The effects of oxygen fugacity and sulfur on the pressure of vapor-saturation of magma

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Abstract

Geobarometers are commonly used to determine the pressure (and hence depth) of magmatic bodies. For instance, at equilibrium, the concentration of dissolved volatiles in a vapor-saturated melt can be used as a barometer: this is the pressure of vapor-saturation ($P_{\text{sat}}^v$). Most determinations of $P_{\text{sat}}^v$ assume that melt and vapor contain only oxidised C-O-H species. However, sulfur is the third most abundant volatile element in magmas and oxygen fugacity ($f_{O2}$) exerts a strong influence on the speciation of the melt and vapor. To explore how S and $f_{O2}$ affect calculations of $P_{\text{sat}}^v$, we model a Hawaiian tholeiite that contains both reduced and oxidised C-O-H-S species in the melt and vapor. We find that excluding reduced C-O-H species in the system can result in significant underestimations of $P_{\text{sat}}^v$ under reducing conditions ($\Delta FMQ < 0$). The
effect of S on $P_{\text{sat}}^v$ is small except in the vicinity of the “sulfur solubility minimum” ($SS_{\text{min}}^\text{SS} < 0 < \Delta \text{FMQ} < +2$), where excluding S-bearing species can result in underestimates of $P_{\text{sat}}^v$.

The implications of these results depend on the volatile concentration of the system being investigated, its $f_{O_2}$, and the melt composition and temperature. Our results suggest there will be little impact on $P_{\text{sat}}^v$ calculated for mid-ocean ridge basalts because their $f_{O_2}$ is above where reduced C-O-H species become important in the melt and vapor, and yet below the SS$_{\text{min}}$.

However, the $f_{O_2}$ of ocean island and arc basalts are close enough to the SS$_{\text{min}}$ and their S concentrations high enough to influence $P_{\text{sat}}^v$. However, high CO$_2$ and H$_2$O concentrations are predicted to reduce the effect of the SS$_{\text{min}}$. Hence, $P_{\text{sat}}^v$ calculated for shallowly trapped melt inclusions and matrix glass are more affected by the SS$_{\text{min}}$ than deeply trapped melt inclusions. Lunar and martian magmas are typically more reduced than terrestrial magmas, and therefore accurate $P_{\text{sat}}^v$ calculations for them require the inclusion of reduced C-O-H species.

**Keywords:** pressure of vapor saturation, thermodynamics, oxygen fugacity, carbon, hydrogen, sulfur

1 **Introduction**

The concentrations of dissolved volatiles (e.g., H$_2$O, CO$_2$) in the melt phase of magma are widely used to determine total pressure ($P$) (e.g., Anderson et al. 1989; Blundy and Cashman 2008). Such determinations are based on analyses of volatile components in quenched glasses coupled with the assumption that the melt from which the glass formed was in equilibrium with a

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vapor prior to quenching. The basis of this approach is that for a given temperature ($T$) and assumed value of $P$, the partial pressure of each species in vapor ($p_i$) coexisting with melt can be calculated from the concentrations of volatile components dissolved in the melt. The pressure of vapor-saturation of the melt ($P_{\text{sat}}^v$) is then the unique $P$ at which the sum of all the $p_i$'s matches the total $P$.

This approach to determining $P_{\text{sat}}^v$ for magmas has been widely applied to melt inclusions and matrix glasses, subject to several caveats (e.g., issues related to the fidelity with which glassy melt inclusions preserve the volatile concentrations present at the time of their entrapment: Anderson 1974; Roedder 1979; Anderson and Brown 1993; Portnyagin et al. 2008; Steele-Macinnis et al. 2011; Gaetani et al. 2012; Bucholz et al. 2013; Maclennan 2017; and the possibility of supersaturation of erupting melts with respect to vapor: Fine and Stolper 1986; Dixon et al. 1988; Jendrzejewski et al. 1997; Saal et al. 2002; Soule et al. 2012; Le Voyer et al. 2015, 2019; Aubaud 2022). For melt inclusions, this approach has led to many minimum estimates of the $P$ (and therefore depth) of inclusion entrapment (e.g., Anderson Jr et al. 1989; Blundy and Cashman 2008), and such estimates have also been used to “image” magmatic plumbing systems (e.g., Colman et al. 2015; Wanless et al. 2015; Camejo-Harry et al. 2018, 2019; Black and Andrews 2020; Wieser et al. 2021). When applied to sub-aqueously erupted matrix glass, it has been used to estimate eruption depths (e.g., Seaman et al. 2004; Coombs et al. 2006; Lund et al. 2018; Belgrano et al. 2021). This approach also returns the composition of the vapor phase in equilibrium with the melt at $P_{\text{sat}}^v$. This vapor composition can be used to understand whether the melt has undergone closed- or open-system degassing or has been buffered by a large volume of fluid (e.g., Spilliaert et al. 2006; Caricchi et al. 2018; Moretti et al. 2018). The vapor composition can also be used to reconstruct bulk melt inclusion compositions.
at entrapment if a “shrinkage” vapor bubble has developed during cooling, provided that $P_{v\text{sat}}$ and
the corresponding vapor composition are calculated at the closure $T$ of bubble formation (e.g.,
Maclennan 2017; Tucker et al. 2019; Rasmussen et al. 2020).

Most efforts to calculate $P_{v\text{sat}}$ using this approach have assumed that the vapor contains only
H$_2$O and CO$_2$ and the melt only contains H as hydroxyl ions (OH$^-$) and/or H$_2$O molecules
(H$_2$O$_{\text{mol}}$), and C as carbonate ions (CO$_3^{2-}$) and/or CO$_2$ molecules (CO$_2_{\text{mol}}$) (e.g.,
VolatileCalc/MIMiC by Newman and Lowenstern, 2002; Rasmussen et al., 2020; MagmaSat by
Ghiorso and Gualda, 2015; VESIcal by Iacovino et al., 2021; EVo by Liggins et al. 2020, 2022;
Yip et al. 2022; MafiCH by Allison et al., 2022; and various unnamed models such as those
presented by Papale et al. 2006; Iacono-Marziano et al. 2012; and Duan 2014). These
calculations do not generally consider the effects on $P_{v\text{sat}}$ and the corresponding vapor
composition of the presence of reduced C-O-H (e.g., H$_2$, CO, CH$_4$) and S-bearing species in the
vapor and melt. However, oxygen fugacity ($f_{O_2}$) can play a significant role in the speciation and
abundances of C-O-H-S volatile components in coexisting vapor and melt, and S is the third
most abundant volatile element in most naturally occurring silicate magmas (e.g., Holloway and
Blank 1994). Some studies have considered the importance of S and/or the effects of $f_{O_2}$ during
degassing (e.g., Carroll and Webster 1994; Moretti and Papale 2004; Scaillet and Pichavant
2004; Kress et al. 2004; Gaillard et al. 2011; Burgisser et al. 2015; Wetzel et al. 2015; Lesne et
al. 2015; Newcombe et al. 2017a; Liggins et al. 2020, 2022; Lo et al. 2021; Métrich 2021; Sun
and Lee 2022; Wieser et al. 2022; Hughes et al. 2023). However, there has to our knowledge not
yet been a systematic or quantitative investigation of these effects on calculations of $P_{v\text{sat}}$.

We are particularly interested in the effects of the so-called “sulfur solubility minimum”
(referred to here as the SS$^{\text{min}}$ – see Hughes et al., 2023) on calculated values of $P_{v\text{sat}}$ and vapor
composition. The SS$^{\text{min}}$ corresponds to a minimum in the dissolved sulfur content of vapor-saturated melt with increasing $f_{O_2}$ at constant $P$ and $T$ in the $f_{O_2}$ range over which the speciation of S dissolved in the melt changes from S$^{2-}$- to S$^{6+}$-dominated. This phenomenon for melt + vapor equilibrium has been observed experimentally (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) and in various calculations (e.g., Fincham and Richardson 1954; Katsura and Nagashima 1974; Carroll and Rutherford 1985; Moretti et al. 2003; Moretti and Ottonello 2005; Backnaes and Deubener 2011; Baker and Moretti 2011; Lesne et al. 2015; Matjuschkin et al. 2016; Nash et al. 2019; Cicconi et al. 2020; Papale et al. 2022; Hughes et al. 2023). Hughes et al. (2023) used a simplified S-O system (i.e., without C-O-H species) to analyse the factors leading to the SS$^{\text{min}}$. They found the SS$^{\text{min}}$ resulted in a maximum in $P_{v_{\text{sat}}}$ with increasing $f_{O_2}$ at constant $T$ and total S-content of the melt due to a maximum in $p_{SO_2}$ where the speciation of S in the melt changed from S$^{2-}$- to S$^{6+}$-dominated. If this $f_{O_2}$-dependent maximum in $P_{v_{\text{sat}}}$ extends to C-O-H-S-bearing systems, magma reservoir depths from melt inclusions and eruption pressures from matrix glasses based on calculations of $P_{v_{\text{sat}}}$ that exclude S will be underestimated for magmas with $f_{O_2}$ values in the vicinity of the SS$^{\text{min}}$. Hence, it is important to understand quantitatively the behaviour of the SS$^{\text{min}}$ in C-O-H-S systems most relevant to natural magmas.

In this paper, we extend the thermodynamic framework of Hughes et al. (2023) to include C-O-H-S vapor and melt species (Section 2), and we apply it to calculating $P_{v_{\text{sat}}}$. The model we use is most closely related to those of Gaillard et al. (2011, 2013), Baumgartner et al. (2017), Iacono-Marziano et al. (2017), Liggins et al. (2020, 2022), and Sun and Lee (2022). Our model is written in Python, can be run using Jupyter Notebook, and is available on github
(https://github.com/eryhughes/Pvsat). Given this thermodynamic model, we explore predicted trends in $P_{\text{sat}}^v$ with varying $f_{O_2}$ for a fixed volatile concentration in the melt (Section 3.1). We then explore: (1) how variations in the total amounts of H, C, and S dissolved in the melt influence the calculated value of $P_{\text{sat}}^v$ (Section 3.2), especially the calculated effects of the predicted build-up of relatively insoluble C-O-H species at low $f_{O_2}$ (Section 3.2.1); and (2) the behavior of the SS$_{\text{min}}$ in C- and H-bearing systems and the quantitative impact of this feature on calculated values on $P_{\text{sat}}^v$ (Section 3.2.2). Finally, we apply the model to natural melt inclusions and matrix glasses from different tectonic settings on Earth, as well as lunar and martian magmas, to evaluate how calculated values of $P_{\text{sat}}^v$ are influenced by these effects (Section 4).

2 Calculating the pressure of vapor-saturation and the vapor composition

Our goal is to calculate $P_{\text{sat}}^v$, the $P$ at which a silicate melt of a fixed chemical composition (including the concentrations of dissolved volatile components in the melt) can coexist with vapor at a given $T$ and $f_{O_2}$. At this $P$, the sum of the $p_i$'s of all species in the vapor ($n$ different species, where each species is denoted with subscript $i$) in equilibrium with the melt equals the $P$ of the system:

$$P = \sum_{i=1}^{n} p_i , #(1)$$

and the mole fraction of each species in the vapor ($x_i^v$) is related to its $p_i$ by:

$$p_i = \frac{f_i}{Y_i} = x_i^v P , #(2)$$
where \( f_i \) is the fugacity of species \( i \), and \( \gamma_i \) is the fugacity coefficient of species \( i \) in the vapor (v). Determining \( P^v_{\text{sat}} \) requires finding the \( P \) that is equal to the sum of the \( p_i \)'s of all molecular species in the vapor: i.e., solving equation (1). At a higher \( P \) than \( P^v_{\text{sat}} \), the system is vapor-undersaturated. Hence, these calculations assume the melt is saturated with a vapor – if the melt is not vapor-saturated, the calculated \( P \) represents a minimum. At a lower \( P \) than \( P^v_{\text{sat}} \), melt with the assumed concentrations of volatiles is supersaturated with respect to vapor and the melt is metastable (or potentially unstable if sufficiently supersaturated; e.g., Allabar and Nowak 2018; Sahagian and Carley 2020; Gardner et al. 2022). Given sufficient time, a vapor phase will exsolve from the supersaturated melt, reducing the volatile concentration of the melt such that equilibrium is achieved (i.e., such that equation (1) is satisfied at the fixed \( P, T \), and bulk composition of the system). Calculating \( P^v_{\text{sat}} \) for a given melt composition requires choosing: (1) the species in the vapor that will contribute significantly to the total \( P \) and the homogenous vapor equilibria that relate them (Section 2.1); and (2) solubility functions that provide relationships between the melt composition and the \( p_i \)'s (Section 2.2).

2.1 Species and homogeneous equilibria in the vapor

If H\(_2\)O and CO\(_2\) are assumed to be the only vapor species, as is typical (see Section 1), equation (1) becomes:

\[
P = \sum_{i=1}^{2} p_i = p_{\text{H}_2\text{O}} + p_{\text{CO}_2}.
\]  

(3)
A review of solubility models used to relate dissolved H$_2$O and CO$_2$ concentrations in the melt to $p_{H_2O}$ and $p_{CO_2}$ is provided by Iacovino et al. (2021), which can be used to calculate $P_{v_{sat}}$ via equation (3). However, to investigate the effects of $f_{O_2}$ and S, we need to consider a C-O-H-S vapor containing species in addition to those in equation (3). Although other species could be added, we have considered the following vapor species: O$_2$, H$_2$, H$_2$O, CO, CO$_2$, S$_2$, SO$_2$, H$_2$S, CH$_4$, and OCS, such that equation (1) becomes:

$$P = \sum_{i=1}^{10} p_i = p_{O_2} + p_{H_2} + p_{H_2O} + p_{CO} + p_{CO_2} + p_{S_2} + p_{SO_2} + p_{CH_4} + p_{H_2S} + p_{OCS}. \ (4)$$

The fugacities of these vapor species are related through the six linearly-independent homogenous vapor equilibria given in Table 1. Details of our choice of equilibrium constants and fugacity coefficients for vapor species are given in Supplementary Material Section 3.1.

2.2 Solubility functions

When melt and vapor are in equilibrium, there is a function (the “solubility function”) that relates the dissolved concentration in the melt of a volatile component to the partial pressure(s) of one (or more) species in the vapor. We use known or likely solubility mechanisms (i.e., chemical reactions between vapor and melt) to constrain the functional forms of the various solubility functions (e.g., Fincham and Richardson 1954; Stolper 1982a; Silver and Stolper 1985; Dixon and Stolper 1995; Gaillard et al. 2011, 2013; Liggins et al. 2020, 2022; Thomas and Wood 2021; Hughes et al. 2023). The key point is that an accurate solubility function allows
calculation of the fugacities of certain vapor species given volatile concentrations in coexisting melt, from which their $p_i$'s can be calculated using equation (2).

Based on our chosen vapor species (Section 2.1) and the assumption of a basaltic melt, we consider the following dissolved C-O-H species in the melt: molecular H$_2$ (H$_2$$_{mol}$; e.g., Gaillard et al. 2003; Kadik et al. 2004; Mysen et al. 2011; Hirschmann et al. 2012), hydroxyl ions (OH$^-$; e.g., Burnham and Davis 1974; Mysen et al. 1980; Stolper 1982a), molecular H$_2$O (H$_2$O$_{mol}$; e.g., Stolper 1982a; Dixon and Stolper 1995; Lesne et al. 2011), molecular CO (CO$_{mol}$; e.g., Brooker et al. 1999; Armstrong et al. 2015; Yoshioka et al. 2019), carbonate ions (CO$_3^{2-}$; e.g., Stolper and Holloway 1988; Blank and Brooker 1994; Dixon et al. 1995), and molecular CH$_4$ (CH$_4$$_{mol}$; e.g., Ardia et al. 2013; Mysen 2013). For dissolved S, we assume sulfide ions (*S$_2^-$, where * refers to sulfide complexes in the melt other than H$_2$S), sulfate ions (SO$_4^{2-}$), and molecular H$_2$S (H$_2$S$_{mol}$) are the dominant S-bearing species in the melt (e.g., Fincham and Richardson 1954; Paris et al. 2001; O’Neill and Mavrogenes 2002, 2022; Clemente et al. 2004; Métrich et al. 2009; Wilke et al. 2011; Klimm et al. 2012; Lesne et al. 2015; O’Neill 2021; Boulliung and Wood 2022). Although other S-bearing species have been observed spectroscopically, they are not thought to be significant in natural Fe-bearing melts (e.g., Métrich et al. 2009; Wilke et al. 2011). For each dissolved species in the melt, the corresponding solubility mechanism (heterogeneous melt-vapor equilibrium) is given in Table 2.

The solubility of a particular volatile species can depend on $P$, $T$, melt composition, and the presence of other volatile species. To illustrate our approach and the trends that it predicts, we have chosen solubility functions appropriate for a Hawaiian tholeiite (detailed in Table 2). However, other solubility functions can be incorporated into our framework (see Supplementary Material Section 3.2 for details) and we emphasize that tailored solubility functions for specific
melt compositions are required if the goal is detailed petrologic interpretations of particular samples. For $H_{2,mol}$, we use the solubility function of Hirschmann et al. (2012) for basalt but modify it to relate $H_{2,mol}$ in ppm to $f_{\text{H}_2}$ in bar (equation (11) in Table 2; see Supplementary Material Section 3.2.3 for details). For the solubility of $H_2O$, we use the approximation of Sievert’s law; i.e., that $f_{\text{H}_2O}$ is proportional to the square of the mole fraction or concentration of the total H dissolved as oxidised species (i.e., combination of $OH^-$ and $H_2O_{\text{mol}}$, expressed as $H_2O: H_2O_T$; see equation (12) in Table 2); this has been shown to be a good approximation up to $\lesssim 6.4$ wt% $H_2O$ (e.g., Burnham 1979; Stolper 1982b; Ghiorso and Gualda 2015). We use the data compilation of Allison et al. (2019) to calibrate this solubility function for basaltic melts (see Supplementary Material Section 3.2.2 for details). For $CO_{\text{mol}}$, we reparameterise the solubility function of Armstrong et al. (2015) (equation (13) in Table 2) using data from Wetzel et al. (2013), Stanley et al. (2014), and Armstrong et al. (2015) (see Supplementary Material Section 3.2.3 for details). The solubility of $CO_3^{2-}$ is highly dependent on melt composition (e.g., Spera and Bergman 1980; Blank and Brooker 1994; Holloway and Blank 1994; Shishkina et al. 2014; Allison et al. 2019). We use the solubility function of Dixon et al. (1995) (equation (14) in Table 2), which is based on data for Hawaiian tholeiites and MOR basalts, although this can be modified for other basaltic compositions (e.g., data from Allison et al. (2019); see Supplementary Material Section 3.2.1 for details). For $CH_4_{\text{mol}}$, we use the solubility function of Ardia et al. (2013) (equation (15) in Table 2). We use O’Neill (2021) for the *$S^{2-}$* solubility function and O’Neill and Mavrogenes (2022) for $SO_4^{2-}$ (equation (16) and (17), respectively, in Table 2). We reparameterise a solubility function for $H_2S_{\text{mol}}$ from Clemente et al. (2004) and Lesne et al. (2015) (equation (18) in Table 2) using basaltic data from Moune et al. (2009) and Lesne et al. (2015) (see Supplementary Material Section 3.2.5 for details). We include $H_2S_{\text{mol}}$ as
a separate species because it is simpler to ensure (compared to its inclusion as another \( \text{S}^{2-} \)

species; see, O’Neill 2021) that H mass balance is satisfied (i.e., H in the melt is partitioned

between \( \text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2, \) and \( \text{CH}_4 \) species) and thus that we do not overestimate the S content of

the melt.

In addition to the solubility functions, our thermodynamic model includes homogeneous

equilibrium between \( \text{Fe}^{2+} \) (FeO) and \( \text{Fe}^{3+} \) (FeO\(_{1.5}\)) in the melt, where melt \( \text{Fe}^{3+}/\text{Fe}^{2+} \) is related to

\( f_{\text{O}_2} \), melt composition, \( P \), and \( T \) (we use Kress and Carmichael 1991, but other parameterisations

can be used). Finally, we check if the melt is supersaturated with respect to sulfide melt,
anhydrite, or graphite; if so, the calculations we present are metastable relative to precipitation of

one or more of these phases and we state this whenever it is the case. The melt is supersaturated

with respect to sulfide melt if the \( \text{S}^{2-} \) content of the melt is greater than the sulfide content at

sulfide saturation (\( \text{S}^{2-} \text{CSS}, \) assuming the sulfide is pure FeS; O’Neill 2021); with respect to

anhydrite if the \( \text{SO}_4^{2-} \) content of the melt is greater than the sulfate content at anhydrite saturation

(\( \text{S}^{6+} \text{CAS}, \) Zajacz and Tsay 2019); and with respect to graphite if \( f_{\text{CO}_2}/f_{\text{O}_2} \) is greater than the

equilibrium constant for \( \text{C}_{\text{graphite}} + \text{O}_2 = \text{CO}_2 \) (Holloway \textit{et al.} 1992) (other parameterisations for

saturation of additional phases can be included in our model).

2.3 Deriving melt speciation to calculate fugacities and partial pressures

Given \( P, T, \) and \( f_{\text{O}_2} \), the fugacities of most species in the coexisting vapor can be calculated

from concentrations of dissolved volatile species in the melt via equations (11–18) in Table 2.
The homogeneous equilibria in the vapor phase described by equations (7) and (10) in Table 1

can then be used to calculate fugacities of the assumed insoluble species \( \text{SO}_2 \) and \( \text{OCS}, \)
respectively. These fugacities can be converted to partial pressures using equation (2) and summed together to calculate $P_{\text{sat}}^{v}$ as in equation (4). However, typically only the bulk concentrations of H, C, and S dissolved in the melt are known, not the concentration of individual H, C, and S-bearing species. For instance, some analytical techniques used to measure volatile concentrations (e.g., secondary ion mass spectrometry) provide no information on the identity or concentrations of different melt species. However, even if an analytical technique can quantify the concentrations of some species (e.g., Fourier transform infrared spectroscopy for $\text{H}_2\text{O}_{\text{mol}}$ vs. $\text{OH}^{-}$ or $\text{CO}_2\text{mol}$ vs. $\text{CO}_3^{2-}$), other dissolved species (e.g., $\text{H}_2$, $\text{CO}$, $\text{CH}_4$) are typically not quantifiable at natural abundances. Moreover, the measured speciation could have changed on quenching to a glass (e.g., Stolper 1989; Dingwell and Webb 1990; Morizet et al. 2001; Behrens and Nowak 2010; Konschak and Keppler 2014; Nash et al. 2019).

To deal with this, we solve for the speciation of the melt, subject to the constraints of: the heterogeneous melt-vapor equilibria in Table 2; homogeneous vapor equilibria in Table 1; mass balance given the specified bulk concentrations of H, C, and S in the melt; and the intensive parameters $T$, $f_{O2}$, and $P$. In this way, the total H, C, and S concentrations measured in the glass are distributed into equilibrium concentrations of the various dissolved species. This is done iteratively, assuming an initial value of $P$ (details of the choice of $P$ are given in the next section). Firstly, all H is assumed to be $\text{H}_2\text{O}_T$, all C is $\text{CO}_3^{2-}$, and all S is $\text{S}^{2-}$. Then the concentrations of the other melt species ($\text{H}_2\text{mol}$, $\text{CO}_{\text{mol}}$, $\text{CH}_4\text{mol}$, $\text{H}_2\text{S}_{\text{mol}}$, and $\text{SO}_4^{2-}$) are calculated at the given $f_{O2}$, $T$, and $P$ using the equations in Tables 1 and 2. The total amounts of H, C, and S in the melt is then calculated by summing the amounts of these elements in all the melt species. The calculated totals will be higher than the known bulk composition of the melt: e.g., for H, all H dissolved in the melt was initially assumed to be $\text{H}_2\text{O}_T$, but after the first iteration, there is
additional H in the melt in form of H\textsubscript{2,mol}, CH\textsubscript{4,mol}, and H\textsubscript{2S,mol}. Based on the difference between these, new values for the concentrations of H\textsubscript{2}O\textsubscript{2}, CO\textsubscript{3}\textsuperscript{2-}, and S\textsuperscript{2-} are estimated, and the process is repeated until H, C, and S satisfies mass balance within a defined limit. Note that oxygen is not mass balanced as \textit{f}\textsubscript{O2} is an independent variable in these calculations and different choices of \textit{f}\textsubscript{O2} lead to different bulk oxygen contents of the melt. Further details are provided in Supplementary Material Section 4.

These calculations require \textit{f}\textsubscript{O2} as an input. When trying to determine \textit{P}\textsubscript{sat} for a natural sample, this could be constrained from measurements of Fe\textsuperscript{3+}/Fe\textsubscript{T} or S\textsuperscript{6+}/S\textsubscript{T} in the glass (e.g., Carroll and Rutherford 1988; Kress and Carmichael 1991; although changes may occur on the quench: Nash \textit{et al.} 2019) or by independent oxybarometry. Here, we have chosen \textit{f}\textsubscript{O2} as an independent variable to evaluate the effects of variation in \textit{f}\textsubscript{O2} on \textit{P}\textsubscript{sat} at constant total dissolved volatile contents. Details are given in Supplementary Material Section 3.2.6 for how \textit{f}\textsubscript{O2} is chosen and the reference buffers we use in reporting \textit{f}\textsubscript{O2}.

2.4 Solving for \textit{P}\textsubscript{sat} and vapor composition

It is important to note that \textit{y}\textsubscript{f}, \textit{C}i, and \textit{f}\textsubscript{O2} all depend on the \textit{P} chosen for the calculations described in Section 2.3. Therefore, \textit{P}\textsubscript{sat} must also be calculated iteratively. The initial guess for \textit{P} (\textit{P}0) is chosen to be high (e.g., 40,000 bars). The speciation of the melt is iteratively solved at the given \textit{f}\textsubscript{O2}, \textit{T}, \textit{P}_n, and bulk volatile content of the melt (H, C, and S) as described in Section 2.3. This gives the concentration of specific dissolved species in the melt; \textit{f}i (including insoluble vapor species); \textit{p}i using equation (2); and \textit{P}\textsubscript{sat} using equation (4). The next guess for \textit{P} (\textit{P}1) is set as the sum of the partial pressures given by the previous guess for \textit{P} (i.e., \textit{P}\textsubscript{sat}[\textit{P}0]) and then the
iteration is repeated. After each iteration, the difference between $P_n$ and $P_v^{sat}$ is evaluated: $dP = P_n - P_v^{sat}[P_n]$. If $dP$ after the iteration is less than the specified tolerance (here we use 0.1 bar), $P_v^{sat}$ is taken to have been found. If $dP$ is greater than the specified tolerance, $P_{n+1} = P_v^{sat}[P_n]$ and the calculations of melt speciation and $P_v^{sat}$ are repeated until $dP$ is less than the specified tolerance. Once the calculation has converged, the concentration of all species in the melt and vapor are calculated at $P_v^{sat}$.

3 Effects of $f_{O_2}$ and H, C, and S concentrations on vapor-saturation pressures and vapor compositions

To isolate and analyze the effects of $f_{O_2}$ and H, C, and S concentrations on $P_v^{sat}$ and on the composition of the saturating vapor, we use the same base melt composition and $T$ for all calculations in this section. The melt composition is the Hawaiian tholeiite used in Hughes et al. (2023) at $T = 1200$ °C.

3.1 $P_v^{sat}$ for a reference case with fixed total volatile concentrations in the melt

In this section, we describe the calculated $P_v^{sat}$ with varying $f_{O_2}$ for a melt containing fixed total dissolved C and H contents (Figure 1). The total concentration of C is 273 ppm (all ppm are by weight, corresponding to 1000 ppm of CO$_2$ if all C were dissolved as CO$_2$: we refer to this CO$_2$ equivalent concentration as CO$_2$-eq) and H is 3357 ppm (corresponding to 3 wt% H$_2$O-eq). In case 1, all C-O-H species in the melt and vapor are oxidized. Hence, H$_2$O and CO$_2$ are assumed to be the only vapor species and H$_2$O$_T$ (i.e., the combination of both OH$^-$ and H$_2$O$_{mol}$) and CO$_3^{2-}$ are the only volatile-bearing melt species (Section 3.1.1). This is equivalent to most $P_v^{sat}$-calculators currently in use (e.g., Newman and Lowenstern 2002; Papale et al. 2006;
In case 2, both oxidized and reduced C-O-H species are present in the melt and vapor phase (Section 3.1.2). Lastly, we add a fixed amount of S to case 2 (1000 ppm S-eq), leading to case 3 where S-bearing species are present in addition to the C-O-H species included in case 2 (Section 3.1.3). Two additional cases are described in Supplementary Material Section 6.3: case 2’, which is the same as case 2 except reduced C-O-H species are assumed to be completely insoluble in the melt; and case 3’, which is the same as case 3 except H$_2$S$_{mol}$ is treated as insoluble in the melt.

### 3.1.1 Case 1: only oxidised C-O-H species in the melt and vapor.

This case will be used as a reference for comparison to the other cases that we consider. For this case, $P_{v}^{\text{sat}}$, $p_i$’s ($p_{\text{CO}_2}$ and $p_{\text{H}_2\text{O}}$), melt speciation, and vapor composition ($x_{v}^{\text{H}_2\text{O}}$ and $x_{v}^{\text{CO}_2}$) are independent of $f_{O_2}$ (black lines in Figure 1 and Figure 2). If the solubility functions for CO$_3^{2-}$ and H$_2$O$_T$ were dependent on the Fe$^{3+}$/Fe$_T$ of the melt, $P_{v}^{\text{sat}}$, $p_i$’s, and vapor composition would depend on $f_{O_2}$. However, melt speciation would still be independent of $f_{O_2}$ because of the assumption that there are no other dissolved C-O-H species. Wieser et al. (2022) found that available models (e.g., Papale et al. 2006; Shishkina et al. 2014; Ghiorso and Gualda 2015) suggest H$_2$O solubility is relatively insensitive to Fe$^{3+}$/Fe$_T$ (also observed by Newcombe et al., 2017), whereas CO$_2$ solubility is sensitive to Fe$^{3+}$/Fe$_T$. However, they found the effects are highly uncertain due to a lack of experimental data to calibrate the Fe$^{3+}$/Fe$_T$ dependence of H$_2$O and CO$_2$ solubility. We show a comparison to VolatileCalc in Figure 1 (and other models in...
Supplementary Material Section 5, Figures S7 and S8), which highlights how much different solubility functions (especially for CO2) can affect calculations of $P'_\text{sat}$.

### 3.1.2 Case 2: oxidised and reduced C-O-H species in the melt and vapor.

For case 2, decreasing $f_{O2}$ results in the fractions of the total H and C dissolved in the melt as reduced species increasing and as oxidised species decreasing (Figure 2c), which is reflected in the corresponding $p_i$’s and $x_i'$’s (Figure 2a and e). H and C behave differently at $\Delta FMQ < -1$, with a large decrease in $p_{CO2}$ but very little change in $p_{H2O}$. This is because the equilibrium constants for homogeneous equilibria (5) and (6) in Table 1 result in $p_{CO}$ beginning to increase significantly with decreasing $f_{O2}$ (from ~0 to ~1200 bars from $\Delta FMQ=0$ to -3) at a higher $f_{O2}$ than that at which $p_{H2}$ begins to increase. Hence, the amount of $CO_3^{2-}$ in the melt decreases substantially over the $f_{O2}$ range covered in the figure, whereas there is less change in the amount of $H_2O_T$ (i.e., compare the solid blue and red curves in Figure 2c).

For $\Delta FMQ \gtrsim 0$, $P'_\text{sat}$ is approximately equal to that assuming the vapor only contains CO2 and H2O (Figure 1) because the $p_i$’s and $x_i'$’s of H2, CO, and CH4 are negligible in the vapor (red and blue curves in Figure 2a and e). With decreasing $f_{O2}$ below $\Delta FMQ \approx 0$, the $p_i$’s of these reduced vapor species increase, while those of H2O and CO2 decrease, but the increases for the reduced species are larger (Figure 2a). Hence, there is a significant increase in $P'_\text{sat}$ with decreasing $f_{O2}$ when the reduced C-O-H species are included (Figure 1). This is due to the buildup of reduced C-O-H species in the system that are less soluble than oxidised C-O-H species (e.g., Scaillet and Pichavant 2004; Wetzel et al. 2015; Newcombe et al. 2017a). If the reduced C-O-H species are assumed to be completely insoluble in the melt, the increase in $P'_\text{sat}$ is even
greater (see Supplementary Material Section 6.3.1). For the conditions shown in Figure 2, graphite is not stable.

3.1.3 Case 3: S-bearing species in the melt and vapor.

The variations with \( f_{O2} \) for the C- and H-bearing vapor and melt species for the S-bearing case 3 are similar to those for the S-free case 2 (i.e., compare the blue and red curves Figure 2). This reflects: (1) the relatively low concentration of S in the melt (i.e., \( H_2O\)-eq = 3 wt% vs. S-eq = 0.1 wt%); and (2) the relatively high solubility of S in the melt compared to CO\(_2\) such that the vapor has a high C/S ratio relative to the melt. Hence, the \( p_i \)'s of S-bearing species are small and a small fraction of \( P_{sat}^v \) under all conditions shown in Figure 2b. Another factor is the assumed insolubility of OCS species in the melt for this case, which means dissolved S has a negligible effect on the concentrations of C-bearing species in the melt. For the conditions shown in Figure 2, graphite, sulfide, and anhydrite are not stable.

Sulfur is dissolved in the melt nearly entirely as S\(^{2-}\) at low \( f_{O2} \) (\( \Delta FMQ \leq 0 \)) and SO\(_4^{2-}\) at high \( f_{O2} \) (\( \Delta FMQ \geq 2 \)) (Figure 2d; 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). Additionally, at low \( f_{O2} \) (\( \Delta FMQ \leq 0 \)), \( H_2S_{mol} \) and *S\(^{2-}\) are present in roughly equal molar concentrations in the melt (Figure 2d). By combining equations (9), (16), and (18) in Table 1 and Table 2, we obtain the following expression for the ratio of S\(^{2-}\) dissolved in the melt as \( H_2S_{mol} \) to that dissolved as *S\(^{2-}\):

\[
\frac{x_{H_2S_{mol}}^{m}}{x_{S^{2-}}^{m}} = \frac{K_{HSC_{H_2S_{mol}}}}{c_{S^{2-}}} f_{H_2O}.
\]  \( (20) \)
Therefore, \( H_2S_{\text{mol}}/^S^{2-} \) increases linearly with increasing \( f_{H_2O} \) (or equivalently with \( (x_{H_2O}^m)^2 \) based on equation 12) if the melt composition is otherwise fixed (i.e., at given \( f_{H_2O}, P, \) and \( T, \) the \( H_2S_{\text{mol}}/^S^{2-} \) ratio depends only on the ratio of the solubilities in equation 19). The ratio is independent of \( f_{S_2} \) and \( f_{O_2} \) (except through the dependence of \( f_{H_2O} \) on \( f_{O_2} \) and \( f_{H_2} \) through reaction 5). The relationship between \( S^{6+}/S^{2-}_T \) and \( f_{O_2} \) (where \( S^{2-}_T \) is the total S dissolved as sulphide, given by \(^S^2- + H_2S\)) can be derived by combining equations (17) (Table 2) and (20):

\[
\frac{x_{SO_4}^m}{x_{S^{2-}_T}^m} = \frac{x_{SO_4}^m}{x_{H_2S_{mol}}^m + x_{S^{2-}^m}} = \frac{c_{SO_4}^m}{c_{H_2S_{mol}}K_{SHS_{H_2O}^m + C_{S^{2-}_T}}} \left( f_{O_2} \right)^2 \approx \frac{c_{SO_4}^m}{K_{HS}c_{HS}S_{H_2O}^m + C_{S^{2-}_T}} \left( f_{O_2} \right)^2. \quad (21)
\]

Hence, \( SO_4^{2-}/S^{2-}_T \) depends on \( (f_{O_2})^2 \), as is the case for \( SO_4^{2-}/^S^{2-} \) (e.g., Wallace and Carmichael 1994; Matthews et al. 1999; Moretti and Ottonello 2005; Métrich et al. 2009; Jugo et al. 2010; Moretti 2021; Hughes et al. 2023), but with different slopes.

At all values of \( f_{O_2} \) covered by our modeling, \( p_{S_2} \) contributes negligibly to the sum of the \( p_i \)’s of the S-bearing species (Figure 3). At \( f_{O_2} \) lower than \( \Delta FMQ \sim +0.4 \), \( H_2S \) is predicted to become the dominant S-bearing vapor species, followed by OCS (Figure 3). The decreases in \( p_{H_2S} \) and \( p_{OCS} \) with increasing \( f_{O_2} \) seen in Figure 3 between \( +0.40 \lesssim \Delta FMQ \lesssim +1.5 \) results from the proportionality of both \( f_{H_2S} \) (equation 9; Table 1) and \( f_{OCS} \) (equations 6, 7, and 9; Table 1) to \( (f_{O_2})^{-0.5} \). As \( p_{H_2S} \) and \( p_{OCS} \) decrease, \( p_{SO_2} \) increases with increasing \( f_{O_2} \), with \( p_{SO_2} \) surpassing \( p_{H_2S} \) at \( \sim \Delta FMQ+0.4 \) (Figure 3). For this melt composition, there is a maximum in \( p_{SO_2} \) at \( \Delta FMQ+1.28 \), where both \( S^{2-}_T \) and \( SO_4^{2-} \) species are dissolved in the melt in subequal amounts (Figure 3; there is also a much smaller maximum in \( p_{S_2} \) at \( \Delta FMQ+0.77 \)). When \( S^{2-}_T \) is the dominant form of S dissolved in the melt, \( p_{S_2} \) and \( p_{SO_2} \) are respectively proportional to \( (f_{O_2})^4 \) and...
In contrast, when \( \text{SO}_4^{2-} \) dominates, \( p_{\text{S}_2} \) and \( p_{\text{SO}_2} \) are respectively proportional to \((f_{\text{O}_2})^{-3}\) and \((f_{\text{O}_2})^{-0.5}\) (equations 6, 7, and 17 in Table 2). As discussed in Hughes et al. (2023), this change in the sign of the dependence of the derivative of \( p_{\text{SO}_2} \) and \( p_{\text{S}_2} \) with respect to \( f_{\text{O}_2} \) results in a maximum in \( p_{\text{SO}_2} \) and \( p_{\text{S}_2} \) in a \( \text{C-} \) and \( \text{H-free} \) system. The same effect produces the maximum in \( P'_{\text{sat}} \) at \( \Delta_{\text{FMQ}}+1.19 \) demonstrating the SS\text{min} is a general feature of \( \text{S-bearing} \) basaltic magmas at relatively oxidising conditions (Figure 3).

Even though \( \text{S-bearing} \) species are minor components of the vapor \((x^i < 0.03, \text{where } i = \text{S}_2, \text{SO}_2, \text{H}_2\text{S}, \text{OCS}; \text{Figure 2f})\), their presence in case 3 influences \( P'_{\text{sat}} \). At all the \( f_{\text{O}_2} \) values shown, \( P'_{\text{sat}} \) for case 3 is greater than case 2 (compare the yellow and blue curves in Figure 1). At low \( f_{\text{O}_2} \) \((\Delta_{\text{FMQ}} < 0)\), this is due to the addition of \( \text{H}_2\text{S} \) and \( \text{OCS} \) to the vapor for case 3 (by up to ~20 bars at \( \Delta_{\text{FMQ}} = 0) \), which are not present in case 2. Additionally, the changing behaviour of \( \text{S-bearing} \) species in the melt and vapor with \( f_{\text{O}_2} \) (mainly \( \text{H}_2\text{S} \) and \( \text{SO}_2 \)) results in the SS\text{min} seen in Figure 1. The overall behaviour of case 3 shown in Figure 3 is similar to that calculated for the \( \text{S-O} \) (i.e., \( \text{H-} \) and \( \text{C-absent} \), referred to as case 4) system presented in Hughes \textit{et al.} (2023). However, the magnitude and \( f_{\text{O}_2} \)-position of the maximum in \( P'_{\text{sat}} \) are different, reflecting the influence of \( \text{C} \) and \( \text{H} \) on the system (more details in Supplementary Material Section 6.2).

Lesne \textit{et al.} (2015) calculated \( p_{\text{H}_2\text{S}} + p_{\text{SO}_2} \) for vapor coexisting with a basaltic melt in a \( \text{C-free} \) system (i.e., the vapor was assumed to contain only \( \text{S-O-H} \) species) for varying \( f_{\text{O}_2} \) at constant dissolved \( \text{S-eq} \), dissolved \( \text{H}_2\text{O-eq} \), \( T \), and \( P \). They predicted that ignoring \( \text{S-bearing} \) vapor species could lead to underestimates of \( P'_{\text{sat}} \) of \( 10^2 \sim 10^3 \) bars at \( \sim 2000 \) bars. However, in contrast to our results, their model produced a local \textit{minimum} in \( P'_{\text{sat}} \), stating: "It is only within the minimum of sulfur solubility, i.e. around \( \text{NNO} \pm 0.5 \) \([\sim \Delta_{\text{FMQ}}+0.2 \text{ to } +1.2]\), that ignoring partial
pressure of S-bearing species does not greatly affect gas saturation calculations”. The behaviour predicted by Lesne et al. (2015) assumes that the only S-bearing species in the melt are H\textsubscript{2}S\textsubscript{mol} and SO\textsubscript{2,\textsubscript{mol}}. However, there is evidence for other dissolved S\textsuperscript{2-} species under reducing conditions in addition to H\textsubscript{2}S\textsubscript{mol} in natural silicate melt compositions (e.g., FeS, CaS; O’Neill 2021). Additionally, there is no evidence for SO\textsubscript{2,\textsubscript{mol}} in natural silicate melt compositions under oxidising conditions, whereas SO\textsubscript{4,\textsuperscript{2-}} has been observed spectroscopically (e.g., Wilke et al. 2011). Therefore, we infer that SS\textsubscript{min} will result in a local maximum in \( P_{\text{v, sat}} \) for silicate melts in nature, rather than a local minimum. However, if there are systems where the dominant oxidised S-bearing species in the melt is SO\textsubscript{2,\textsubscript{mol}} and H\textsubscript{2}S\textsubscript{mol} dominates over other dissolved sulfide species at reduced conditions, a minimum in \( P_{\text{v, sat}} \) might occur.

### 3.2 Varying the concentration of volatiles

We now investigate how variations in the concentrations of volatiles (i.e., bulk concentrations of C, H, and S in the melt) affect the relationship between \( P_{\text{v, sat}} \) and \( f_{O_2} \). This calculation uses the full C-O-H-S system with the same melt and vapor species as in case 3, but we allow the dissolved total volatile contents to vary between 0–5 wt% H\textsubscript{2}O-eq, 0–2000 ppm CO\textsubscript{2}-eq, and 0–2000 ppm S-eq.

We first calculate \( P_{\text{v, sat}} \) for a fully-oxidised, S-free reference system comparable to case 1 between 0–5 wt% H\textsubscript{2}O-eq and 0–2000 ppm CO\textsubscript{2}-eq, shown as isobars in Figure 4a. The differences between this reference case and the full C-O-H-S system are contoured in Figure 4b–d, where the contours are for constant values of \( \Delta P_{\text{v, sat}} = P_{\text{v, sat}}[\text{C-O-H-S}] - P_{\text{v, sat}}[\text{oxidised C-O-H reference state}] \). Case 3 (3 wt% H\textsubscript{2}O-eq, 1000 ppm CO\textsubscript{2}-eq, and 1000 ppm S-eq) described in
Section 3.1.3 is shown by the dashed grey horizontal lines in Figure 4b–d. Figure 4b has variable S (0–2000 ppm S-eq) at constant H (3 wt% H2O-eq) and C (1000 ppm CO2-eq); Figure 4c has variable H (0–5 wt% H2O-eq) at constant S (1000 ppm S-eq) and C (1000 ppm CO2-eq); and Figure 4d has variable C (0–2000 ppm CO2-eq) at constant H (3 wt% H2O-eq) and S (1000 ppm S-eq). In the following two subsections, we emphasize two features of Figure 4: (1) The increase in $P_{\text{sat}}^v$ with decreasing $f_{O_2}$ at low $f_{O_2}$ ($\Delta F_{\text{MQ}} \lesssim 0$) due to the build-up of relatively insoluble reduced C-O-H species in the vapor (Section 3.2.1); and (2) the local maximum in $P_{\text{sat}}^v$ at intermediate $f_{O_2}$ ($\Delta F_{\text{MQ}} \approx +0.5$ to $+1.5$ for this melt composition), which is a manifestation of the SS$^{\text{min}}$ (Section 3.2.2).

### 3.2.1 Build-up of relatively insoluble reduced C-O-H species in the vapor.

At any given y-value on Figure 4b–d (i.e., a horizontal slice), $\Delta P_{\text{sat}}^v$ increases with decreasing $f_{O_2}$ for $\Delta F_{\text{MQ}} \lesssim 0$. This is due to the build-up of reduced C-O-H species in the vapor because these species are less soluble in the melt than their oxidised counterpart species (e.g., Scaillet and Pichavant 2004; Wetzel et al. 2015; Newcombe et al. 2017a; discussed in Section 3.1.2). The contours of $\Delta P_{\text{sat}}^v$ also get closer together with decreasing log$_{10}(f_{O_2})$, reflecting the concave up shapes of the curves shown in Figure 1. However, the magnitude of the predicted effects – and even their signs – could be changed if future experiments were to demonstrate significantly lower or higher solubilities of these reduced species.

Contours of $\Delta P_{\text{sat}}^v$ with constant H and C contents but variable S contents are near-vertical; i.e., variations in the S content of the melt have only small effects on $\Delta P_{\text{sat}}^v$ (Figure 4b). This is because S-bearing species represent such small proportions of the vapor at low $f_{O_2}$ (e.g., $<30$ bars...
with 1000 ppm S-eq for $\Delta$FMQ $\leq 0$; black solid curve in Figure 3). Although the S content of the melt is changing along each contour in Figure 4b, neither the direct impact of these changes through variations of the $p_i$'s of S-bearing species nor their indirect effects on the $p_i$'s of the C-O-H species result in significant effects on $P_{\text{sat}}$.

Contours of $\Delta P_{\text{sat}}$ with constant S and C contents but variable H contents are also near-vertical (Figure 4c), whereas for constant H and S but variable C they are steeply, positively sloped and concave up (Figure 4d). Therefore, increasing the C content of the melt has a greater effect on increasing $\Delta P_{\text{sat}}$ with decreasing $f_{O_2}$ than increasing the H content of the melt, even though the absolute concentration of C is far smaller. This reflects the increase in the relatively insoluble CO-species in the vapor with decreasing $f_{O_2}$ by conversion from CO$_2$ to CO (reaction 6) occurs at a higher $f_{O_2}$ than the increase in the H$_2$ species by conversion from H$_2$O with decreasing $f_{O_2}$ (reaction 5) (see Section 3.1.2).

Graphite and anhydrite are not stable under the conditions shown in Figure 4. However, sulfide is stable above the white dotted curves in Figure 4b and c (but nowhere in Figure 4d because the S and H content of the melt are too low) and hence the calculations are metastable in this region (see Hughes et al., 2023, for explanations of the shape of the sulfide-stable curve). This shows that sulfide is stabilised at low $f_{O_2}$ ($\Delta$FMQ < 0), high dissolved S (>1000 ppm S), and high dissolved H$_2$O (>3.5 wt% H$_2$O-eq because of the effect of dilution on S$^2$-CSS).
The sulfur solubility minimum in C- and H-bearing melts.

A near-vertical “ridge” defining a maximum in $\Delta P^{v}_{sat}$ at $+0.5 < \Delta FMQ < +1.5$ is visible in Figure 4b–d. The trace of this ridge with varying volatile contents is shown in each panel as a black curve. For ease of comparison, these three traces are superimposed in Figure 5b where volatile concentrations along the “ridge” are plotted vs. the $f_{O2}$-position of the ridge. Figure 5a also superimposes these three traces of the ridge, in this case plotting volatile concentration vs. $\Delta P^{v}_{sat}$, the height of the ridge.

The $\Delta P^{v}_{sat}$ maximum in Figure 4b–d is the signature of the SS$_{min}$, and it is also closely associated with maxima in the sum of the $p_i$’s of S-bearing vapor species (especially $p_{SO2}$; Figure 3; and Hughes et al., 2023). Hence, the ridge in calculated $\Delta P^{v}_{sat}$ disappears in the S-free systems (i.e., near the x-axis in Figure 4b) and increases in height with increasing total dissolved S in the melt coexisting with vapor (e.g., with increasing S in Figure 4b). The interactions among C-, H-, and S-bearing species in the melt and vapor result in the systems described here being more complex than the simple cases considered by Hughes et al. (2023) (Sections 3.1.3). Nevertheless, our modeling predicts that this feature persists robustly in basaltic systems saturated with C-O-H-S vapor.

The $f_{O2}$ value of the maximum in $\Delta P^{v}_{sat}$ varies little ($+0.97 < \Delta FMQ < +1.38$) over the ranges in S-eq, H$_2$O-eq, and CO$_2$-eq explored here (Figure 5b). In contrast, the height of the $\Delta P^{v}_{sat}$ maximum does depend on the volatile contents of the melt (Figure 5a). The maximum in $\Delta P^{v}_{sat}$ reflects competing reactions involving dissolved S (Section 3.1.3; e.g., Hughes et al., 2023). Hence, its magnitude increases with increasing S-eq because $p_{SO2}$ is proportional to the total sulfur content of the melt (yellow line in Figure 5a; derivation in Supplementary Material).
Section 6.1). However, $\Delta P_{\text{sat}}^v \neq 0$ at $S$-eq = 0 ppm, reflecting the presence of small but non-negligible quantities of reduced C-O-H species in the vapor such that $\Delta P_{\text{sat}}^v > 0$. The build-up of relatively insoluble C-O-H species (especially CO) contributes sufficiently to the $\Delta P_{\text{sat}}^v$ value that it begins to interfere with and obscure the SS$_{\text{min}}$ at low S such that the maximum in $\Delta P_{\text{sat}}^v$ disappears before $S_T$ reaches zero (e.g., yellow curves in Figure 5 terminate at $S_T > 0$). Increasing CO$_2$-eq in the melt causes the magnitude of the $\Delta P_{\text{sat}}^v$ maximum to decrease. The magnitude of the $\Delta P_{\text{sat}}^v$ maximum first increases then decreases with increasing H$_2$O-eq, highlighting the complex interplay between H-, C-, and S-bearing melt and vapor species.

### 4 Implications

Figure 4 emphasizes that calculations of the magnitude and exact position of the SS$_{\text{min}}$ and their impact on calculations of $P_{\text{sat}}^v$ will depend on precise knowledge of the volatile solubility functions, through which the complex interplay discussed in Section 3 must ultimately be modeled. Complete and accurate parameterizations of the solubilities in Table 2 in terms of the major element composition of the melt, $f_{\text{O2}}$, and the concentrations of each volatile component are needed for accurate calculations of $P_{\text{sat}}^v$. It is important to be aware of these uncertainties to avoid over-interpretation of the calculated absolute values of $P_{\text{sat}}^v$. For example, uncertainty in the parameters used in the model (e.g., solubilities and their parameterization, vapor fugacity coefficients) and analytical errors on the melt composition (major, minor, and volatile species, as well as iron oxidation state) can result in significant uncertainties in the accuracy of calculated values of $P_{\text{sat}}^v$ (see Supplementary Material Sections 7.6 and 7.7). The largest source of uncertainty in calculations of $P_{\text{sat}}^v$ are the carbonate solubilities and their significant dependence...
on major element composition of the melt and errors on measurements of CO$_2$-eq (and H$_2$O-eq) concentration, which can dwarf variations due to $f_{O_2}$ and S (Supplementary Material Figure S17). Despite these uncertainties, we are confident that our modeling captures the overall trends in the effects of S and $f_{O_2}$ on calculations of $P_{v_{\text{sat}}}$ and $\Delta P_{v_{\text{sat}}}$ for basaltic melt compositions (see Supplementary Material Section 7.2). We describe these potential limitations of our model in detail in Supplementary Material Section 7.

As emphasized in the Introduction, values of $P_{v_{\text{sat}}}$ are routinely and widely calculated based on the volatile contents of glasses to provide minimum estimates of the $P$ at which the volatile contents were set (e.g., Anderson et al. 1989; Blundy and Cashman 2008; Colman et al. 2015; Wanless et al. 2015; Camejo-Harry et al. 2018, 2019; Black and Andrews 2020; Wieser et al. 2021). With advances in microanalysis, melt inclusion and matrix glass studies are increasingly co-determining the concentrations of a more complete suite of volatiles in the samples (H, C, S, Cl, F, etc.) and Fe$^{3+}$/Fe$_T$ and/or S$^{6+}$/S$_T$ to constrain $f_{O_2}$. However, few such calculations of $P_{v_{\text{sat}}}$ include the effects of dissolved S or $f_{O_2}$ (e.g., Carroll and Webster 1994; Newman and Lowenstern 2002; Lesne et al. 2015; Iacovino et al. 2021; Yip et al. 2022).

To investigate the magnitude of these effects in nature, we collated literature data on glassy melt inclusions and matrix glasses where CO$_2$, H$_2$O, S, and Fe$^{3+}$/Fe$_T$ have been measured for the same glass sample. We have restricted our compilation to low-alkali basaltic glass compositions similar to the Hawaiian tholeiite we have adopted as a reference as the carbonate solubility is highly dependent on melt composition and is fixed in these calculations (e.g., Supplementary Material Figure S15). However, to examine magmas formed at the low $f_{O_2}$ extreme of our calculations we include lunar and martian samples. These have much higher FeO than a Hawaiian tholeiite and hence the carbonate solubility function we use here may not be
appropriate. For each terrestrial glass sample included in our compilation, we calculate \( P_{v_{\text{sat}}} \) at \( T = 1200 \, ^\circ\text{C} \) using the known \( f_{O_2} \) based on measured \( \text{Fe}^{3+}/\text{Fe}^\text{T} \) ratios and measured melt composition (which can influence \( C_{\text{S}_{2-}} \) and \( C_{\text{SO}_4^{2-}} \) in our model, but not other solubilities). For lunar and martian glasses, we calculate \( P_{v_{\text{sat}}} \) using a range of \( f_{O_2} \) appropriate for these magmas (-5 < \( \Delta \text{FMQ} < -1 \); e.g., Shearer et al. 2006; Gaillard et al. 2021). As well as \( P_{v_{\text{sat}}} \), we also calculate the vapor composition in equilibrium with the measure melt composition at \( P_{v_{\text{sat}}} \): we do not discuss the vapor composition in the main text, but this can be found in Supplementary Material Section 8. Calculated vapor compositions could be compared to natural volcanic gas samples and fluid inclusions or used to reconstruct bulk melt inclusion compositions when a bubble is present.

Most modern terrestrial magmas have \( f_{O_2} \) levels corresponding to \(-1 \leq \Delta \text{FMQ} \leq +2 \) (e.g., Cottrell et al. 2021) and contain significant S (typically 900–1200 ppm S for MORBs, 1100–6000 ppm S for intraplate hotspots, and 1200–7000 for arcs; Wallace and Edmonds 2011; Gaillard et al. 2021). Hence, the \( SS_{\text{min}} \), which for our calculations is between \(+1 \leq \Delta \text{FMQ} \leq +2 \) (Figure 1) could influence calculated \( P_{v_{\text{sat}}} \) values for hotspot and arc magmas that have \( f_{O_2} \) values overlapping the calculated range of the \( SS_{\text{min}} \). The build-up of relatively insoluble reduced C-O-H species in the vapor described previously (Figure 1) is unlikely to be important for typical terrestrial magmas but is likely to be important for extra-terrestrial settings. Although we also discuss values of absolute \( P_{v_{\text{sat}}} \), we focus on \( \Delta P_{v_{\text{sat}}} \), the difference between \( P_{v_{\text{sat}}} \) for full C-O-H-S-bearing system and the \( P_{v_{\text{sat}}} \) value for the oxidized C-O-H reference (i.e., case 1, which has been used widely in existing calculations of \( P_{v_{\text{sat}}} \)).
4.1 Mid-ocean ridge basalts

Figure 6a–c shows measured volatile contents and calculated \( P^v_{\text{sat}} \) and \( \Delta P^v_{\text{sat}} \) for MORB submarine matrix glasses. These MORBs have an \( f_{O_2} \leq \Delta \text{FMQ}+0.4 \), so their calculated values of \( P^v_{\text{sat}} \) are relatively insensitive to \( f_{O_2} \) and S at the S contents observed (\( \Delta P^v_{\text{sat}} \leq 33 \) bars, Figure 6c). Thus, calculations of \( P^v_{\text{sat}} \) for MORB that do not include the effects of \( f_{O_2} \) and S would only underestimate \( P^v_{\text{sat}} \) by \( \lesssim 30 \) bars (Figure 6c). Reykjanes Ridge glasses have low CO\(_2\) and H\(_2\)O concentrations due to degassing to shallow depths (\( \leq 100 \) ppm CO\(_2\)-eq and \( \leq 0.3 \) wt% H\(_2\)O-eq; Figure 6a; e.g., Nichols et al., 2002), but they have not degassed significant S (\( \sim 1200 \) ppm S-eq, Figure 6b; e.g., Nichols et al. 2002; Shorttle et al. 2015) and their \( f_{O_2} \) is roughly where the SS\(_{\text{min}}\) can start to affect \( P^v_{\text{sat}} \) (Figure 6b). The combination of relatively high \( f_{O_2} \) and \( S_T \) and low \( H_T \) and \( C_T \) leads to large values of \( \Delta P^v_{\text{sat}}/P^v_{\text{sat}} \) (i.e., 10–40% based on the lines of constant \( 100*(\Delta P^v_{\text{sat}}/\Delta P^v_{\text{sat}}) \) shown in Figure 6c). Thus, including the effects of S and \( f_{O_2} \) in calculations of \( P^v_{\text{sat}} \) result in only small absolute values of \( \Delta P^v_{\text{sat}} \), but when compared to the low \( P^v_{\text{sat}} \) (due the low CO\(_2\)-H\(_2\)O abundances) this leads to a large relative effect on \( \Delta P^v_{\text{sat}} \) (i.e., 10–40%; Figure 6c).

4.2 Ocean island basalts

Basalts related to hotspots have an \( f_{O_2} \) range that straddles the SS\(_{\text{min}}\) calculated for the reference basalt used in this study (e.g., \( \Delta \text{FMQ}+1 \) to +3 using global compilations; Moussallam et al. 2019; Cottrell et al. 2021) and can have much higher \( S_T \) contents than MORB glasses (e.g., Ding and Dasgupta 2018). Hence S could significantly influence calculated values of \( P^v_{\text{sat}} \). The broad positive correlation between S and \( f_{O_2} \) seen in Figure 6e (and also h for Marianas samples) is caused by progressive reduction during S degassing (e.g., Anderson and Wright 1972; Carmichael and Ghiorso 1986; Burgisser and Scaillet 2007; Métrich et al. 2009; Gaillard et al.
Due to the $f_{O_2}$ range of the submarine matrix glasses from Mauna Kea and melt inclusion data from Kīlauea, and their low H$_2$O and CO$_2$ concentrations (<240 ppm CO$_2$-eq and ≤0.81 wt% H$_2$O-eq; Figure 6d), the calculated $\Delta P^v_{sat}$ is up to 150 bars (the yellow symbols in Figure 6f). Both these factors enhance the effect of the SS$^{\text{min}}$ on calculated $P^v_{sat}$, leading to relatively large absolute and relative differences in $P^v_{sat}$ (i.e., $\Delta P^v_{sat}$ = 30–120 bars such that the relative effect is 20–60%; Figure 6e and f).

Melt inclusions from Iceland also show the effect of elevated $f_{O_2}$ on absolute differences in $\Delta P^v_{sat}$ (Figure 6i), but a smaller effect on the relative increase in $P^v_{sat}$ (i.e., $\Delta P^v_{sat}$ is <20% of the value of $P^v_{sat}$; Figure 6f). This is due to the higher CO$_2$ concentrations of the Icelandic melt inclusions (Figure 6d). Given the dominant influence of CO$_2$ on $P^v_{sat}$ in these water-poor samples, $P^v_{sat}$ for the Icelandic samples is generally higher than for the Hawaiian samples. Thus, while the increase in $P^v_{sat}$ (which is approximately equal to $\Delta P^w_{sat}$) is similar (several 10’s of bars) for the most oxidized samples from both groups as they approach the SS$^{\text{min}}$, when normalized to the absolute value of $P^v_{sat}$, the percentage increase in $P^v_{sat}$ for the most oxidized sample of the two sets of OIBs is smaller for the Icelandic samples (20% rather than 60%). This is likely a general rule: although $\Delta P^v_{sat}$ is similar in deeply trapped melt inclusions that have not experienced significant degassing of CO$_2$ and H$_2$O relative to shallowly trapped melt inclusions/matrix glasses, the relative effect on $\Delta P^v_{sat}$ will be lower in deep, undegassed melts than in shallow, degassed melts (Figure 6f).
4.3 Arc basalts

Melt inclusion and matrix glasses from basalts from the Marianas arc have $f_{O_2}$ values on the low $f_{O_2}$-limb of the SS$_{min}$ (Figure 6h). Thus, similar to OIB-related melt inclusions, arc-related melt inclusions with sufficient S also show higher calculated values of $\Delta P_{\text{sat}}^v$ with increasing $f_{O_2}$ as S-bearing species contribute progressively more to the value of $P_{\text{sat}}^v$. For the Marianas samples, H$_2$O and CO$_2$ positively correlate and the CO$_2$ concentrations are high (Figure 6g). For the melt inclusions, this results in the negative correlation of $\Delta P_{\text{sat}}^v$ with $P_{\text{sat}}^v$ (Figure 6i), reflecting the larger impact of S in the $f_{O_2}$ range of arc magmas when H$_2$O and CO$_2$ contents are lowest (see Section 3.2). The matrix glasses do not show this trend because of their lower $f_{O_2}$ and S (Figure 6h and i). However, as also observed for OIBs, $\Delta P_{\text{sat}}^v$ is small relative to $P_{\text{sat}}^v$ (relative effect on $\Delta P_{\text{sat}}^v \lesssim 20\%$, and mostly $\lesssim 10\%$ for melt inclusions and matrix glasses from the Marianas samples; Figure 6i) due to their overall high CO$_2$ and H$_2$O contents (Figure 6g). Conversely, matrix glasses from the Bonin islands are too reduced for the SS$_{min}$ to be important and therefore $\Delta P_{\text{sat}}^v$ is small (blue diamonds in Figure 6h and i).

4.4 Lunar and martian basalts

Lunar and martian basalts formed and evolved under significantly reduced conditions relative to modern terrestrial settings, with an $f_{O_2}$ range of $-5 \lesssim \Delta \text{FMQ} \lesssim -1$ (e.g., Shearer et al. 2006; Gaillard et al. 2021). As has been pointed out previously (e.g., Section 3.2.1; Scaillet and Pichavant 2004; Wetzel et al. 2015; Newcombe et al. 2017; Lo et al. 2021), not including the effects of $f_{O_2}$ as an independent variable can lead to significant underestimations in $P_{\text{sat}}^v$ at the
low \( f_{O_2} \) experienced by lunar and martian magmas due to the low solubility of reduced C-O-H species. Calculated \( P^v_{\text{sat}} \) is very sensitive to \( f_{O_2} \) in this \( f_{O_2} \) range, so accurate \( f_{O_2} \) estimates are vital for accurate \( P^v_{\text{sat}} \) estimates. Additionally, primary magmas from both bodies are estimated to contain non-negligible S (up to \( \sim \)900 and \( \sim \)3500 ppm S-eq for the Moon and Mars, respectively, e.g., Gaillard et al. 2021). However, given that the SS\text{min} is only likely to be observed at more oxidising conditions than those prevalent on the Moon or Mars, this effect is unlikely to be important. However, the low H and C concentrations of these magmas (\( \leq \)1500 ppm H\text{O} and \( \leq \)6 ppm CO\text{2} in lunar melt inclusions; \( \leq \)2000 ppm H\text{O} and \( \leq \)200 ppm CO\text{2} in Martian magmas; Gaillard et al. 2021; Saal and Hauri 2021) suggest that S-bearing species could be an important component of the vapor released by lunar and martian magmas on ascent.

Usui et al. (2012) and Saal and Hauri (2021) analyzed CO\text{2}-eq, H\text{2}O-eq, and S-eq in melt inclusions and matrix glasses from martian and lunar samples (Figure 7a and b), but no measurements or estimates of \( f_{O_2} \) are available for the glasses. Hence, we calculated \( P^v_{\text{sat}} \) values for each glass at \( f_{O_2} \) values spanning the range \(-5 < \Delta \text{FMQ} < -1 \) at 1200°C (e.g., Herd et al. 2002; Shearer et al. 2006), which generates the curves shown in Figure 7c and d (each curve is for a single analysed glass). The range in \( \Delta P^v_{\text{sat}} \) from Figure 7c and d are shown as vertical lines in Figure 7e and f. For both lunar and martian samples, H\text{2}O-eq < 0.2 wt% but the lunar samples have low CO\text{2}-eq (<16 ppm) and S-eq (900 ppm) relative to the martian samples (<240 ppm CO\text{2}-eq and <3500 ppm S-eq) (Figure 7a and b). The lunar samples record low pressures (i.e., \( P^v_{\text{sat}} < 50 \) bars; Figure 7c and e), and excluding S and reduced C-O-H species leads to underestimates of \( P^v_{\text{sat}} \) by up to 130% at \( \Delta \text{FMQ}=5 \) (Figure 7e). The martian samples record much higher pressures but the relative change in \( P^v_{\text{sat}} \) by including S and reduced C-O-H species is still large, up to 100% at \( \Delta \text{FMQ}=5 \) (Figure 6p). Based on our calculations, neither sulfide- nor
graphite-saturation is indicated for lunar samples but most of our calculations for martian samples suggest sulfide (and sometimes graphite) saturation are reached; in such cases, the calculated equilibrium between melt and vapor is metastable, indicated by dashed curves (Figure 7d and f). Care must be taken applying these results as the carbonate solubility used may not be applicable to lunar and martian compositions (although sulfide and sulfate solubilities are appropriate).

Our results are in general agreement with Wetzel et al. (2015) and Newcombe et al. (2017a), who calculated $P_{v}^{w}$ for lunar glasses including reduced C-O-H species in the system: OH$^-$, H$_2$O$_{mol}$, and Fe(CO)$_5$ in the melt and CO and H$_2$O in the vapor (Wetzel et al. 2015); and OH$^-$, CO$_3^{2-}$, and CO in the melt and H$_2$, H$_2$O, CO, and CO$_2$ in the vapor (Newcombe et al. 2017a). In general, this highlights that modelling lunar and martian magmas requires inclusion of both reduced and oxidised C-O-H-S species (Newcombe et al. 2017a) and this will have implications for where magmas are stored and eruption dynamics (e.g., Lo et al. 2021). Also, these calculations of $P_{v}^{w}$ are highly-dependent on the $f_{O2}$ used to calculate $P_{v}^{w}$ and accurate $f_{O2}$ estimates are needed for accurate $P_{v}^{w}$ estimates (e.g., Figure 7e and f). However, quantitative results are sensitive to the solubilities in the melt of the reduced species, and more work is necessary to ensure their accuracy, but the trends shown here are robust.

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7 Figure captions

Figure 1 Calculated values of $P'_\text{sat}$ vs. $\log_{10}(f_{\text{O}_2})$ for a Hawaiian tholeiitic melt at 1200 °C with 
$\text{H}_2\text{O-eq} = 3$ wt%, $\text{CO}_2\text{-eq} = 1000$ ppm, and $\text{S-eq} = 0$ ppm (cases 1 and 2, black horizontal lines 
and blue curves, respectively, from this study; and the horizontal black-dashed line is similar to 
the lower solid line) and blue curves, respectively, from this study; and the horizontal black-dashed line is similar to 
H2O-eq = 3 wt%, CO2-eq = 1000 ppm, and S-eq = 0 ppm (cases 1 and 2, black horizontal lines 
and blue curves, respectively, from this study; and the horizontal black-dashed line is similar to 
case 1 but calculated using VolatileCalc (Newman and Lowenstern 2002)) or S-eq = 1000 ppm 
(case 3, yellow curve). For these conditions, none of the melt compositions are supersaturated 
with respect to graphite, sulfide, or anhydrite. The $f_{\text{O}_2}$ ranges for different tectonic settings from 
Cottrell et al. (2021) are shown by horizontal blue bars below the main figure (the extent of each 
bar shows the range and the black vertical line shows the mode) for mid-ocean ridge (MORB: 
light blue), ocean island (OIB: intermediate blue), and arc (Arc: dark blue) basalts based on 
XANES measurements of Fe$^{3+}$/FeT of glass. The upper limit of $f_{\text{O}_2}$ for lunar and martian magmas 
(L/M) is shown by a capped black horizontal arrow (Wadhwa 2008; Gaillard et al. 2021)

Figure 2 Calculated values of $p_i$'s (top row), species fraction in the melt (middle row), and $x_i$'s 
(bottom row) vs. $\log_{10}(f_{\text{O}_2})$ for cases 1–3 discussed in the text. All calculations are for a Hawaiian 
tholeiitic melt at 1200 °C with $\text{H}_2\text{O-eq} = 3$ wt%, $\text{CO}_2\text{-eq} = 1000$ ppm, and $\text{S-eq} = 0$ ppm (case 1 
shown in both columns and case 2 shown in column 1) or S-eq = 1000 ppm (case 3 shown in 
column 2). The red curves in both columns are for H-bearing species (including CH$_4$, but not 
H$_2$S); blue curves for C-bearing species (including OCS, but not CH$_4$); and yellow curves in 
column 2 are for S-bearing species (including H$_2$S, but not OCS). Results for case 1 (indicated 
by a superscript circle, °) are shown for reference in (a–b) and (e–f): H$_2$O is a dashed horizontal 
black line and CO$_2$ is a dotted horizontal black line. For melt speciation in (c–d), the blue curves 
show the fractions of C in different C-bearing species as a fraction total C in the melt (i.e., CO$_2$ =
solid, CO = dash, CH₄ = dot), and these fractions sum to one. The red curves show the fractions of H in different H-bearing species as a fraction total H in the melt (H₂OT = solid, H₂ = dash, CH₄ = dot, H₂S = dot-dash), which also sum to one. The yellow curves show the fractions of S in different S-bearing species as a fraction total S in the melt (SO₄²⁻ = solid, *S²⁻ = dash, H₂S = dot-dash, S²⁻ₜ = *S²⁻ + H₂S = dot). For the S-bearing melt species shown in (d), both [SO₄²⁻ + *S²⁻ + H₂S] and [SO₄²⁻ + S²⁻ₜ] equal one. For the vapor speciation in (e–f), the sum of all coloured curves is one at any given f_0₂, and likewise for the horizontal black reference lines representing case 1. The pᵢ’s and xᵢ’s of S₂, H₂S, and OCS in (b,f) are always near zero (i.e., close to the x-axis) on this scale (see Figure 3 for a zoomed in version). For these conditions, none of the melt compositions are supersaturated with respect to graphite, sulfide, or anhydrite. The f_0₂ ranges for different settings are as described in Figure 2.

**Figure 3** Variations with log₁₀(f_0₂) for a Hawaiian tholeiitic melt at 1200 °C with H₂O-eq = 3 wt%, CO₂-eq = 1000 ppm, and S-eq 1000 ppm (case 3) of the partial pressures of individual S-bearing vapor species (S₂ – dash, SO₂ – solid, and H₂S – dot in yellow; OCS in blue dash), their sum (ΣS-species = p_S₂ + p_SO₂ + p_H₂S + p_OCS in solid black), ΔPᵥ_sat (dash black), and Pᵥ_sat[case 4] ([S-O] = grey; i.e., p_S₂ + p_SO₂ + p_O₂ for S-eq = 1000 ppm, CO₂-eq = 0 ppm, and H₂O-eq = 0 wt%; Hughes et al., 2023). For these conditions, none of the melt compositions are supersaturated with respect to graphite, sulfide, or anhydrite. The f_0₂ ranges for different settings are as described in Figure 2.

**Figure 4** Effects of varying volatile concentrations (S, H, and C) and f_0₂ on Pᵥ_sat for a Hawaiian tholeiitic melt at 1200 °C. (a) CO₂ against H₂O dissolved in vapor-saturated melt contoured for Pᵥ_sat (bars; black solid curves) calculated assuming case 1. The grey dashed lines in (a) are the H₂O-CO₂ concentrations shown in (b–d) and the grey star is case 1 described in Section 3.1.1.
(b–d) Contours of $\Delta P^\text{sat}$ (bars, difference between case 3 [C-O-H-S] and case 1 [oxidised C-O-H]): (b) H$_2$O-eq = 3 wt%, CO$_2$-eq = 1000 ppm, and S-eq = 0–2000 ppm; (c) H$_2$O-eq = 0–5 wt%, CO$_2$-eq = 1000 ppm, and S-eq = 1000 ppm; and (d) H$_2$O-eq = 3 wt%, CO$_2$-eq = 0–2000 ppm, and S-eq = 1000 ppm. The grey dashed lines in (b–d) correspond to case 3 described in Section 3.1.3 and illustrated in Figure 1, Figure 2b,d,f, and Figure 3 (H$_2$O-eq = 3 wt%, CO$_2$-eq = 1000, and S-eq = 1000 ppm), and the black solid curves are the trace of the maximum in $P^\text{sat}$. For these conditions, none of the melt compositions are supersaturated with respect to graphite or anhydrite, but are supersaturated with respect to sulfide above the white dotted curve. The $f_{O2}$ ranges for different settings are as described in Figure 1.

Figure 5 The (a) magnitude and (b) position of the maximum in $P^\text{sat}$ for a Hawaiian tholeitic melt at 1200 °C using case 3 [C-O-H-S] containing: H$_2$O-eq = 3 wt%, CO$_2$-eq = 1000 ppm, and S-eq = 0–2000 ppm (yellow); H$_2$O-eq = 0–5 wt%, CO$_2$-eq = 1000 ppm, and S-eq = 1000 ppm (red); and H$_2$O-eq = 3 wt%, CO$_2$-eq = 0–2000 ppm, and S-eq = 1000 ppm (blue). The x-axis is the concentration of volatile species that is changing for each curve (e.g., for the yellow curves it is S-eq). Although rotated, the curves in (b) are the same as the black curves in Figure 4b–d.

Figure 6 Melt inclusion (mi, circles) and matrix glass (mg, diamonds) data for natural terrestrial samples from the literature, for which H$_2$O-eq, CO$_2$-eq, and S-eq and Fe$^{3+}$/Fe$^T$ have been measured. (a–c) Mid Ocean Ridge Basalts (MORB): American-Antarctic Ridge = grey, Kolbeinsey Ridge = black, Mid-Atlantic Ridge = blue, Reykjanes Ridge = red, and South-West Indian Ridge = yellow; (d–f) Ocean Island Basalts (OIB): Hawai’i = yellow, and Iceland = red; and (g–i) arc basalts: Bonin = blue, and Marianas = grey. (a,d,g) Measured CO$_2$-eq vs. H$_2$O-eq, with calculated isobars (in kbar) using case 1; and (b,e,h) measured S-eq vs. calculated $f_{O2}$ from measured Fe$^{3+}$/Fe$^T$, with an indication of the location of the sulfur solubility minimum using case
4 [S-O, 1000 ppm S-eq] in grey – it does not use the y-axis values and is there to show the \( f_{O2} \)-position of the SS\textsuperscript{min.} (c,f,i) \( \Delta P^w_{sat} \) vs. \( P^w_{sat} \) (using case 1: only oxidised C-O-H species), where \( \Delta P^w_{sat} \) is the difference between case 3 (all C-O-H-S species; calculated using measured volatile contents and melt composition at 1200 °C) and case 1. The grey solid lines show relative % errors (i.e., 100\*[\( \Delta P^w_{sat}/P^w_{sat} \)]) as labelled on the line. None of the melt compositions are supersaturated with respect to graphite, sulfide, or anhydrite. MORB matrix glasses are from American-Antarctic Ridge (Le Voyer et al. 2019), Kolbeinsey Ridge (Le Voyer et al. 2019), Mid-Atlantic Ridge (Le Voyer et al. 2019), Reykjanes Ridge (Nichols et al. 2002; Shorttle et al. 2015), and South-West Indian Ridge (Wang et al. 2021). Hawai‘i melt inclusions are from Kīlauea (Moussallam et al. 2016) and matrix glasses are from Mauna Kea (Brounce et al. 2017). Iceland melt inclusions are from 1783–84 Laki eruption (Hartley et al. 2015, 2017). Marianas melt inclusions are from Agrigan, Sarigan, and Alamagan volcanoes (Kelley and Cottrell 2012; Brounce et al. 2014) and matrix glasses are from the Mariana Trough and Fina Nagu (Brounce et al. 2014, 2016). Bonin matrix glasses are forearc basalts (Brounce et al. 2021; Coulthard Jr et al. 2022).

Figure 7 Melt inclusion (mi, circles) and matrix glass (mg, diamonds) data for natural lunar (blue; Saal and Hauri 2021) and martian (red; Usui et al. 2012) samples from the literature, where H\(_2\)O-eq, CO\(_2\)-eq, and S-eq have been measured. Measured H\(_2\)O-eq against (a) CO\(_2\)-eq and (b) S-eq. \( \Delta P^w_{sat} \) (difference between cases 3 and 1) calculated for each measured glass composition at 1200 °C against (c–d) log[\( f_{O2} \)] and (e–f) \( P^w_{sat} \) (case 1), where for the solid region of each curve the melt is not supersaturated with respect to graphite, sulfide, or anhydrite (labelled “stable”) but the dashed regions indicate the melt is supersaturated with respect to sulfide and/or graphite (labelled “metastable”; for these conditions the melt is never
supersaturated with respect to anhydrite). The extent of each vertical line in (e–f) corresponds to the vertical range of a single curve in (c–d). Lunar samples are shown in (c,e) and martian samples in (d,f). In (e–f) the grey solid lines show relative % errors as labelled on the line (see Figure 6).
### Table 1 Homogeneous vapor equilibria considered in our model.

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<tr>
<th>Reaction</th>
<th>Equilibrium constant</th>
<th>Eq no.</th>
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<tbody>
<tr>
<td>$\text{H}_2 + 0.5\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$</td>
<td>$K_H = \frac{\tilde{f}_{\text{H}<em>2\text{O}}}{\tilde{f}</em>{\text{H}<em>2}\tilde{f}</em>{\text{O}_2}^{0.5}}$</td>
<td>(5)</td>
</tr>
<tr>
<td>$\text{CO} + 0.5\text{O}_2 \rightleftharpoons \text{CO}_2$</td>
<td>$K_C = \frac{\tilde{f}_{\text{CO}<em>2}}{\tilde{f}</em>{\text{CO}}^{0.5}}$</td>
<td>(6)</td>
</tr>
<tr>
<td>$0.5\text{S}_2 + \text{O}_2 \rightleftharpoons \text{SO}_2$</td>
<td>$K_S = \frac{\tilde{f}_{\text{SO}<em>2}}{\tilde{f}</em>{\text{S}<em>2}^{0.5}\tilde{f}</em>{\text{O}_2}}$</td>
<td>(7)</td>
</tr>
<tr>
<td>$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>$K_{\text{CH}} = \frac{\tilde{f}_{\text{CO}<em>2}\tilde{f}</em>{\text{H}<em>2\text{O}}^2}{\tilde{f}</em>{\text{CH}<em>4}^{\frac{3}{2}}\tilde{f}</em>{\text{H}_2\text{O}}}$</td>
<td>(8)</td>
</tr>
<tr>
<td>$0.5\text{S}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + 0.5\text{O}_2$</td>
<td>$K_{\text{HS}} = \frac{\tilde{f}_{\text{H}<em>2\text{S}}^{0.5}\tilde{f}</em>{\text{O}<em>2}}{\tilde{f}</em>{\text{S}<em>2}^{0.5}\tilde{f}</em>{\text{H}_2\text{O}}}$</td>
<td>(9)</td>
</tr>
<tr>
<td>$2\text{CO}_2 + \text{OCS} \rightleftharpoons 3\text{CO} + \text{SO}_2$</td>
<td>$K_{\text{SC}} = \frac{\tilde{f}<em>{\text{OCS}}^{\frac{3}{2}}\tilde{f}</em>{\text{SO}<em>2}}{\tilde{f}</em>{\text{CO}_2}^2}$</td>
<td>(10)</td>
</tr>
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</table>

**Notes:** $K_{X(Y)}$ are equilibrium constants, which depend on $T$ but are independent of $P$ and are given in Supplementary Material Section 3.1; and $\tilde{f}_i$ is the fugacity of species $i$.

### Table 2 Solubility mechanisms and functions considered in our model.

<table>
<thead>
<tr>
<th>Solubility mechanism</th>
<th>Solubility function</th>
<th>Eq no.</th>
</tr>
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<tbody>
<tr>
<td>$\text{H}_2(v)$ $\rightleftharpoons \text{H}_2\text{mol}(m)$</td>
<td>$\tilde{f}_\text{H}<em>2 = \frac{w</em>{\text{H}<em>2\text{mol}}^m}{C</em>{\text{H}_2\text{mol}}}$</td>
<td>(11)</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(v)$ $\rightleftharpoons \text{H}<em>2\text{O}</em>{\text{mol}}(m)$</td>
<td>$\tilde{f}_{\text{H}<em>2\text{O}} \approx \left(\frac{x</em>{\text{H}_2\text{O}<em>T}^m}{C</em>{\text{H}_2\text{O}_T}}\right)^2$</td>
<td>(12)</td>
</tr>
<tr>
<td>Reaction</td>
<td>Fugacity Equation</td>
<td>Notes</td>
</tr>
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<td>-----------------------------------------------</td>
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<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\text{CO}(v) \rightleftharpoons \text{CO}_{\text{mol}}(m)$</td>
<td>$f_{\text{CO}} = \frac{w_{\text{CO}<em>{\text{mol}}}}{C</em>{\text{CO}_{\text{mol}}}}$</td>
<td>$f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$</td>
</tr>
<tr>
<td>$\text{CO}_2(v) + \text{O}^2(m) \rightleftharpoons \text{CO}_3^{2-}(m)$</td>
<td>$f_{\text{CO}<em>2} = \frac{x</em>{\text{CO}<em>3^{2-}}^m}{C</em>{\text{CO}_3^{2-}}}$</td>
<td>$f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$</td>
</tr>
<tr>
<td>$\text{CH}_4(v) \rightleftharpoons \text{CH}_4\text{,mol}(m)$</td>
<td>$f_{\text{CH}<em>4} = \frac{w</em>{\text{CH}<em>4\text{,mol}}}{C</em>{\text{CH}_4\text{,mol}}}$</td>
<td>$f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$</td>
</tr>
<tr>
<td>$0.5\text{S}_2(v) + \text{O}^2(m) \rightleftharpoons ^*\text{S}^{2-}(m) + 0.5\text{O}_2(v)$</td>
<td>$f_{\text{S}<em>2} = \left(\frac{w</em>{\text{S}^{2-}}^m}{C_{\text{S}^{2-}}}</td>
<td></td>
</tr>
</tbody>
</table><p>ight)^2 f_{\text{O}_2}$ | $f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$ |
| $0.5\text{S}_2(v) + 1.5\text{O}_2(v) + \text{O}^2(m) \rightleftharpoons \text{SO}<em>4^{2-}(m)$ | $f</em>{\text{S}<em>2} = \left(\frac{w</em>{\text{SO}<em>4^{2-}}^m}{C</em>{\text{SO}<em>4^{2-}}}ight)^2 f</em>{\text{O}<em>2}^{-3}$ | $f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$ |
| $\text{H}<em>2\text{S}(v) \rightleftharpoons \text{H}<em>2\text{S}</em>{\text{mol}}(m)$ | $f</em>{\text{H}<em>2\text{S}} = \frac{w</em>{\text{H}<em>2\text{S}</em>{\text{mol}}}}{C</em>{\text{H}<em>2\text{S}</em>{\text{mol}}}}$ | $f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$ |</p>

Notes: $v = \text{vapor}; m = \text{melt}; \text{mol} = \text{molecular}; f_i = \text{fugacity of species } i$; $x_i^m = \text{mole fraction or } w_i^m$ = concentration (depending on the units) of species $i$ in the melt; $C_i = \text{solubility of species } i$, which is the constant of proportionality between the fugacity(ies) and the mole fraction/concentration of species $i$ in the melt; $^*\text{S}^{2-} = \text{sulfide associated with cations in the silicate melt, rather than associated with H, i.e., H}_2\text{S}_{\text{mol}}$. Details of solubilities are given in Supplementary Material Section 3.2.
9 Figures

Figure 1
Figure 2

**case 1: oxidised C-O-H**

Hawaiian tholeiite, 1200 °C: 1000 ppm CO₂-eq

**case 2: oxidised+reduced C-O-H**

+ 3 wt% H₂O-eq ± 1000 ppm S-eq

**case 3: oxidised+reduced C-O-H-S**

$\text{SO}_2$, $\text{H}_2\text{S}$, OCS <0.01
Figure 3
Figure 4
Figure 5

Hawaiian tholeite, 1200 °C: reduced-oxidised C-O-H-S

(a) Graph showing changes in ΔPaw (bars) as a function of H₂O-eq (wt%) for different CO₂-eq and S-eq concentrations. The graph includes lines for 0-2000 ppm CO₂-eq, 0-3 wt% H₂O-eq, 1000 ppm S-eq, and 1000 ppm CO₂-eq + 0-3 wt% H₂O-eq + 1000 ppm S-eq.

(b) Graph showing log₁₀[δf₀, ΔFMQ] as a function of H₂O-eq (wt%) for different CO₂-eq or S-eq (ppm).
Figure 6
Figure 7

(a)玻璃挥发成分
(b) H₂O-eq (wt%)
(c) 单独玻璃分析
(d) 稳定
(e) ΔPₓₑₑ vs. Pₓₑₑ
(f) ΔPₓₑₑ (bar)

ΔFMO-5
ΔFMO-1
10%
200
150
100
50
0

ΔPₓₑₑ (bar)

Pₓₑₑ [oxidised C-O-H] (bar)