt.

Figure 2 Different dependent variables (Z) versus oxygen fugacity (fO₂) relative to the Fayalite-Magnetite-Quartz (FMQ) buffer (shown as ΔFMQ) for silicate melt + vapour: (a, c, e) concentration of dissolved S-bearing species in the silicate melt (w^im), where i = total sulfur (S⁰, white solid), sulfide (S²⁻, black dot), or sulfate (S⁶⁺, black dash); and (b, d, f) pressure (P, white solid) or partial pressure (p), where i = sulfur (S₂, black dot), sulfur dioxide (SO₂, black dash), or oxygen (O₂, black dot dash). In each column a different independent variable (Y) is fixed (indicated by the horizontal line in either the top or bottom row): (a–b) fS₂ = 10⁴↑ bar; (c–d) w^mST = 400 ppm; and (e–f) P = 1 bar. The background colour indicates the S speciation of the silicate melt and vapour, where boundaries are defined at [S⁶⁺/S⁰]^m = 0.1 and 0.9 ([S²⁻]^m < 0.1, [S²⁻]+S⁶⁺)^m where 0.1 ≤ [S⁶⁺/S⁰]^m ≤ 0.9, and [S⁶⁺]^m where [S⁶⁺/S⁰]^m > 0.9) and x^SO₂ = 0.1 or 0.9 ([S²⁻]^m where x^SO₂ < 0.1, [S₂+SO₂]^v where 0.1 ≤ x^SO₂ ≤ 0.9, or [SO₂]^v where x^SO₂ > 0.9): purple = [S²⁻]^m+[S₉²]; blue = [S²⁻]^m+[S₂+SO₂]^v; turquoise = [S²⁻]^m+[SO₂]^v; green = [S²⁺+S⁶⁺]^m+[SO₂]^v; and yellow = [S⁶⁺]^m+[SO₂]^v. The vertical grey lines show where sulfide melt (solid) or anhydrite (dashed) would saturate. Slopes (ζ) are labelled in boxes outlined in black. α (in panels b, d, and f) indicates when pO₂ = pS₂, and β in panel (d) indicates a change in slope of P from ζ = +1 to +1.5 with increasing fO₂. Note that to the right of α in (b) that γS₂ = 2.14 at P = 4507 bar, causing pS₂ to deviate noticeably from fS₂, just visible as the slight downturn in the black dotted curve at high fO₂. Abbreviations: sil⁰, silicate melt; v, vapour; sulf⁰, sulfide melt; and anh, anhydrite.
Figure 3 Sulfur fugacity ($Y = f_{S2}$) versus oxygen fugacity ($f_{O2}$) for silicate melt + vapour at $T = 1200 \, ^\circ\text{C}$. Contours of $Z$ are shown for: (a) sulfur dioxide fugacity ($f_{SO2}$); (b) pressure ($P$), and (c) total S content of the silicate melt ($w_{ST}^{\text{sil}}$). (d) Sulfur speciation of the vapour ($S_2$ and/or $SO_2$) and silicate melt ($S^{2-}$ and/or $S^{6+}$), where boundaries are defined for the vapour at $x_{SO2} = 0.1$ or $0.9$ (black dashed curves) and for the silicate melt at $[S^{6+/S1}]^m = 0.1$ and $0.9$ (black solid curves): purple = $[S^{2-}]^m + [S^{2+}]^v$; blue = $[S^{2-}]^m + [S^{2+} + SO_2]^v$; turquoise = $[S^{2-}]^m + [SO_2]^v$; green = $[S^{2-} + S^{6+}]^m + [SO_2]^v$; yellow = $[S^{6+}]^m + [SO_2]^v$. (as in Figure 2, although the light turquoise section was not previously intersected). (e) Paths followed in $f_{O2}$-$f_{S2}$ space for different processes (overlain on contours of $Z = w_{ST}^{\text{sil}}$): dark turquoise is constant $f_{S2} = 10^{-4}$ bar (Figure 2a–b); purple is constant $w_{ST}^{\text{sil}} = 400$ ppm (Figure 2c–d); blue is constant $P = 1$ bar (Figure 2e–f); yellow, green, and light turquoise are constant bulk $O_2 = 3.26, 3.87, and 4.23 \, \text{wt}\%$, respectively (Figure 8); and grey is constant $\mu_{FeS}$ and/or $\mu_{CaSO_4}$ equal to sulfide melt- and anhydrite-saturation, respectively (Figure 6a–b). In the white region at very low and very high $f_{O2}$ and high $f_{S2}$, $w_{ST}^{\text{sil}} > 10 \, \text{wt}\%$ and hence calculations are terminated. The value of the slopes of the curves and contours ($\sigma$) are labelled in boxes with a thick black outline. The grey curve indicates the boundary above which silicate melt + vapour is metastable, which is solid when sulfide melt would saturate, dashed when anhydrite would saturate, and the grey star indicates the silicate melt is multiply-saturated with vapour, sulfide melt, and anhydrite. The $f_{O2}$ for different tectonic settings from Cottrell et al. (2021) is shown by horizontal blue bars (extent of the bar shows the range and black vertical line shows the mode) for mid-ocean ridge (light blue), ocean island (intermediate blue), and arc (dark blue) basalts. Abbreviations: $sil^m$, silicate melt; $v$, vapour; $sulf^m$, sulfide melt; $anh$, anhydrite; MORB, mid-ocean ridge basalts; OIB, ocean island basalts; and Arc, arc basalts.

Figure 4 Total S content of the silicate melt ($Y = w_{ST}^{\text{sil}}$) versus oxygen fugacity ($f_{O2}$) for silicate melt + vapour at $T = 1200 \, ^\circ\text{C}$. Contours of $Z$ are shown for: (a) sulfur fugacity ($f_{S2}$); (b) sulfur dioxide fugacity ($f_{SO2}$); and (c) pressure ($P$). (d) Sulfur speciation of the silicate melt and vapour. (e) Paths followed in $f_{O2}$-$f_{S2}$ space for different processes (overlain on contours of $Z = P$). See Figure 3 for details of the coloured regions, different curves, annotations, abbreviations, and $f_{O2}$ ranges. Note: anhydrite is not stable at these $w_{ST}^{\text{sil}}$ and therefore $anh$ does not appear.

Figure 5 Pressure ($Y = P$) versus oxygen fugacity ($f_{O2}$) at $T = 1200 \, ^\circ\text{C}$ for (a–e) silicate melt + vapour and (f–g) silicate melt + (vapour and/or sulfide melt and/or anhydrite) (indicated using *). Contours of $Z$ are shown for: (a) sulfur fugacity ($f_{S2}$); (b) sulfur dioxide fugacity ($f_{SO2}$); and (c, g) total S content of the silicate melt ($w_{ST}^{\text{sil}}$). (d, f) Sulfur speciation of the silicate melt and vapour. In the vapour-undersaturated region of (f): dark grey indicates $S^{2-}$-dominated silicate melt + sulfide melt; medium grey indicated silicate melt (both $S^{2-}$ and $S^{6+}$ in similar concentrations) and sulfide melt; and light grey indicates $S^{6+}$-dominated silicate melt + anhydrite. (e, g) Paths followed in $f_{O2}$-$f_{S2}$ space for different processes (overlain on contours of $Z = w_{ST}^{\text{sil}}$). In the white region at high $f_{O2}$ and low $P$, calculations are unfeasible as $x_{SO2} > 1$. See Figure 3 for details of the coloured regions, different curves, annotations, abbreviations, and $f_{O2}$ ranges. Note: the blue horizontal dotted and dashed lines in (g) are the $P = 200$ and $2000 \, \text{bar}$, respectively, slices shown in Figure 6c–f. 

Figure 6 (a, c, e) Total S content of the silicate melt ($w_{ST}^{\text{sil}}$) and (b, d, f) pressure ($P$) versus oxygen fugacity ($f_{O2}$) against at $T = 1200 \, ^\circ\text{C}$. When the silicate melt is vapour-saturated, the background is coloured (no vapour is present in the white regions) and the silicate melt and vapour speciation are shown by the background colour (see Figure 3 for details). Grey or black solid curves indicate sulfide melt-saturation and dashed curves indicate anhydrite-saturation. (a–b) Silicate melt +

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f (sulfide melt and/or anhydrite) with independent variables of $T$, $fO_2$, and $\mu_{FeS}$ and/or $\mu_{CaSO_4}$. At the grey star, both sulfide melt and anhydrite are saturated; hence, both $\mu_{FeS}$ and $\mu_{CaSO_4}$ are specified and $fO_2$ is no longer independent. The white horizontal lines and annotations ($\alpha$, $\beta$, and $\gamma$) are for the melt inclusion example containing 400 (solid), 3000 (dash), and 13000 (dot) ppm $ST$ described in “Using $wmST$ as an oxybarometer”. (c–d) Vapour-undersaturated silicate melt + (sulfide melt and/or anhydrite) with independent variables of $T$, $fO_2$, $P$, and $\mu_{FeS}$ and/or $\mu_{CaSO_4}$; when both $\mu_{FeS}$ and $\mu_{CaSO_4}$ are specified, $fO_2$ or $P$ is no longer independent. Silicate melt speciation is indicated by the green vertical lines ($[S^{6+}/S_T]^{m} = 0.1$ or 0.9); $[S^{2-}]^{m}$ at low $fO_2$. $[S^{2+}+S^{6+}]^{m}$ at intermediate $fO_2$, and $[S^{6+}]^{m}$ at high $fO_2$. At the vertical grey line, both sulfide melt and anhydrite are saturated. (e–f) Silicate melt + (vapour and/or sulfide melt and/or anhydrite) with independent variables of $T$, $fO_2$, $P$, and $\mu_{FeS}$ and/or $\mu_{CaSO_4}$; when both $\mu_{FeS}$ and $\mu_{CaSO_4}$ are specified, $fO_2$ or $P$ is no longer independent. The green vertical line indicates the boundary between $[S^{2-}]^{m}$ (lower $fO_2$) and $[S^{2+}+S^{6+}]^{m}$ (higher $fO_2$) when vapour is not present ($[S^{6+}/S_T]^{m} = 0.1$). At the solid grey vertical line, sulfide melt + vapour are saturated; along the dotted segment, vapour is saturated; and at the dashed grey vertical line, vapour + anhydrite are saturated. Annotations ($\delta$, $\epsilon$, and $\zeta$) indicate maxima and minima described in “Silicate melt + (vapour and/or sulfide melt and/or anhydrite)”. $fO_2$ ranges are shown as described in Figure 3. Abbreviations: $sil^m$, silicate melt; $v$, vapour; $sulf^m$, sulfide melt; $anh$, anhydrite; MORB, mid-ocean ridge basalts; OIB, ocean island basalts; and Arc, arc basalts.

**Figure 7** Closed-system degassing: pressure ($P$) versus bulk $O_2$ content of the system for silicate melt + vapour at $T = 1200$ °C with a bulk S content of 5000 ppm. Contours of $Z$ are shown for: (a) sulfur fugacity ($f_{S_2}$); (b) sulfur dioxide fugacity ($f_{SO_2}$); (c) total S content dissolved in the silicate melt ($w^{m}_{ST}$); (d) oxygen fugacity ($f_{O_2}$); (e) total vapour content of the system ($w^{v}_{T}$) – this includes both S and O in the vapour and hence can exceed 0.5 wt%. (f) Sulfur speciation of the silicate melt and vapour. (g) Paths followed in $P$-bulk O2 space for closed-system degassing and the white circle and square connected by a black-long dashed-horizontal line is the mixing example described in “Magma mixing and crustal assimilation” (overlain on contours of $Z = w^{m}_{ST}$). The solid black curve is equal to the 5000 ppm $w^{m}_{ST}$ contour and $P^s_{sat}$, and $SS^m_{min}fO_2$ is indicated by a white diamond. The bulk $O_2$ ranges shown below each figure correspond to the $fO_2$ by tectonic setting bars in other figures at $P^s_{sat}$. See Figure 3 for details of the coloured regions, different curves, annotations, and abbreviations. Note: anhydrite is not stable at these conditions and therefore $anh$ does not appear.

**Figure 8** Closed (solid) and open (black dash) -system depressurisation paths for silicate melt + vapour at $T = 1200$ °C: (a) sulfur fugacity ($f_{S_2}$); (b) oxygen fugacity ($f_{O_2}$); and (c) total S content dissolved in the silicate melt ($w^{m}_{ST}$). Three initial bulk compositions are used, as shown on Figure 7g: 3.26 (yellow), 3.87 (green), and 4.23 (turquoise) wt% O2.

**Figure 9** Pressure of vapour-saturation ($P^s_{sat}$) versus oxygen fugacity ($f_{O_2}$) for a Hawaiian basaltic melt + vapour at 1200 °C containing different $w^{m}_{ST}$: 400 (solid), 2000 (dash), and 5000 (dot) ppm. The background colour indicates the speciation of the silicate melt and vapour and the bars indicate $fO_2$ of different tectonic settings (see Figure 3 for details).
Figures

Figure 1

(a) Diagram of the system showing the relationship between silicate melt, silicate melt, bulk system, vapor, sulfide melt, and anhydrite. The triangle represents the composition of the system with S₂, SO₂, and O₂ as the axes.

(b) Diagram showing the transition between reduced and oxidized states of S₂, SO₂, and FeO ↔ FeO₁.₅. The symbols indicate the presence of sulfide melt (sulf°) and anhydrite (anh).

(c) Diagram illustrating the sulfur solubility showing minimum and maximum conditions. The reliability of the petrologic method is discussed with large SO₂ emissions during explosive eruptions. The fO₂ of surface emissions and degassing depth are also shown. The gas release from magma mixing/crustal assimilation and S content of partial mantle melts are highlighted.
Figure 2

Y = f_{SO}_2 = 10^{-4} \text{ bar}

Y = w_{SO}_2 = 400 \text{ ppm}

Y = P = 1 \text{ bar}

Figure 3

(a) $\log_{10}[Z = f_{SO}_2, \text{ bar}]

(b) $\log_{10}[Z = P, \text{ bar}]

(c) $\log_{10}[Z = w_{SO}_2, \text{ ppm}]

Figure 4

sulfur speciation

paths of constant

closed-system degassing paths
Figure 4

(a) $\log_{10}[Z = f_{S_2}, \text{bar}]$

(b) $\log_{10}[Z = f_{SO_2}, \text{bar}]$

(c) $\log_{10}[Z = P, \text{bar}]$

(d) sulfur speciation

- $[S^{II}]^+[S]^{II}$
- $[S^{III}]^+[S_2+SO_2]^I$
- $[S^{IV}]^+[SO_4]^{II}$
- $[S^{VI}]^++[SO_2]^{IV}$
- $[S^{VIII}]^++[S_2+SO_2]^{V}$

- $\chi^{SO_2} = 0.1 \text{ or } 0.9$
- $[S^{II}]/S_2^{II} = 0.1 \text{ or } 0.9$

- $\text{closed-system degassing paths}$
  - $O_2 = 3.25 \text{ wt\%}$
  - $O_2 = 3.87 \text{ wt\%}$
  - $O_2 = 4.23 \text{ wt\%}$

(e) paths ($\log_{10}[Z = P, \text{bar}]$)
Figure 6

Vapour-saturated

\[ Y = \mu_{FeS} \text{ and/or } \mu_{CaSO_4} \]

Vapour-undersaturated

\[ Y = \mu_{FeS} \text{ and/or } \mu_{CaSO_4}, P = 2000 \text{ bar} \]

Vapour

\[ Y = \mu_{FeS} \text{ and/or } \mu_{CaSO_4}, P = 200 \text{ bar} \]

- \[ f_{o_2} \text{ by tectonic setting} \]

- MORB

- OIB

- Arc

Vapour-saturated

- \([S^{2-}]^{+}+[S_2]^{2+}\]
- \([S^{2-}]^{+}+[S_2+SO_3]^{2+}\]
- \([S^{2-}]^{+}+[SO_3]^{2-}\]
- \([S^{2-}]^{+}+[SO_4]^{2-}\]

- \([S^{2-}]^{+}+[S_2+SO_3]^{2+}\]
- \([S^{2-}]^{+}+[SO_3]^{2-}\]
- \([S^{2-}]^{+}+[SO_4]^{2-}\]

- \([S^{2-}]^{+}+[S_2+SO_3]^{2+}\]
- \([S^{2-}]^{+}+[SO_3]^{2-}\]
- \([S^{2-}]^{+}+[SO_4]^{2-}\]

\[ f_{o_2} \text{ from } w_{s}^{ST} \]

\[ \text{multiply-saturated as labelled} \]

Vapour-undersaturated

- \([S^{2-}]^{+}+(\text{silf} \text{ and/or anh})\]
- \([S^{2-}]^{+}+(\text{silf} \text{ and/or anh}) \approx 0.1 \text{ or } 0.9\]
- \([S^{2-}]^{+}+(\text{silf} \text{ and/or anh}) \approx 0.9\]

- \([S^{2-}]^{+}+(\text{silf} \text{ and/or anh}) \approx 0.9\]

- \([S^{2-}]^{+}+(\text{silf} \text{ and/or anh}) \approx 0.9\]
Figure 8

Figure 9