**Supplementary Material for “The effects of oxygen fugacity and sulfur on the pressure of vapor-saturation of magma” by Hughes *et al.***

# Terminology

|  |  |
| --- | --- |
| Variable/parameter/abbreviation | Symbol |
| Vapor | *v* |
| Melt | *m* |
| Temperature | *T* |
| Pressure | *P* |
| Pressure of vapor-saturation | | *Pv*sat |
| Partial pressure of species *i* | *pi* |
| Fugacity of species *i* | *fi* |
| Activity of species *i* in phase *j* | | *aij* |
| Mole fraction of species *i* in phase *j* | | *xij* |
| Weight fraction of species *i* in phase *j* | | *wij* |
| Fugacity or activity coefficient of species *i* in phase *j* | | *γij* |
| Equilibrium constant for reaction *j* | *Kj* |
| Solubility for reaction *j* | *Cj* |
| Sulfur solubility minimum | SSmin |
| Fayalite-Magnetite-Quartz | FMQ |

# Melt composition used for calculations

We model a Hawaiian tholeiite melt, which is the same as the silicate melt component used in Hughes et al. (2023) (Table S1).

Table S1 Hawaiian tholeiite melt composition.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| SiO2 | TiO2 | Al2O3 | FeOT | MnO | MgO | CaO | Na2O | K2O | P2O5 |
| 51.29 | 2.50 | 13.70 | 11.04 | 0.02 | 6.70 | 11.03 | 2.27 | 0.43 | 0.21 |

*Notes*: Average of high-SiO2 pillow-rim glasses in HSDP from Mauna Kea volcano from Brounce et al. (2017)*.* All concentrations in wt% and FeOT is all Fe as FeO.

# Thermodynamic framework and parameters

## Vapor

We approximate the vapor as an ideal mixture of non-ideal gases (i.e., the Lewis-Randall rule): i.e., each γ*vi*, although dependent on *P* and *T*, does not depend on the bulk composition of the vapor. Fugacity coefficients of the pure vapor species are calculated from Holland and Powell (1991) for H2O; Shaw and Wones (1964) for H2; and Shi and Saxena (1992) for O2, CO, CH4, S2, OCS, and CO2. We used the modified fugacity coefficient by Hughes et al. (2023) for SO2 based on Shi and Saxena (1992) (Figure S1). Using Shi and Saxena (1992), the fugacity coefficient for H2S increases and then sharply decreases with decreasing *P* for *P* < 500 bars (Figure S1). Hence, as for SO2, we linearly interpolate from 500 bar so that γ*v*H2Scontinuously decreases for 1 < *P* < 500 bar and is equal to 1 when *P* ≤ 1 bar (Figure S1). Equilibrium constants for the homogeneous vapor equilibria depend only on *T* and are taken from Ohmoto and Kerrick (1977) for equations (5–9) in the main text (i.e., *K*H, *K*C, *K*S, *K*CH, and *K*HS) and from Moussallam et al. (2019) for equation (10) in the main text (i.e., *K*SC). *T* and *P* ranges (where appropriate) for fugacity coefficients and equilibrium constants are summarised in Table S2.



Figure S1 Fugacity coefficients for SO2 and H2S. Black horizontal line is for an ideal gas (i.e., γ = 1). Solid curves are calculated using Shi and Saxena (1992) [γi SS92] for i = SO2 (blue) and H2S (red). Dashed lines are a linear interpolations from the value of Shi and Saxena (1992) at 500 bar to γ = 1 at P = 1 bar (γi linear), which is used in this study.

Table S2 Summary of range in composition, P, and T for parameters (fugacity coefficients, equilibrium constants, and solubilities) used in this study for the Hawaiian tholeiite.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Composition | *P* range (bar) | *T* range (°C) | Reference |
| *Fugacity coefficients* | | | | |
|  | n/a | 51–20000 | -118–2227 | Shi and Saxena (1992) |
|  | n/a | 1–3040 | 0–1000 | Shaw and Wones (1964) |
|  | n/a | 1–50000 | 100–1400 | Holland and Powell (1991) |
|  | n/a | 35–20000 | -140–2227 | Shi and Saxena (1992) |
|  | n/a | 74–20000 | 31–2227 | Shi and Saxena (1992) |
|  | n/a | 46–20000 | -82–2227 | Shi and Saxena (1992) |
|  | n/a | 73–20000 | -65–2227 | Shi and Saxena (1992) |
|  | n/a | 78–20000 | 158–2227 | Modified from Shi and Saxena (1992) as in Hughes et al. (2023) |
|  | n/a | 90–20000 | 101–2227 | Modified from Shi and Saxena (1992) for this study |
|  | n/a | 66–20000 | 105–2227 | Shi and Saxena (1992) |
| *Equilibrium constants for homogeneous vapor equilibria* | | | | |
|  | n/a | n/a | Not stated | Ohmoto and Kerrick (1977) |
|  | n/a | n/a | Not stated | Ohmoto and Kerrick (1977) |
|  | n/a | n/a | Not stated | Ohmoto and Kerrick (1977) |
|  | n/a | n/a | Not stated | Ohmoto and Kerrick (1977) |
|  | n/a | n/a | Not stated | Ohmoto and Kerrick (1977) |
|  | n/a | n/a | Not stated | Moussallam et al. (2019) |
| *Solubilities* | | | | |
|  | MORB, Hawaiian tholeiite | 200–15000 | 1200–1600 | Dixon et al. (1995) |
|  | Basalts | 109–5000 | 1050–1250 | This study |
|  | MOR, lunar, and martian basalts | 350–32000 | 1340–1617 | This study |
|  | Basalt | 7000–30000 | 1400–1450 | Modified from Hirschmann et al. (2012) for this study |
|  | Haplobasalt | 7000–30000 | 1400–1450 | Ardia et al. (2013) |
|  | Silicates | 1 | 1200–1500 | O’Neill (2021) |
|  | Silicates | 1 | 1200–1500 | O’Neill and Mavrogenes (2022) |
|  | Basalt | 2040–3120 | 1050 | This study |
| *Other* | | | | |
| Fe3+/FeT | Silicates | 1–?30000 | 1200–1630 | Kress and Carmichael (1991) |

*Notes:* Composition, *P*, and *T* range are stated in the reference paper or based on the range of experimental conditions used. n/a = not applicable. Although not stated in the papers, equilibrium constants for homogeneous reactions will be applicable at magmatic temperatures.

## Melt

In the following sections, we detail the solubility functions used in our framework and Table S2 summarises the compositional, *P*, and *T* range for the solubilities. Other functions for the solubilities can be added to our framework, as long as they are for the solubility functions included.

### Carbon dioxide (CO2) solubility

We describe the solubility of CO2 in basaltic melts using the following equilibrium (e.g., Blank and Brooker, 1994; Dixon et al., 1995; Stolper and Holloway, 1988):

where O2- refers to a reactive oxygen in the silicate melt. To begin with, if we assume that there is a single type of O2-, reaction (S1) has an equilibrium constant (*K*) given by:

where *K*CO32- depends only on *P* and *T*; *ami* is activity of the *i*th component in the silicate melt (denoted with superscript *m*), which depends on *P*, *T*, and *xmi*; *xmi* is the mole fraction of the *i*th component in the silicate melt; and *γmi* is the activity coefficient of the *i*th component in the silicate melt, which also depends on *P*, *T*, and *xmi*. These definitions (*Ki*, *ami*, *xmi*, and *γmi*) are also valid for the equilibria developed below involving other volatile components.

If we make the approximation that the carbonate ion behaves ideally in the silicate melt, then *γm*CO32-=1 and *am*CO32- = *xm*CO32-. Additionally, we can assume the concentration of CO32- in the silicate melt is sufficiently small that a negligible quantity of O2- in the silicate melt is consumed by its formation. This is typically the case in natural silicate melts due to the low solubility of CO32- (e.g., Dixon and Stolper, 1995; Jendrzejewski et al., 1997; Pan et al., 1991; Shishkina et al., 2010; Stolper and Holloway, 1988). In this case, *am*O2- can be taken as a constant (*am,0*O2-) and *f*CO2 is directly proportional to *xm*CO32-:

By combining the oxide activity and equilibrium constant, equation (S3) becomes:

where *C*CO32- is the solubility of carbonate. We use the Dixon et al. (1995) for parameterisation of *C*CO32- for MORB melts in our calculations, which incorporates a *P*-dependence using a volume term, assumed to be constant:

where ln*K* is ln*Ci*, ln*K*0 is ln*Ci*at a reference set of conditions (*P*0, *T*0), and Δ*V* is the volume change of the reaction of the condensed phases: *K*0 = 3.8 × 10-7; *P*0 = 1 bar; and Δ*V* = 23.0 cm3/mol. The parameterisation uses data from Dixon et al. (1995) and Pan et al. (1991) on Hawaiian tholeiite and MOR basalt compositions at 200–15000 bar and 1200–1600 °C experimental conditions. Options for other basaltic compositions (i.e., Δ*V* and ln*K*0) are compiled from Table 2 of Allison et al. (2022) and shown in Table S3.

Table S3 Thermodynamic parameters to calculate carbonate solubility for different basaltic melt compositions.

|  |  |  |  |
| --- | --- | --- | --- |
| Composition | Δ*V* (cm3/mol) | ln*K*0 | Reference |
| Hawaiian tholeiite/MORB | 23.0 | -14.78 | Dixon et al. (1995) |
| Sunset Crater | 16.40 | -14.67 | Allison et al. (2019) |
| SFVF | 15.02 | -14.87 | Allison et al. (2019) |
| Erebus | 15.83 | -14.65 | Allison et al. (2019) |
| Vesuvius | 24.42 | -14.04 | Allison et al. (2019) |
| Etna | 21.59 | -14.28 | Allison et al. (2019) |
| Stromboli | 14.93 | -14.68 | Allison et al. (2019) |
| Basanite | 21.72 | -14.32 | Allison et al. (2022) |
| Leucite | 21.53 | -13.36 | Allison et al. (2022) |
| AH3 phonotephrite | 30.45 | -13.26 | Allison et al. (2022) |
| N72 basalt | 19.05 | -14.86 | Allison et al. (2022) |

We only consider carbonate in our calculations. However, molecular CO2 can also dissolve in silicate melts: it occurs as well as carbonate in andesite and dacite compositions and is the only species in rhyolites (e.g., Blank et al., 1993; Blank and Brooker, 1994; Botcharnikov et al., 2006). Molecular CO2 has a different heterogeneous melt-vapor equilibrium to carbonate, with its associated equilibrium constant:

Using similar assumptions to before (*γm*CO2,mol = 1, therefore *am*CO2,mol = *xm*CO2,mol) and by combining the activity coefficients and equilibrium constants :

When both CO2,mol and CO32- are present (e.g., andesites and dacites; Behrens et al., 2004; Botcharnikov et al., 2006; Konschak and Keppler, 2014), the total amount of oxidised carbon in the melt is the sum for the amount of CO2,mol and CO32-:

We can subtract equation (S1) from equation (S6) to generate the following homogeneous melt equilibrium and its associated equilibrium constant:

where there is only a single type of reactive O2- to describe the conversion of CO2,mol to CO32- within the silicate melt. By combining the activity coefficients, equilibrium constants, and oxide concentration, this becomes:

Using pair-wise combinations of equations (S3, S6, and S12) – as only two out of the three reactions are needed to describe the system – we obtain:

### Water (H2O) solubility

In silicate melts H2O dissolves as molecular H2O (H2Omol) and hydroxyl ions (OH-) (e.g., Dixon and Stolper, 1995; Lesne et al., 2011; Stolper, 1982a). We describe the solubility of H2Omol as follows, with its associated equilibrium constant,

Additionally, assuming only one type of O2- in the silicate melt, H2O in the vapor or H2Omol in the melt can react with O2- to form OH- by the following heterogeneous or homogeneous melt(-vapor) equilibria with their associated equilibrium constants,

As developed in Stolper (1982), if we assume all species are ideal (all *γmi* = 1) we can apply an ideal mixing model (no energetic interactions between these groups and with O2- ions) and calculate *f*H2O from the total amount of H2O dissolved as H2Omol and OH-. Other models have been applied, such as a regular solution model, which must be solved numerically to calculate *xm*H2O,mol for a given *xm*H2O,T (Silver and Stolper, 1989). However, at relatively low total water contents OH- dominates and therefore *am*H2O,mol *k*(*xm*H2O,T)2 (where *k* is a constant; Stolper, 1982b). This relationship is known as Siefert’s law, and can be used to provide a reasonable approximation to *f*H2O up to ~6.4 wt. % dissolved water (Stolper, 1982b). This results in the following equilibrium constant:

which becomes the following when combining the oxide activity, equilibrium constant, and *k*-constant:

|  |  |
| --- | --- |
|  | (S21) |

The solubility of water does not appear to depend heavily on *P*, *T*, or melt composition (e.g., Allison et al., 2022; Iacono-Marziano et al., 2012; Lesne et al., 2011; Moore et al., 1998): hence, we do not incorporate any dependency on these parameters into *C*H2OT (e.g., there is no Δ*V* term). To calculate *C*H2OT, we take the experimental data compiled by Allison et al. (2022), which contains a wide range of basaltic melt compositions. We filter out data with H2O contents higher than 6 wt% (remaining experimental conditions are 1050–1250 °C and 109–5000 bars) and convert weight fraction to mole fraction on a singular oxygen basis assuming a molecular weight of 36.594 g/mol (this is the value used by Dixon et al. (1995) for their MORB composition, but it does not vary greatly between basalts). We fit a straight line through the origin for *f*H2O against (*xm*H2OT)2, which gives *C*H2OT = 4.6114 × 10-6 (Figure S2). Our water solubility is very similar to that of Dixon et al. (1995), which uses a regular solution model with H2Omol and OH-, and Lesne et al. (2011), which uses a power-law fit between *f*H2O and wt% H2O (Figure S2).



Figure S2 Fitting the water solubility function for basaltic melt compositions [fH2O against (xmH2OT)2, where xmH2OT is in mole fraction]. Grey circles (n = 177) are the experimental data on basalts compiled by Allison et al. (2022) with H2OT < 6 wt%. The red solid curve is the model of Lesne et al. (2011), the blue solid curve is the model of Dixon et al. (1995) [their table 5], and the black solid line is our fit to the data. For reference, (xmH2OT)2 of 0.005 corresponds to 3.48 wt% H2O, 0.010 to 4.92 wt% H2O, and 0.015 to 6.03 wt% H2O.

### Hydrogen (H2), carbon monoxide (CO), and methane (CH4) solubility

Under sufficiently reducing conditions (e.g., lunar and some martian magmas) additional carbon- and hydrogen-bearing species can dissolve in silicate melts: molecular H2 (Gaillard et al., 2003; Hirschmann et al., 2012; Kadik et al., 2004; Mysen et al., 2011), molecular CO (COmol; e.g., Brooker *et al.* 1999; Armstrong *et al.* 2015; Yoshioka *et al.* 2019), and molecular CH4 (CH4,mol; e.g., Ardia *et al.* 2013; Mysen 2013). We consider dissolution via the following reactions, with their associated equilibrium constants and solubilities, which are summarised in Table S4.

Table S4 Thermodynamic parameters to calculate the solubility of reduced C-O-H species in different melt compositions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Species | Composition | Δ*V* (cm3/mol) | ln*K*0 | References |
| H2,mol | Basalt | 10.6 | -0.9624 | Hirschmann et al. (2012) |
| H2,mol | Andesite | 11.3 | -0.1296 | Hirschmann et al. (2012) |
| COmol | Basalt | 15.2 | -2.11 | Armstrong et al. (2015); Stanley et al., (2014); Wetzel et al., (2013) |
| CH4,mol | Basalt | 26.85 | 4.93 | Ardia et al. (2013) |

For molecular H2:

We parameterise *C*H2,mol using equation (S5) to include the effects of *P* with experimental data on a basalt at 1400–1450 °C and 7000–30000 bar (Hirschmann et al., 2012; Figure S3). We use = 10.6 cm3/mol from Hirschmann et al. (2012) where *P*0 = 1 bar; but calculate ln*K*0 = -0.9624 where H2,mol is in ppm and *f*H2 is in bar. Values for the andesite composition in the same experimental study have = 11.3 cm3/mol (Hirschmann et al., 2012) and ln*K*0 = -0.1296. The basalt value is used in the calculations in our study.

Chart, scatter chart

Description automatically generated

Figure S3 Fitting the molecular H2 solubility function using equation (S5). Blue circles are the experimental data on basalt and red squares on andesite from Hirschmann et al. (2012). The solid lines are the fit to the data.

For molecular CO:

We parameterise *C*COmol using equation (S5) to include the effects of *P* (but not *T*) with experimental data on basalts (MOR, lunar, and martian basalt compositions) at 1340–1617 °C and 350–32000 bar (Armstrong et al., 2015; Stanley et al., 2014; Wetzel et al., 2013; Figure S4). This gives ln*K*0 = -2.11; *P*0 = 1 bar; and = 15.2 cm3/mol where COmol is in ppm and *f*CO is in bar.

Chart, scatter chart

Description automatically generated

Figure S4 Fitting the molecular CO solubility function for basaltic melt compositions using equation (S5). Experimental data are from Wetzel et al. (2013) [square], Stanley et al. (2014) [circle], and Armstrong et al. (2015) [diamond]. The black solid line is the fit to the data, excluding the blue squares at 9000 bars.

For molecular CH4:

We use the parameterisation of *C*CH4,mol by Ardia et al. (2013), which is based on equation (S5) to include the effects of *P*: ln*K*0 = 4.93; *P*0 = 1 bar; and = 26.85 cm3/mol, where CH4,mol is in ppm and *f*CH4 is in bar. This is based on experimental data on a haplobasalt at 1400–1450 °C and 7000–30000 bar (Ardia et al., 2013).

### Sulfur (S2) solubility

There are two mechanisms for S2 dissolution into silicate melt to form either sulfide (S2-) and/or sulfate (SO42-) species (e.g., Boulliung and Wood, 2022; Fincham and Richardson, 1954; Métrich et al., 2009; O’Neill, 2021; O’Neill and Mavrogenes, 2022, 2002; Paris et al., 2001; Wilke et al., 2011). There is currently no evidence for other valence states or species (e.g., S4+) in silicate melts (Wilke et al., 2008). Hence, the total dissolved sulfur content (ST) of the silicate melt is:

Sulfur dissolution as S2- replaces O2- 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) according to:

which, assuming there is a single type of O2-, has the following equilibrium constant:

Making similar assumptions as previously (e.g., *γm*S2- = 1 and *am*O2- = *am*,0O2-):

Likewise, sulfur dissolving as SO42- species in silicate melts (e.g., Fincham and Richardson 1954; Moretti and Ottonello 2003, 2005; Moretti and Papale 2004; Baker and Moretti 2011; Moretti 2021) can be simply described via the following reaction (again assuming there is a single type of reactive O2-) with its associated equilibrium constant,

Using similar approximations to before (*γm*SO42- = 1 and *am*O2- = *am*,0O2-):

Typically, only the total sulfur content (ST) dissolved in the silicate melt (or glass) is known, rather than distinguishable concentrations of S2- and SO42-. Substituting equations (S34) and (S37) for *xm*S2- and *xm*SO42- respectively, into the mass balance equation (S31) and rearranging gives:

The solubility of sulfur depends on melt composition, *P*, and *T* (e.g., Boulliung and Wood, 2022; Moretti, 2021; Moretti and Ottonello, 2005; Nash et al., 2019; O’Neill, 2021; O’Neill and Mavrogenes, 2022, 2002; Webster et al., 2009; Webster and Botcharnikov, 2011). The dependence of sulfide and sulfate solubility on silicate melt composition can be described using the concepts of sulfide and sulfate capacity (e.g., Fincham and Richardson, 1954; O’Neill, 2021; O’Neill and Mavrogenes, 2022, 2002; Wagner, 1975). For simplicity in the above description, we assumed there was only one type of O2- in the silicate melt, which is not generally a valid assumption or approximation. Instead, we can write a reaction such as equation (S22) for each the different oxide components in the melt (e.g., FeO, CaO, etc.). For example, for FeS with its associated equilibrium constant:

This can be rearranged to give the concentration of sulfur dissolved in the silicate melt as the FeS species:

where *C*FeS (equivalent to the term in [] brackets) is known as the “sulfide capacity” for Fe2+, which we could simplify further if we assume melt species mix ideally (i.e., *γmi* = 1). We can write equations similar to (S39–S41) for all oxide and associated sulfide species in the silicate melt (e.g., CaO → CaS, etc.: *n* different oxide species with cation of element *M* of charge *z*) and the total amount of sulfide dissolved in the silicate melt is the sum of the concentrations of each of the sulfide species (where = 1 has been applied):

where *C*S2- is the “sulfide capacity”. As the equilibrium constants for each reaction only depend on *P* and *T*, *C*S2- is a constant for a given melt composition, *P*, and *T*.

A similar approach can be applied to the sulfate capacity, where in equation (S35) we also assumed a single type of O2- in the silicate melt. For CaSO4 the equivalent equations to (S39–S41) are:

where *C*CaSO4 (equivalent to the term in [] brackets) is the sulfate capacity for Ca2+, which we could simplify further if we assume melt species mix ideally (i.e., *γmi* = 1). As with sulfide capacity, this can be extended to all oxide components and their associated sulfate species in the silicate melt (e.g., Na2O → Na2SO4, etc.) to calculate the total concentration of sulfate dissolved in the silicate melt. Assuming the melt species behave ideally (*γmi* = 1) gives:

Again, as described above for the sulfide capacity, *C*SO42- is a constant for a given melt composition, *P*, and *T*.

We adopt the parameterization of *C*S2- from O’Neill (2021), which although more complex than a simple linear combination of mole fractions (as denoted in equation S42) – reflecting ultimately the complex dependence of the activity coefficients on *T* and *xmi* – is well calibrated for silicate compositions. Although O’Neill (2021) includes the dependence of *T* (based on data between 1200–1500 °C), the parameterisation does not include a *P*-dependence because the experiments used to calibrate the parameterisation are typically conducted at one atmosphere. This parameterisation does include a term for the effect of H2O on *C*S2-, but O’Neill (2021) emphasizes that the dataset used for its calibration is limited. We instead model the effect of H2S using a separate H2S solubility mechanism detailed in Supplementary Material Section 2.2.5, but do include the effects of dilution by H2O on melt composition in the*C\**S2-.

When we began this work there had not been a similarly comprehensive treatment for sulfate capacity. Hence, we developed an expression from available literature data, as described in Hughes et al. (2023). Briefly, we calculated *C*S6+ from glasses with known *T*, measured S6+/ST and Fe3+/FeT, and used O’Neill (2021) to calculate *C*S2-: these are the symbols in Figure S5. The *T*-relationship was derived by fitting the *C*S6+ calculated for Kīlauea glasses (Figure S5). This gave a value of the Hawaiian basalt used in our model of log10(CS6+) = +13.24 at 1200 °C (Figure S5) and is independent of *P*. This value agrees well with the parameterisations of Boulliung and Wood (2022) and O’Neill and Mavrogenes (2022) (Figure S2). However, we now use the parameterisation of O’Neill and Mavrogenes (2022) for our modelling, which is based on experiments covering a wide range of silicate compositions at 1200–1500 °C and 1 bar. For both sulfide and sulfate capacity using O’Neill (2021) and O’Neill and Mavrogenes (2022), the sulfur content is calculated as ppm weight, rather than mole fraction.



Figure S5 Calculated sulfate capacities against temperature for natural samples where CS6+ has been calculated by Hughes et al. (2023) from Hawai’i: Mauna Kea in purple squares (Brounce et al., 2017), Kīlauea in yellow diamonds (Lerner, 2020), and Lōʻihi Seamount in green circles (Dixon et al., 1991; Jugo et al., 2010; Wallace and Carmichael, 1992). Modelled temperature dependence for the sulfate capacity of the Hawaiian tholeiite in Table S1 using parameterisations by Nash et al. (2019) (N+19, black long-dashed curve), Hughes et al. (2023) (H+23, solid black curve), O’Neill and Mavrogenes (2022) (OM22, black short-dashed curve), and Boulliung and Wood (2022) (BW22, black dot-dash curve – uses the version in Boulliung and Wood, 2023).

### Hydrogen sulfide (H2S) solubility

Rather than including the effect of water on sulfide solubility using a H2O term in the sulfide capacity approach described in Section 3.2.4, we consider the following dissolution mechanism of molecular H2S and its associated equilibrium constant:

|  |  |
| --- | --- |
| H2S(*v*) ⇄ H2Smol(*m*) | (S47) |
|  | (S48) |
|  | (S49) |

Clemente et al. (2004) and Lesne et al. (2015) assumed H2Smol was an S-bearing species in the silicate melt and calculated equilibrium constants for this reaction for rhyolites and basalts, respectively, including effects of *T*, *P*, and FeO contents of the melt based on the limited available data. For simplicity, we regress the literature data (*f*H2S and dissolved H2S in ppm) from Lesne et al. (2015) and Moune et al. (2009) for basaltic and basaltic-andesite melts to calculate *C*H2Smol without including the effects of *T*, *P*, and FeO contents of the melt (Figure S6). This is based on experimental data at 2040–3120 bar and 1050 °C. We use the value for basalt in our modelling.



Figure S6 Fitting the H2S solubility function based on H2S vs. fH2S calculated by Lesne et al. (2015) using data from Moune et al. (2009) for basaltic (blue circles) and basaltic andesite (red squares) melt composition. Linear regressions for each composition are used to calculate CH2Smol.

### Oxygen fugacity and iron redox

Conversion between absolute oxygen fugacity and ΔFMQ (relative to the Fayalite-Magnetite-Quartz buffer) uses FMβQ from Frost (1991). We use the relationships given in the appendix of Kress and Carmichael (1991) to relate *f*O2 to melt Fe3+/Fe2+ (i.e., their equations A-1 through A-6 and Table A1), which is calibrated on a wide range of silicate compositions at 1200–1630 °C and appropriate for high pressures (30000 bar according to figures made in their paper).

# Calculating *Pv*sat, vapor composition, and melt speciation

Here we outline the approach for calculating *Pv*sat, vapor composition, and melt speciation described in Sections 2.3 and 2.4 of the main text in more detail (a flow chart of this calculation is shown in Figure S7).

1. The inputs for the calculation of *Pv*sat , vapor composition, and melt speciation are *T*, major element composition of the melt, concentrations of volatile components in the melt (H2O-eq, CO2-eq, and S-eq), *f*O2 or Fe3+/FeT, tolerance of convergence of *Pv*sat (d*x*; e.g., 0.1 bar), and step size and tolerance for the Newton Raphson solver for calculating melt speciation.
2. First, an initial value for *P* is assumed: *Pn* refers to the assumed *P* at guess *n*. The first *P* (i.e., *P*0) in all calculations described in the text is 40000 bars, which helps to ensure convergence.
3. The melt speciation is then calculated:
   1. Initially, all C is assumed to dissolve as CO32-, all H as H2OT, and all S as \*S2-.
   2. Solubilities, equilibrium constants, and *f*O2 are calculated at the given *T*, *P*, and melt composition.
   3. Using these values, the concentrations of CO32-, H2OT, and \*S2- are used to calculate *f*CO2, *f*H2O, and *f*S2 using equations (12, 14, and 16) given in Table 2 of the main text.
   4. The fugacities calculated in step 3c (i.e., *f*CO2, *f*H2O, *f*S2) and a value for *f*O2 (either specific relative to FMQ or based on measured Fe3+/FeT for natural glasses) are used to calculate *f*CO, *f*H2, *f*CH4, and *f*H2S using equations (5, 6, 8, 9) in Table 1 of the main text.
   5. From the fugacities obtained in step 3c and d, the concentrations of H2,mol, COmol, CH4,mol, SO42-, and H2Smol in the melt are then calculated using equations (11, 13, 14, 17, and 18) in Table 3 of the main text.
   6. There are three mass balance equations across all volatile species dissolved in the melt: one each for C, H, and S (note that O is not mass balanced because *f*O2 is an independent variable). The total dissolved C, H, and S content of the melt are then determined from the concentrations of CO32-, H2OT, \*S2-, H2,mol, COmol, CH4,mol, SO42-, and H2Smol in the melt. The difference between these sums of C, H, and S and the known total C, H, and S of the melt are then calculated.
   7. The value of the differentials of each of the mass balance equations with respect to C, H, and S is calculated (nine values in total).
   8. A Newton Raphson method is used to converge on concentrations of CO32-, H2OT, and \*S2- that satisfy the mass balance equations by repeating 3c–g.
4. Next, *Pv*sat is calculated:
   1. The calculated melt speciation is used to calculate *f*CO2, *f*H2O, *f*S2, *f*CO, *f*H2, *f*CH4, and *f*H2S as described in 3c–d.
   2. *f*O2 and *f*S2 are used to calculate *f*SO2 using equation (7) in Table 1 of the main text, then *f*SO2, *f*CO2, and *f*CO are used to calculate *f*OCS using equation (10) in Table 1 of the main text.
   3. All these fugacities are converted to partial pressures using equation (2) in the main text.
   4. *Pv*sat is calculated by summing all the *pi*’s (i.e., using equation (4) in the main text).
   5. Convergence of this iterative calculation is achieved when d*x* = *Pn* – *Pv*sat(*Pn*) → 0. In practice, we halt the iterations and declare *Pv*sat to have been determined when d*x* is less than a specified tolerance. If after a given iteration, d*x* exceeds the specified tolerance, *Pn*+1is set to *Pv*sat for the next iterations, and steps 3–4 are repeated (i.e., the melt speciation is recalculated at the new *P*, as is *Pv*sat) until d*x* is within the specified tolerance. In this study, d*x* = 0.1 bar.
5. Once *Pv*sat has been found based on the criteria of step 4e, the melt speciation and vapor composition are calculated at *Pv*sat and we check whether the melt is supersaturated with graphite, sulfide, or anhydrite

*Notes*:

* For case 1 (only oxidised C-O-H species in the melt and vapor), melt speciation does not have to be calculated: only steps 1; 2; 3b–c (excluding references to *f*S2 and \*S2-); 4a (excluding references to species other than CO2 and H2O) and 4c–e; and 5 are used.
* For case 2 (reduced and oxidised C-O-H species in the melt and vapor), melt speciation does have to be calculated: steps 1; 2; 3a–h (excluding references to S-bearing species); 4a (excluding references to S-bearing species) and 4c–e; and 5 are used.
* For case 2’ (reduced and oxidised C-O-H species in the vapor, only oxidised C-O-H species in the melt), melt speciation does not have to be calculated: only steps 1; 2; 3b–c (excluding references to *f*S2 and \*S2-); 4a (excluding references to S-bearing species) and c–e; and 5 are used.
* For case 3 (all C-O-H-S species in the melt and vapor), melt speciation does have to calculated: all steps are included.
* For case 3’ (all C-O-H-S species in the melt and vapor, except H2Smol is insoluble in the melt), melt speciation does have to be calculated: all steps are included, except H2Smol is not calculated in step 3e and therefore does not contribute to the mass balances or values of the derivatives.
* For case 4 (only S-O species in the melt and vapor), see Supplementary Material in Hughes et al. (2023): “2.1 Silicate melt + vapor: *T*, *f*O2, and *f*S2, *wm*ST, *µ*FeS, or *µ*CaSO4” using step 2b in that description.
* The model is available on github (<https://github.com/eryhughes/Pvsat>).

Shape

Description automatically generated with medium confidence

Figure S7 Flow chart describing the calculation of Pvsat.

# Comparison to other models

We compare our calculated *Pv*sat assuming only oxidised C-O-H species in the melt and vapor (i.e., case 1 – no S) to several available *Pv*sat calculators. All calculations are at 1200 °C. For VolatileCalc (Newman and Lowenstern, 2002), we set SiO2 to 49 wt%. For MagmaSat (Ghiorso and Gualda, 2015) and MafiCH (Allison et al., 2022), we use the Hawaiian tholeiite composition in Table S1. *Pv*sat was calculated for 0.01, 1, 2, 3, 4, and 5 wt% H2O with 1000 ppm CO2 (Figure S7) and 1, 500, 1000, 1500, and 2000 ppm CO2 and 3 wt% H2O (Figure S8). We could not achieve convergence with MafiCH for 1 ppm CO2, hence 2 ppm CO2 was used. Likewise, we were unable to achieve convergence with MagmaSat for 1 ppm CO2 and 3 wt% H2O or 1000 ppm CO2 and 0.01 or 5 wt% H2O; no results are presented for these volatile contents using this model.



Figure S8 Pressure of vapor saturation (Pvsat) calculated for varying H2O concentrations at 1000 ppm CO2 using different models: VolatileCalc (yellow), MagmaSat (orange), MafiCH (blue), and this study (grey). This is equivalent to case 1 (only oxidised C-O-H species in the melt and vapor).



Figure S9 Pressure of vapor saturation (Pvsat) calculated for varying CO2 concetrations at 3 wt% H2O using different models: VolatileCalc (yellow), MagmaSat (orange), MafiCH (blue), and this study (grey). This is equivalent to case 1 (only oxidised C-O-H species in the melt and vapor).

All models show similar trends. For constant CO2 and increasing H2O, all models are slightly concave up; whereas for constant H2O and increasing CO2, all models essentially linearly increase. However, the models differ in their absolute values of *Pv*sat for the different combinations of H2O-CO2. The model used in this study and VolatileCalc are most similar, reflecting that they use similar carbonate solubilities (the curves converge as H2O → 0 wt% at 1000 ppm CO2; Figure S8) and similar water solubilities (the curves have similar values at 0 ppm CO2 at 3 wt% H2O; Figure S9). MafiCH also has a similar water solubility (Figure S9). The carbonate solubility functions of MafiC and MagmaSat differ considerably from those of VolatileCalc and the one used in this study, as shown by the large difference in *Pv*sat at 0 wt% H2O and 1000 ppm CO2 (or 1 wt% H2O for MagmaSat; Figure S8). This highlights the sensitivity of *Pv*sat calculations to carbonate solubility and that an accurate model for carbonate solubility in basalts is still to be found (e.g., Wieser et al., 2022).

# Additional discussion for “*Pv*sat for a reference case with fixed total volatile concentrations in the melt”

## Derivation of proportionality between pSO2 and wmST

In Section 3.2.2 of the main text, where we discussed the SSmin in C- and H-bearing melts, we state that the magnitude of maximum in Δ*Pv*sat is proportional to S-eq because *p*SO2 is proportional to the total sulfur content of the melt. We prove this statement here.

The total S in the melt (*wm*ST) is a combination of the sulfur dissolved as \*S2-, SO42-, and H2Smol:

|  |  |
| --- | --- |
| . | (S50) |

where *wm*\*S2 is the sulfur dissolved in the melt as \*S2-, *wm*S|H2S is the sulfur dissolved in the melt as H2S, and *wm*S|SO42- is the sulfur dissolved in the melt as SO42-. Substituting equations (7, 9, 16–18) from the main text into equation (S50) gives:

|  |  |
| --- | --- |
|  | (S51) |

Hence, *p*SO2 is proportional to *wm*ST.

## Comparison between case 3 and 4 for position and magnitude of Pvsat

The overall behaviour of case 3 shown in Figure 3 of the main text is similar to that calculated for the S-O (i.e., H- and C-absent, referred to as case 4) system presented in Hughes *et al.* (2023), where there is also a maximum in *Pv*sat in the *f*O2 range in which both \*S2- and SO42- are present in the melt in similar quantities. In the S-O system, the maximum reflects entirely a maximum in *p*SO2 (the positions of the maxima in *Pv*sat and *p*SO2 are at the same *f*O2). Here, the maximum reflects primarily the behaviour of SO2 in the vapor, but there are small influences from the other S-bearing species (e.g., H2S and OCS) as well. Thus, its position is influenced by the presence of C-O-H species (Figure 3 in the main text). Additionally, the presence of C-O-H species changes both the magnitude and position of the maximum in *Pv*sat; i.e., for the same S-eq, the sum of the *pi*’s of the S-bearing species is roughly half when C-O-H species are included compared to only S-O species, and the position of the maximum shifts to lower *f*O2s.

## Additional cases exploring the effect of insoluble C-O-H and H2S species on Pvsat

Here we present additional cases not shown in the main text that explore the effects of assuming reduced C-O-H and H2S species are insoluble in the melt (Figure S10):

* Case 2’: All dissolved C-O-H species in the melt are oxidized, (i.e., only CO32‑, OH-, and H2Omol are dissolved in the melt), but reduced species (i.e., H2, CO, CH4) are present in the vapor phase, as is O2 (Supplementary Material Section 7.1). This case contrasts with case 2 in the main text in that reduced C-O-H species in case 2’ are assumed to be insoluble in the melt.
* Case 3’: S-bearing species are present in the melt (SO42- and \*S2-) and vapor (S2, SO2, H2S, and OCS) in addition to the oxidised and reduced C-O-H species included in case 2 in the main text, but H2Smol is treated as insoluble in the melt (Supplementary Material Section 7.2). When compared to case 3 described in the main text, this allows quantitative evaluation in the context of our model of how the solubility of H2Smol influences *Pv*sat and the composition of the saturating vapor.

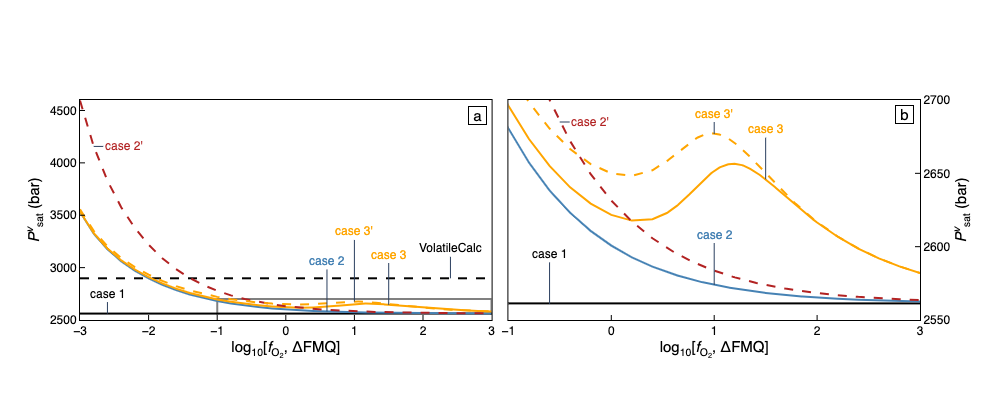


Figure S10 Calculated values of Pvsat vs. log10(fO2) for a Hawaiian tholeiitic melt at 1200 °C with H2O-eq = 3 wt%, CO2-eq = 1000 ppm, and S-eq = 0 ppm (cases 1, 2, and 2’, black-solid, blue-solid, and red-dash, respectively, and using VolatileCalc by Newman and Lowenstern, 2002, black-dash) or S-eq = 1000 ppm (case 3 and 3’, yellow-solid and -dash, respectively), where **(b)** is a zoomed-in version of **(a)** below the black-dash line. For these conditions, there is no saturation with graphite, sulfide, or anhydrite.

### Case 2’: reduced C-O-H species in the vapor but insoluble in the melt.

The increase in *Pv*sat with decreasing *f*O2 when reduced C-O-H species are treated as insoluble (case 2’) is larger than when reduced C-O-H species have a small but finite solubility (case 2) (Figure S10). The concentrations of CO32- and H2OT in the melt do not decrease with decreasing *f*O2 in case 2’ (Figure S11d) because C and H in the melt cannot convert to reduced C-O-H species because they are insoluble. Hence, the sum of the partial pressures of the oxidised C-O-H species decreases less with decreasing *f*O2 for case 2’ than case 2 (Figure S11a). At the same time, the sum of the partial pressures of the reduced C-O-H species increases more with decreasing *f*O2 in case 2’ than case 2 (Figure S11b) because the reduced C-O-H species are insoluble (Figure S11d). Overall, this leads to larger *Pv*sat in case 2’ but the magnitude of this effect depends strongly on the solubility of the reduced species in the melt. As a result, *Pv*sat can be significantly overestimated if the reduced species are treated as completely insoluble in the melt. The comparison between cases 2 and 2’ highlights the importance of including heterogeneous equilibria for reduced species when calculating *Pv*sat at reduced conditions (Figure S11d). Quantifying the magnitude of this effect for natural systems will, however, depend on improved measurements of the solubility in of the reduced species in naturally occurring silicate melts and of their dependence on melt composition.

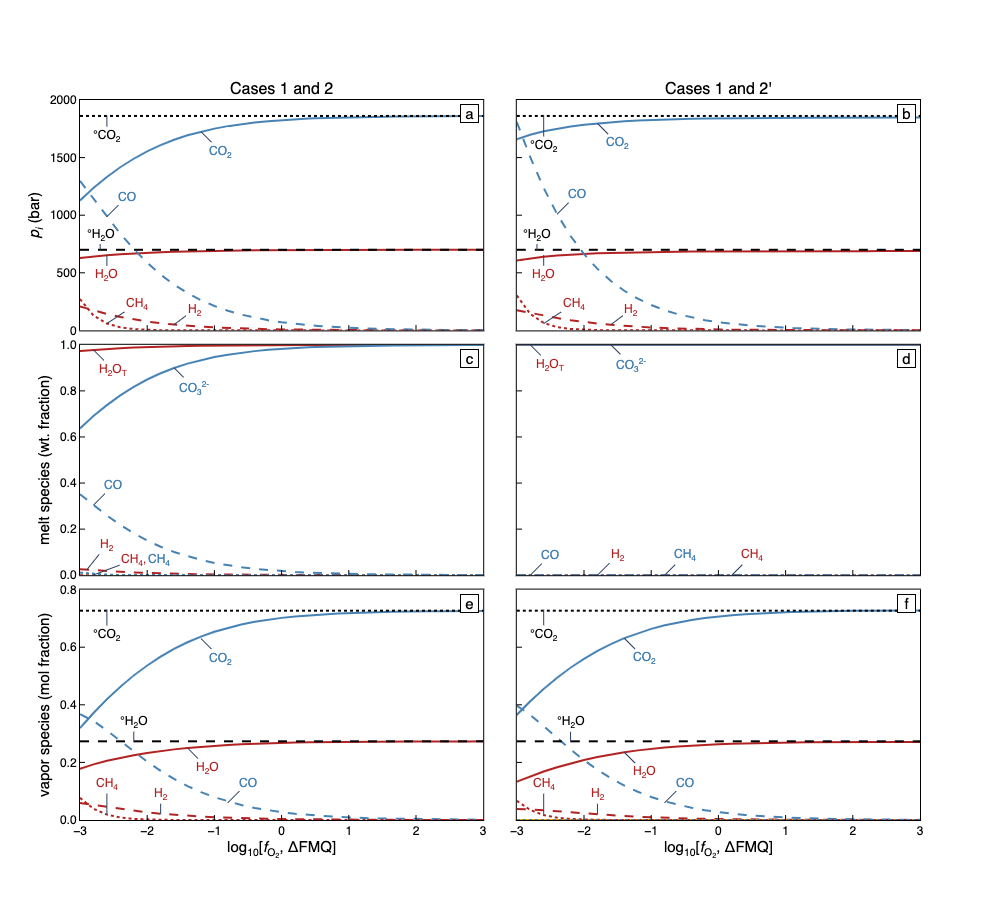


Figure S11 Calculated values of pi’s (top row), species fraction in the melt (middle row), and xvi’s (bottom row) vs. log10(fO2) for cases 1 (only oxidised C-O-H), 2 (oxidised and reduced C-O-H), and 2’ (reduced C-O-H insoluble). All calculations are for a Hawaiian tholeiitic melt at 1200 °C with H2O-eq = 3 wt% and CO2-eq = 1000 ppm. The red curves are for H-bearing species (including CH4); and blue curves for C-bearing species (excluding CH4). Results for case 1 (indicated by a superscript circle, °) are shown for reference in (**a**–**b**) and (**e**–**f**): H2O is a dashed horizontal black line and CO2 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 (CO2 = solid, CO = dash, CH4 = dot), which 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), which also sum to one. For the vapor speciation in (**e**–**f**), the sum of all coloured curves is one at any given fO2, and for the horizontal black lines representing case 1. For these conditions, there is no saturation with graphite, sulfide, or anhydrite.

Diagram, histogram

Description automatically generated with medium confidence

Figure S12 Variations with log10(fO2) for a melt with H2O-eq = 3 wt%, CO2-eq = 1000 ppm and S-eq = 0 ppm of the sum of the pi’s of the various C-O-H vapor species: **(a)** oxidised (H2O and CO2); and (**b**) reduced (H2, CO, and CH4). Case 1 = black-solid, 2 = blue-solid, and 2’ = red-dash.

Scaillet and Pichavant (2004) used the same melt and vapor species as case 2’. Equivalent to our calculations, they calculated *Pv*sat at constant *T*, constant H2O in the melt, various choices of constant total CO2 in the melt, and varying *f*O2. Despite different values for the various thermodynamic parameters that were used, both studies find that not including the presence of reduced C-O-H species in the vapor results in significant underestimates of *Pv*sat at low *f*O2. They also found that this effect increases with increasing CO2 content of the melt, in agreement with our model results shown in the main text. They also calculated the composition of the vapor (*xv*H2O and *xv*CO2) and melt (CO2-eq and H2O-eq) at constant *P* (400 bar), *T* (1200 °C), and *f*H2 (either 0.01 or 1 bar) whilst varying *f*H2O, which allowed them to look at the effects of *f*O2 on vapor and melt composition. At H2O-eq < 1 wt%, the melt and vapor calculated using their model contained less CO2 under reducing conditions compared to oxidising conditions. However, at H2O-eq >1 wt%, their calculated melt and vapor compositions were essentially independent of *f*O2, from which they concluded that calculations of *Pv*sat for high water contents were not affected by *f*O2. This contrasts with our results at 3 wt% H2O-eq. However, this likely reflects the high *f*O2 (ΔFMQ > 0.5) of their calculations at H2O > 1 wt% such that the effects of adding reduced C-O-H species at low *f*O2 were not observed.

### Case 3’: H2S is insoluble in the melt.

As for case 3, the behaviour of the purely C-O-H species is essentially unchanged in case 3’ compared to case 2 (Figure S13). Likewise, the S-speciation of the melt in both case 3 and 3’ is dominated by SO42- at ΔFMQ > +1 and \*S2- species below this *f*O2 (Figure S13c and d), resulting in the well-known sigmoidal shape of S6+/ST with *f*O2 documented by previous experimental and modeling studies (e.g., Wallace and Carmichael 1994; Carroll and Rutherford 1998; Matthews *et al.* 1999; Jugo *et al.* 2005, 2010).

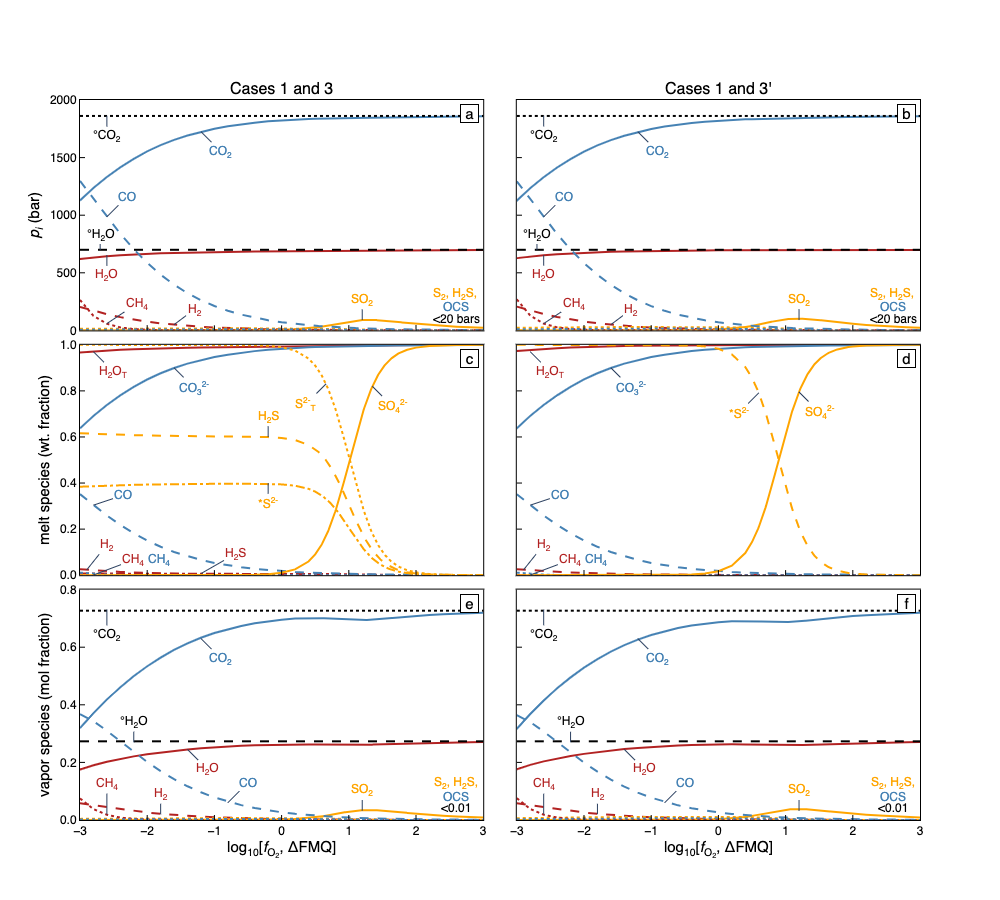


Figure S13 Calculated values of pi’s (top row), species fraction in the melt (middle row), and xvi’s (bottom row) vs. log10(fO2) for cases 1 (oxidised C-O-H only), 3 (full C-O-H-S), and 3’ (H2Smol insoluble) discussed in the text. All calculations are for a Hawaiian tholeiitic melt at 1200 °C with H2O-eq = 3 wt%, CO2-eq = 1000 ppm, and S-eq = 1000 ppm. The red curves are for H-bearing species (including CH4, but not H2S); blue curves for C-bearing species (including OCS, but not CH4); and yellow curves are for S-bearing species (including H2S, but not OCS). Results for case 1 (indicated by a superscript circle, °) are shown for reference in (**a**–**b**) and (**e**–**f**): H2O is a dashed horizontal black line and CO2 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 (CO2 = 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 (**c**), 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 fO2, and likewise for the horizontal black reference lines representing case 1. The pi’s and xvi’s of S2, H2S, and OCS in (**a,b,e,**f) are always near zero (i.e., close to the x-axis) on this scale – a zoom in is shown Figure S14. For these conditions, there is no saturation with graphite, sulfide, or anhydrite.

Although the effect is not large, the maximum in *p*SO2 for case 3 is smaller and at a higher *f*O2 relative to case 3’ (Figure S14). This reflects that at ΔFMQ < +1, a higher proportion of sulfur is dissolved in the melt as \*S2 for case 3’ relative to case 3 due to the lack of dissolved H2Smol in case 3'. As a result, both *p*S2 (through equation (16) in Table 2 of the main text) and *p*SO2 (through equation (7) in Table 2 of the main text) are higher in case 3’ than case 3. In contrast, at higher *f*O2 (i.e., ΔFMQ > +1.5), *f*H2S is negligible for both cases 3 and 3’ based on equation (9) in Table 2 in the main text, and as a result, *p*S2 and *p*SO2 are essentially indistinguishable for cases 3 and 3’ under these conditions. The combination of these two effects results in a higher *p*SO2 at its maximum and shifts the maximum to lower *f*O2 for case 3’ compared to 3. As H2Smol is treated as insoluble in the melt in case 3’, *p*H2S is higher (for the same value of S-eq) than in case 3 where it is treated as soluble. Because H2S and OCS are larger fractions of the S-bearing vapor species in case 3’ relative to case 3, the maximum in the sum of the *pi*’s of the S-bearing species is both displaced to lower *f*O2 and is higher relative to the maximum in *p*SO2 in case 3’ relative to case 3. There is also a larger shift between the maxima in the sum of the *pi*’s of the S-bearing species and Δ*Pv*sat in case 3’ relative to case 3. Hence, the solubility of H2Smol influences the position and magnitude of the sulfur solubility minimum.

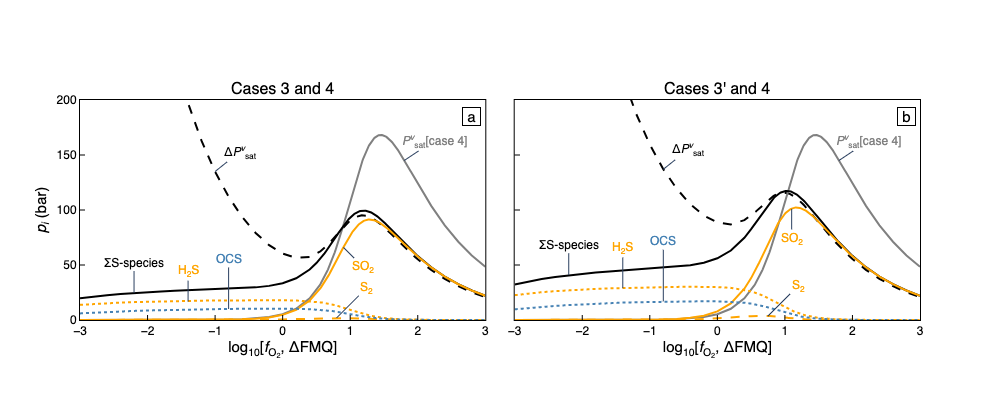
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Figure S14 Variations with log10(fO2) for a Hawaiian tholeiitic melt at 1200 °C with H2O-eq = 3 wt%, CO2-eq = 1000 ppm, and S-eq 1000 ppm for **(a)** case 3 and **(b)** case 3’ of the partial pressures of individual S-bearing vapor species (S2 – dash, SO2 – solid, and H2S – dot in yellow; OCS in blue dash), their sum (ΣS-species = pS2 + pSO2 + pH2S + pOCS in solid black), ΔPvsat (dash black), and Pvsat[case 4] ([S-O] = grey; i.e., pS2 + pSO2 + pO2 for S-eq = 1000 ppm, CO2-eq = 0 ppm, and H2O-eq = 0 wt%; Hughes et al., 2023). For these conditions, there is no saturation with graphite, sulfide, or anhydrite.

# Limitations

In this section, we describe some of the consequences for the accuracy of calculated *Pv*sat values that arise from limitations of our model. We emphasise, however, that our focus is on the *trends* in *Pv*sat as *f*O2, S, C, and H vary. We are confident that the dominant trends predicted by our model provide useful insights into the influence of these parameters on *Pv*sat. Nevertheless, this discussion serves to emphasize the importance of further experiments that investigate the effects of melt composition, *T*, and *P* on the solubilities of vapor species in melt by reactions such as (11–18) in Table 2 of the main text, on the activity-composition relationships of the dominant melt species, and on the fugacity coefficients of species in compositionally complex vapor. In our view, current knowledge of all of these factors influences the accuracy of all available models that might be used to calculate *Pv*sat for naturally occurring magmas, including ours.

## Choice of volatile-bearing species in vapor and melt

We included only a subset of known C-O-H-S species in the thermodynamic description of the vapor and melt. At homogenous equilibrium, additional species (e.g., SO3, SO, CS2, SOH, etc.) must be present at some level and could be significant in a C-O-H-S vapor depending on the *P*, *T*, and H/C/O/S ratios in the vapor (e.g., Henley and Fischer, 2021; Henley and Seward, 2018; Kress et al., 2004). However, our chosen species: (1) are those commonly measured in volcanic gases (e.g., Fischer and Chiodini, 2015; Giggenbach, 1996; Moussallam et al., 2019); and (2) have available fugacity coefficients (e.g., Shi and Saxena, 1992), which becomes progressively more important with increasing *P*.

Additional volatile components could be included in the system (e.g., N, Cl, F, etc.), which would also expand the number of species in the vapor and melt (e.g., N2, HCl, HF, etc.). These other volatile components are less significant than those we have considered in typical mafic to intermediate magmas (e.g., Le Voyer et al., 2015; Wallace, 2005). Although homogeneous and heterogeneous equilibria describing their behaviour in the vapor and their solubility in the melt could in principle be added to our model relatively simply, we expect their contributions to *Pv*sat (and therefore to Δ*Pv*sat) would typically be low relative to those of the species we have considered. In any case, neglecting these other components and species – which will always be present to some degree – will inevitably lead to some level of underestimation of *Pv*sat.

We also have not explicitly included the precipitation of solid or immiscible volatile-bearing species, such as graphite, sulfide melt, anhydrite, etc, although we do indicate conditions at which these phases would be stable based on our calculations. This could alter the magnitude and trends of some of the features we discussed. For example, anhydrite- or sulfide-saturation would limit the ST concentration stably attainable in the melt and influence the major element composition of the silicate (e.g., reduction in FeO and CaO concentrations) at the high- and low-*f*O2 extremes of some of our calculations. If assemblages containing such solid or liquid phases are more stable than the two-phase melt + vapor assemblages we have modelled, the results presented here would represent upper limits on *Pv*sat (e.g., Hughes et al., 2023). At the most reducing conditions we have considered, graphite is a stable C-bearing phase. Hence, the increase in *Pv*sat from reduced C-bearing species in the vapor would be limited by the precipitation of graphite, which would reduce the C content of the melt. However, our calculations, although metastable, are still thermodynamically valid and help us to understand the trends in the regions where melt + vapor is stable.

## Effects of temperature and melt composition on calculated Pvsat

We restricted our modelling to a single volatile-free melt composition (a representative Hawaiian tholeiite) at a single *T* (1200°C). We took this approach to isolate the effects of *f*O2 and S, C, and H on *Pv*sat and the coupled speciation of the melt and composition and speciation of the vapor. However, both melt composition and *T* obviously vary significantly in nature, and these effects have not been considered here.

It is well-known that variations in *T* will influence the solubilities of volatile component in the melt via the *T*-dependence of heterogenous melt-vapor equilibria (equations (11–18) in Table 2 of the main text); the *Ki*’s for homogeneous vapor equilibria (equations (5–10) in Table 1 of the main text); and the γ*vi*‘s for vapor species. These effects are well-constrained for homogeneous vapor equilibria (e.g., Ohmoto and Kerrick, 1977) and γ*vi*‘s (e.g., Shi and Saxena, 1992), but less well known for the solubilities of most volatile components in vapor-saturated melt (e.g., Allison et al., 2022; Lesne et al., 2011; Wieser et al., 2022). For example, there is evidence that both *C*\*S2- and *C*SO42- are strongly dependent on *T* (e.g., Boulliung and Wood, 2022; Moretti and Ottonello, 2005; Nash et al., 2019; O’Neill, 2021; O’Neill and Mavrogenes, 2002, 2022).

Even for a fixed volatile-free melt composition, the Fe3+/FeT in the melt depends on *f*O2 (e.g., Wieser et al., 2022); and this could influence the solubilities of volatile components in the melt via structural changes results from changes in the Fe oxidation state. Additionally, the dependences of sulfide and sulfate capacities on variations of Fe3+/Fe2+ (and therefore on *f*O2) in a melt that is otherwise constant in chemical composition are not currently known (e.g., Moretti and Ottonello, 2005; O’Neill, 2021; O’Neill and Mavrogenes, 2022). Thus, although there are potentially measurable effects of *f*O2 on volatile solubilities over the *f*O2 range observed of commonly occurring magmas, they have not been addressed by our calculations.

More generally, melt composition significantly influences the speciation and solubility of some volatile components in the melt (e.g., CO32-, \*S2-, and SO42-; Allison et al., 2022; O’Neill, 2021; O’Neill and Mavrogenes, 2022; Shishkina et al., 2014), but less so for others (e.g., H2OT; Ghiorso and Gualda, 2015; Wieser et al., 2022). Characterization of such variations on solubility functions is an active area of research. New results can be incorporated into our treatment as they become available, through the compositional dependence of the solubility functions and by adding additional heterogeneous melt-vapor equilibria where required (e.g., CO2,mol for rhyolites; Blank et al., 1993). Similarly, more experimental work needs to be done to model accurately the compositional dependence of the solubilities of H2, CO, CH4, and H2S, which is particularly important to model accurately the behaviour of volatiles in lunar and martian magmas (e.g., Lo et al., 2021; Wetzel et al., 2013). This leads to potentially significant inaccuracy in calculations of absolute values of *Pv*sat. In particular, *Pv*sat calculations are very sensitive to the solubility of CO2 in the melt (i.e., *C*CO32-), which both is strongly dependent on melt composition (e.g., Allison et al., 2022; Wieser et al., 2022) and has an outsized effect on *Pv*sat calculations because of its low solubility.

Some of the details of the trends in *f*O2 that we present in the main test may vary – perhaps strongly – with *T* and the volatile-free melt composition due to their effects on speciation and solubility. This applies particularly to the position and magnitude of the SSmin and to the absolute values of *Pv*sat, which as we have emphasised is strongly dependent on the solubility of CO2. However, there is a lack of: (1) complete experimental data for solubilities even for the most abundant terrestrial magmas; and (2) models that can account fully for the observed effects of melt composition on measured solubilities. Hence, a full investigation of the effect of melt composition on calculations of *Pv*sat are beyond the scope of this paper, especially given the lack of a general model for carbonate solubility. However, to ensure the trends we describe for our Hawaiian tholeiite are generalisable to other melt compositions, we apply our model to other basaltic melt compositions (Table S4) where the carbonate solubility function can be calculated from experiments (Table S3). We calculate *Pv*sat for the same conditions used in case 3 of the main text for the Hawaiian tholeiite (1200 °C, 3 wt% H2O-eq, 1000 ppm CO2-eq, and 1000 ppm S-eq) but vary the melt composition (Table S4) and use the appropriate carbonate solubility (i.e., appropriate ln*K*0 and Δ*V*0; see Supplementary Material Section 2.2.1 for details). The sulfide and sulfate solubilities are therefore calculated for the compositions given in Table S4, as is the relationship between Fe3+/FeT and *f*O2. All other solubilities (i.e., H2OT, H2,mol, COmol, CH4,mol, and H2Smol) are the same in all calculations

Table S4 Basaltic melt compositions.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Composition | SiO2 | TiO2 | Al2O3 | FeOT | MnO | MgO | CaO | Na2O | K2O | P2O5 |
| Sunset Crater | 47.61 | 1.80 | 16.22 | 11.02 | 0.17 | 8.66 | 9.84 | 3.43 | 0.80 | 0.45 |
| SFVF | 52.77 | 1.18 | 17.28 | 7.88 | 0.19 | 5.86 | 9.19 | 3.39 | 1.50 | 0.76 |
| Erebus | 47.49 | 2.79 | 18.83 | 10.36 | 0.29 | 3.31 | 6.95 | 6.03 | 2.78 | 1.17 |
| Vesuvius | 48.69 | 0.98 | 15.26 | 8.15 | 0.23 | 6.68 | 11.60 | 1.93 | 5.86 | 0.62 |
| Etna | 47.46 | 1.81 | 16.17 | 10.47 | 0.20 | 6.74 | 11.42 | 3.48 | 1.72 | 0.52 |
| Stromboli | 48.85 | 0.83 | 16.83 | 8.15 | 0.20 | 7.81 | 12.45 | 2.46 | 1.99 | 0.43 |
| Basanite | 46.20 | 3.18 | 15.27 | 12.05 | 0.00 | 9.10 | 8.26 | 4.35 | 1.33 | 0.27 |
| Leucite | 44.33 | 2.70 | 12.87 | 9.09 | 0.00 | 9.19 | 14.37 | 3.22 | 3.47 | 0.77 |
| AH3 pt | 50.15 | 0.86 | 15.28 | 7.64 | 0.04 | 5.93 | 11.13 | 7.11 | 1.86 | 0.00 |
| N72 basalt | 50.17 | 0.92 | 18.28 | 9.37 | 0.17 | 7.00 | 11.37 | 2.33 | 0.23 | 0.15 |
| Hawaiian | 50.8 | 1.84 | 13.7 | 12.4 | 0.22 | 6.67 | 11.5 | 2.68 | 0.15 | 0.19 |
| MORB | 51.29 | 2.50 | 13.70 | 11.04 | 0.02 | 6.70 | 11.03 | 2.27 | 0.43 | 0.21 |

*Notes*: all oxide concentrations in wt%. Composition for Sunset crater, SFVF, Erebus, Vesuvius, Etna, and Stromboli from Allison et al. (2019); Basanite from Holloway and Blank (1994); Leucite from Thibault and Holloway (1994); AH3 phonotephrite (pt) from Vetere et al. (2014); and N72 basalt from Shishkina et al. (2010); Hawaiian from Table S1; and MORB from Dixon et al. (1995).

As expected, the absolute *Pv*sat is a strong function of melt composition due to the strong dependence of carbonate solubility on melt composition (Figure S15a). There is also an effect of melt composition on the position and magnitude of the sulfur solubility minimum and therefore its influence on Δ*Pv*sat (Figure S15b and c). This is due to changes in the carbonate, sulfide, and sulfate solubilities due to the varying melt composition. However, the trends detailed in the main text are still expressed over this broad range of melt compositions that strongly effect carbonate, sulfide, and sulfate solubility. This applies especially to: (1) the large increase in *Pv*sat at reducing conditions due to the build-up of insoluble C-O-H species, and (2) the local maximum in *Pv*sat at intermediate *f*O2 due to the sulfur solubility minimum. Hence, although the details do depend on melt composition, our results are generalisable to other basaltic compositions, including highly-alkalic compositions.

Graphical user interface, chart, application, histogram

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Figure S15 For a melt containing 3 wt% H2O-eq, 1000 ppm CO2-eq, and 1000 ppm S-eq at 1200 °C for different melt compositions and solubility functions as described in the text: **(a)** pressure of vapor saturation (Pvsat) and **(b,c)** difference between Pvsat calculated using case 1 and 3 (ΔPvsat) against oxygen fugacity (fO2), where **(c)** is a zoom in of the dashed insert in **(b)**: Hawaiian tholeiite (yellow solid), MORB (yellow dot), N72 basalt (yellow dash), SVFV (yellow dot-dash), Sunset Crater (red dash), Erebus (blue dot), Basanite (red dot), Etna (red solid), Vesuvius (blue solid), Leucite (blue dot-dash), and AH3 phonotephrite (blue dash). Details of the calculations are given in the text.

## Effect of one volatile on the solubility of another volatile

An important feature of volatile solubilities is the possibility that the solubility of one volatile species can influence that of another. Our inclusion of the solubility of CH4,mol in the melt is one example of the mutual effects between H and C and how they can be readily incorporated in the approach we have taken to modelling volatile solubilities. We followed a similar approach in our treatment of the effects of H on S speciation and solubility by including H2Smol in the melt (i.e., difference between case 3 and 3’). This example demonstrates the potential for such interactions to have significant effects on the speciation of S in the melt speciation and, in this case, on the SSmin. Another possibly significant interaction between H and S speciation (and therefore solubility) could occur for dissolved sulfate species. For example, by analogy with how we treated the H2S component, H2O and SO2 in the vapor could react to produce an H2SO3 species in the vapor, the solubility of which in the melt could then quantified given an equilibrium constant for the reaction H2SO3(*v*) = H2SO3(*m*). In this case, the melt species would represent a hydrated sulfate species in the melt. Experiments have demonstrated that the sulfate content of melt at anhydrite saturation (a parameter closely related to *C*SO42-) varies with H2OT (e.g., Chowdhury and Dasgupta, 2019; Zajacz and Tsay, 2019), which suggests that H- and SO42‑-bearing species are interacting in the melt. However, we have not included such phenomena in our modeling given the limited experimental data on this effect (e.g., Moretti et al., 2003). Sulfur has been experimentally shown to effect CO2 solubility (Webster et al., 2011), but this effect is not included in our model at present. Finally, the solubility of CO32- is known to be affected by dissolved H2OT (e.g., Ghiorso and Gualda, 2015; King and Holloway, 2002; Papale et al., 2006) and this effect could also in principle be incorporated into our modelling by following a similar approach. This could be approached by adding an additional heterogeneous equilibrium to Table 2 (e.g., CO2(*v or m*) + H2O(*m*) = H2CO3(*m*)). However, we have not included this effect given the sparse data on the effects of H2O on CO2 solubility in basaltic melts.

## Effect of P on solubility

The *P*-dependences of *Ci* for the relatively insoluble CO32-, H2,mol. CH4,mol, and COmol melt species have been included in our model (e.g., Ardia et al., 2013; Armstrong et al., 2015; Dixon et al., 1995; Hirschmann et al., 2012; Stanley et al., 2014; Wetzel et al., 2013). However, the *Ci* functions were assumed to be independent of *P* for \*S2-, SO42-, and H2Smol due to a lack of data (e.g., Clemente et al., 2004; Lesne et al., 2015; Moune et al., 2009; O’Neill, 2021; O’Neill and Mavrogenes, 2022) and for H2OT because available data suggest it is of minor importance over most of the *P* interval for the calculations presented here (e.g., Dixon and Stolper, 1995; Lesne et al., 2011; Shishkina et al., 2014). Therefore, the calculated build-up of relatively insoluble C-O-H species at low *f*O2 incorporates the influence of *P* on *Ci*’s. However, the possible importance of the *P*-dependence of the *Ci*’s of the S-bearing species remains to be quantified, which could influence the magnitude and *f*O2-position of the *Pv*sat maximum.

## Ideal mixing of non-ideal gases

An important uncertainty in our modelling results from the *P*-dependence of fugacity coefficients. The fugacity coefficients for SO2 and H2S are large and the Shi and Saxena (1992) parameterizations that we used for these species are unphysical at low *P* where ideality should be approached and thus required some modification. Additionally, the approximation of ideal mixing between non-ideal pure gases (Lewis-Randall rule), although widely used must introduce inaccuracies (e.g., Holloway, 1977). However, at the *P* and *T* for crustal magmatic systems it appears to be appropriate (e.g., Abramov, 2000; Ferry and Baumgartner, 2019; Ohmoto and Kerrick, 1977). Although changes in these parameters could alter the details of some of the behaviour observed (especially since some of the trends we observed in our calculations reflect the *P*-dependence of γH2S and γSO2), it is unlikely that they would fundamentally affect the results.

## Effect of uncertainty in model parameters

Each parameter in the model will have an associated error with it, which will result in an uncertainty on *Pv*sat and Δ*Pv*sat. We investigate the influence of errors in the solubilities and vapor fugacity coefficients by varying these parameters for all species by ±10% in the same calculation for case 3 (Hawaiian tholeiite, 1200 °C, 3 wt% H2O-eq, 1000 ppm CO2-eq, and 1000 ppm S-eq), which is illustrated in Figure S16. Uncertainties in solubilities and vapor fugacity coefficients have large effects on *Pv*sat (Figure S16a) but small effects on Δ*Pv*sat (Figure S16b and c). Increasing both solubilities and vapor fugacity coefficients causes a decrease in *Pv*sat because species are both more soluble in the melt and more compressible in the vapor phase (Figure S16a). A 10% error in vapor fugacity coefficients has a larger effect on *Pv*sat than for solubilities (Figure S16a). However, despite the potentially large effects of these uncertainties on absolute values of *Pv*sat the broad trends that are our major focus are robust.

Chart, line chart, histogram

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Figure S16 Evaluation of the effects of uncertainties in solubility and fugacity coefficients on calculated values of Pvsat. All curves are for the Hawaiian tholeiite melt containing 3 wt% H2O-eq, 1000 ppm CO2-eq, and 1000 ppm S-eq at 1200 °C for different errors: **(a)** pressure of vapor saturation (Pvsat) and **(b,c)** difference between Pvsat calculated using case 1 and 3 (ΔPvsat) against oxygen fugacity (fO2) when changing vapor fugacity coefficients (red, labelled ) and solubilities (blue, labelled C) for +10% (dash, labelled 1.1) and -10% (dot, labelled 0.9) for all species, where **(c)** is a zoom in of **(b)** within the dashed box. The yellow curve is for case 3. Details of the calculations are given in the text.

## Effect of errors in melt composition

We have also explored aspects of the effects of analytical uncertainties in melt composition on calculated *Pv*sat and *f*O2. We take the anhydrous melt composition in Table S1 and assume the relative errors on each oxide shown in Table S5, which are typical for the electron probe. The melt contains 3 wt% H2O-eq, 1000 ppm CO2, and 1000 ppm S-eq, each with 10% relative error, which is typical for secondary ion mass spectrometry or Fourier transform infrared spectroscopy. We choose four different Fe3+/FeT with 0.01 absolute error that is typical with X-ray absorption near-edge structure spectroscopy (Cottrell et al., 2009), 0.235 (the sulfur solubility minimum); 0.160 (the minimum between the sulfur solubility minimum and the rapid increase due to the build-up of insoluble species); 0.063 (equivalent to ~ΔFMQ-2); and 0.313 (equivalent to ~ΔFMQ+2). When a parameter is varied, we calculate 100 melt compositions assuming a Gaussian probability distribution given the assumed uncertainty of the parameter.

Table S5 Relative error (%) for each oxide.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| SiO2 | TiO2 | Al2O3 | FeOT | MnO | MgO | CaO | Na2O | K2O | P2O5 |
| 0.64 | 5.3 | 0.88 | 1.7 | 14.3 | 1.4 | 1.1 | 3.5 | 2.2 | 13.9 |

We vary these compositional parameters independently as well as all together to understand their influence (Table S6 and Figure S17). Varying anhydrous melt composition only effects sulfide and sulfate capacities and converting Fe3+/FeT to *f*O2: therefore, it has essentially no effect on *Pv*sat or *f*O2 (Figure S17a). Varying Fe3+/FeT has no effect on *Pv*sat and a small effect on *f*O2 (Figure S17b). Varying H2O-eq and CO2-eq have a large effect on *Pv*sat, whilst S-eq as essentially no effect (Figure S17c). Varying all measured parameters highlights that errors in the composition (primarily CO2-eq and H2O-eq) have a large effect on *Pv*sat and *f*O2, and these are more important than the effects of *f*O2 and S (Figure S17d).

Chart

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Figure S17 Pressure of vapor saturation (Pvsat) against oxygen fugacity (fO2), where different aspects of the melt composition have been varied within defined errors 100 times (see text for details). **(a–c)** At the maximum in Pvsat (ΔFMQ+1.19), varying **(a)** anhydrous melt composition; **(b)** Fe3+/FeT; and **(c)** all volatiles (grey), CO2-eq (red circles), H2O-eq (blue circles), and S-eq (yellow circles) [red, blue, and yellow circles have been offset in ΔFMQ for clarity]. **(d)** At various fO2, varying all melt composition parameters (the black-dash box is the region shown in (a–c)). The black star is the true value at a particular fO2 and the yellow curve how the true value of Pvsat varies with fO2.

Table S6 Quantitative effect of analytical errors on melt composition on calculations of Pvsat and fO2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compositional parameter varied | *Pv*sat (bar) | | | *f*O2 (ΔFMQ) | | |
| correct | mean | s.d. | correct | mean | s.d. |
| Melt composition (a) | 2656 | 2657 | 3 | +1.19 | 1.18 | 0.02 |
| Fe3+/FeT (b) | 2655 | 2 | 1.18 | 0.10 |
| CO2-eq (c – red) | 2665 | 163 | 1.19 | 0.00 |
| H2O-eq (c – blue) | 2674 | 119 | 1.19 | 0.00 |
| S-eq (c – yellow) | 2656 | 7 | 1.19 | 0.00 |
| All volatiles (c – grey) | 2683 | 209 | 1.19 | 0.00 |
| All parameters (d) | 2682 | 210 | 1.18 | 0.10 |
| All parameters (d) | 2618 | 2590 | 215 | +0.19 | 0.20 | 0.17 |
| All parameters (d) | 2617 | 2606 | 185 | +2.00 | 1.98 | 0.09 |
| All parameters (d) | 2912 | 2951 | 233 | -2.02 | -2.06 | 0.38 |

# Vapor compositions for natural samples

Figures S18–20 show the calculated vapor compositions in equilibrium with the measured volatile contents of matrix glasses and melt inclusions from MORB, OIB, and arc basalts at *Pv*sat, which are shown as CO2-H2O-SO2 ternary diagrams in Figure S21.

The calculated vapor composition for MORBs is mostly CO2 (>75 mol%) with minor H2O (<17 mol%) and CO (<8 mol%) and traces of other species (<0.02 mol% for each species) (Figure S18). Rekeyanes Ridge samples are an exception, which are still mostly CO2 (>60 mol%) but have up to 22 mol% SO2 (Figure S18). This highlights that even being on the limb of the SSmin influences the vapor composition when the H2O and CO2 concentrations in the melt are low.

Icelandic samples are in equilibrium with a vapor containing mostly CO2 (>73 mol%) and minor H2O (<12 mol%) and SO2 (<15 mol%) (Figure S19). Due to the lower H2O-CO2 contents, and the *f*O2 within 0.5 log units of the SSmin, the vapor for Hawai’ian samples can have up to 40 mol% SO2 in them (Figure S19).

The vapor composition for Bonin samples is mostly CO2 (>77 mol%) with some H2O (<14 mol%) and trace amounts of all other gas species (<5 mol% each) (Figure S20). The Marianas samples, with their high H2O contents, have water- and CO2-rich vapors (24–86 and 8–69 mol%, respectively), with significant SO2 (<26 mol%), again reflecting the influence of the SSmin (Figure S20). However, even with the high H2O contents, H2S is minor component of the vapor (<3 mol%) as they are too oxidised (Figure S20).

The vapor is dominated by CO2 and CO for both lunar and martian samples, with the proportion of CO increasing with decreasing *f*O2 (Figure S22).

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Figure S18 Calculated vapor composition (mole fraction of species i) against log10(fO2) for MORB samples shown in Figure 6 of the main text (same symbol shapes and colours are used: diamond = matrix glass, blue = Mid-Atlantic ridge, red = Rekeyanes ridge, yellow = SW Indian ridge, grey = American-Antarctic ridge, and black = Kolbeinsey ridge). Note the different y-axis scales for the major species (CO2, H2O, and SO2: 0–1) and for the minor/trace species (CO, H2, S2, OCS, CH4, and H2S: 0.0–0.1).

A picture containing diagram

Description automatically generated

Figure S19 Calculated vapor composition (mole fraction of species i) against log10(fO2) for OIB samples shown in Figure 6 of the main text (same symbol shapes and colours are used: diamond = matrix glass, circle = melt inclusion, yellow = Hawai’i, and red = Iceland). Note the different y-axis scales for the major species (CO2, H2O, and SO2: 0–1) and for the minor/trace species (CO, H2, S2, OCS, CH4, and H2S: 0.0–0.1).

Diagram

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Figure S20 Calculated vapor composition (mole fraction of species i) against log10(fO2) for arc basalt samples shown in Figure 6 of the main text (same symbol shapes and colours are used: diamond = matrix glass, circle = melt inclusion, grey = Marianas, blue = Bonin). Note the different in y-axis scales for the major species (CO2, H2O, and SO2: 0–1) and for the minor/trace species (CO, H2, S2, OCS, CH4, and H2S: 0.0–0.1).

|  |  |  |
| --- | --- | --- |
|  |  |  |

Figure S21 Ternary diagrams for calculated vapor composition for samples shown in Figure 6 in the main text for MORB (left-hand panel; Figure S18), OIB (middle panel; Figure S19), and arc basalts (right-hand panel; Figure S20). The same symbols and colours as Figure 6 are used. a = CO2 (top vertex), b = H2O (left-hand vertex), and c = SO2 (right-hand vertex).



Figure S22 Calculated vapor composition (mole fraction CO2 = solid lines, or CO = dashed lines) against log10(fO2) for lunar (blue) and martian (red) samples shown in Figure 7 of the main text.

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