

Rough Draft of Methods

Note, “Appendix X” is stated below are placeholders for when I actually write those parts.

Model for Calculating Volcanic outgassing

Below, we describe our model for predicting the gases produced by an erupting mantle-sourced volcano. We follow the work of Gaillard and Scaillet (2014), and solve for the gas-gas and gas-melt equilibrium in a C-O-H system. Our model differs from Gaillard and Scaillet (2014) because we do not consider nitrogen or sulfur species. Our Python code is published as an open-source software on the Github page URL (placeholder).

When magma reaches the surface of a planet, it will degas. The amount of carbon and hydrogen that is exsolved by the magma is governed by the solubility of CO₂ and H₂O, which we calculate with the solubility relations described in Iacono-Marziano et al. (2012):

$$\ln(x_{\text{CO}_2}) = x_{\text{H}_2\text{O}} d_{\text{H}_2\text{O}} + a_{\text{CO}_2} \ln(P_{\text{CO}_2}) + F_1 \quad (1)$$

$$\ln(x_{\text{H}_2\text{O}}) = a_{\text{H}_2\text{O}} \ln(P_{\text{H}_2\text{O}}) + F_1 \quad (2)$$

All constants and variables are defined in Table 1 and Table 2, respectively. The constants F_1 and F_2 depend on the chemical makeup of the magma, which we fix to the concentration of the lava erupting at Mt. Etna, Italy (See Appendix X). This is a reasonable assumption because solubility of H₂O and CO₂ does not dramatically change with different magmatic compositions or oxygen fugacities of the melt. We show this in Appendix X. In the equations above, volatile abundance in the magma is expressed as a mol fraction, although this can be converted to a mass fraction with the formula

$$m_i = x_i M_i \quad (3)$$

Here, m_i is the mass fraction of volatile i (either H₂O or CO₂).

We assume that after the hot gas exsolves from the magma, it achieves thermodynamic equilibrium from the reactions



At thermodynamic equilibrium, the ratios of the fugacities of volatile species (denoted f_x) are related to the equilibrium constant corresponding to each chemical reaction. For the range of temperatures and pressures we are considering the fugacities of each species are well approximated by partial pressures (denoted P_x). We show that this approximation is valid in Appendix X.

$$K_1 = \frac{f_{\text{H}_2} f_{\text{O}_2}^{0.5}}{f_{\text{H}_2\text{O}}} \approx \frac{P_{\text{H}_2} f_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}} \quad (7)$$

$$K_2 = \frac{f_{\text{CO}} f_{\text{O}_2}^{0.5}}{f_{\text{CO}_2}} \approx \frac{P_{\text{CO}} f_{\text{O}_2}^{0.5}}{P_{\text{CO}_2}} \quad (8)$$

$$K_3 = \frac{f_{\text{CH}_4} f_{\text{O}_2}^2}{f_{\text{CO}_2} f_{\text{H}_2\text{O}}^2} \approx \frac{P_{\text{CH}_4} f_{\text{O}_2}^2}{P_{\text{CO}_2} P_{\text{H}_2\text{O}}^2} \quad (9)$$

We calculate equilibrium constants (e.g. K_1) using the NASA thermodynamic database (Burcat & Ruscic 2005). We assume that the gas is thermally and chemically coupled to the magma so that the oxygen fugacity (f_{O_2}) of the gas is set by the oxygen fugacity of magma. Notice that we have 7 unknowns (x_{CO_2} , $x_{\text{H}_2\text{O}}$, P_{CO_2} , $P_{\text{H}_2\text{O}}$, P_{CO} , P_{H_2} , P_{CH_4}) and only 5 equations. To close the system, we add three more equations and one more unknown. The first equation requires that the partial pressures sum to the total pressure:

$$P_{\text{H}_2} + P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{CO}_2} + P_{\text{CH}_4} = P \quad (10)$$

The final two equations are mass conservation equations:

$$\left(\frac{m_{\text{CO}_2}^{\text{tot}}}{M_{\text{CO}_2} x} \right) = \frac{P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{CH}_4}}{P} \alpha_{\text{gas}} + (1 - \alpha_{\text{gas}}) x_{\text{CO}_2} \quad (11)$$

$$\left(\frac{m_{\text{H}_2\text{O}}^{\text{tot}}}{M_{\text{H}_2\text{O}} x} \right) = \frac{P_{\text{H}_2\text{O}} + P_{\text{H}_2} + 2P_{\text{CH}_4}}{P} \alpha_{\text{gas}} + (1 - \alpha_{\text{gas}}) x_{\text{H}_2\text{O}} \quad (12)$$

Equations (11) and (12) state that the total moles of either species should be equal to the moles of either species in the gas phase plus the moles in the magma. α_{gas} is the final unknown. It is the total moles in the gas phase divided by the total moles in the gas and magma combined. See Appendix X for a full derivation of Equations (11) and (12).

Given a gas/magma temperature (T), pressure (P), oxygen fugacity (f_{O_2}), and the total mol fraction (or mass fraction) of CO_2 and H_2O in the magma ($x_{\text{CO}_2}^{\text{tot}}$, and $x_{\text{H}_2\text{O}}^{\text{tot}}$), Equations (1), (2), (7) - (12) are a system of 8 equations and 8 unknowns (x_{CO_2} , $x_{\text{H}_2\text{O}}$, P_{CO_2} , $P_{\text{H}_2\text{O}}$, P_{CO} , P_{H_2} , P_{CH_4} , α_{gas}). Our method for solving this system (for the unknowns) is explained in a Jupyter Notebook file titled “Explanation_of_model” which can be downloaded from the Github page of the lead author at URL.

In Appendix X validates our model. It shows that we reproduce the work of Gillard 2014, and shows our model outputs predict measured gas speciation.

Table 1
Model Constants

Constant	Value	Units	Definition
$d_{\text{H}_2\text{O}}$	2.3	-	Solubility constant
a_{CO_2}	1	-	Solubility constant
$a_{\text{H}_2\text{O}}$	0.54	-	Solubility constant
F_1	-14.23	-	Solubility constant
F_2	-5.93	-	Solubility constant
x	1.55×10^{-2}	$(\text{mol magma})(\text{g magma})^{-1}$	Inverse molar mass of magma
$M_{\text{H}_2\text{O}}$	18.02	$(\text{g H}_2\text{O})(\text{mol H}_2\text{O})^{-1}$	Molar mass of H ₂ O
M_{CO_2}	44.01	$(\text{g CO}_2)(\text{mol CO}_2)^{-1}$	Molar mass of CO ₂
K_1	$\exp(-29755 / T + 6.65)$	$\text{bar}^{0.5}$	Equilibrium constant for Equation X
K_2	$\exp(-33979 / T + 10.42)$	$\text{bar}^{0.5}$	Equilibrium constant for Equation X
K_3	$\exp(-96444 / T + 0.22)$	-	Equilibrium constant for Equation X

Notes.

^a Constants taken from Ianco...

^b Calculated using the bucat data base.

^c Calculated assuming magmatic composition of Mt. Etna.

Table 2
Model variables

Model Input/output	Variable	Units	Definition
Input	P	bar	Total pressure of degassing
	T	K	Temperature of magma and gas of degassing
	f_{O_2}	bar	Oxygen fugacity of the magma
	$m_{\text{CO}_2}^{\text{tot}}$	(g CO ₂)(g gas and magma) ⁻¹	mass fraction CO ₂ in magma before degassing
	$m_{\text{H}_2\text{O}}^{\text{tot}}$	(g CO ₂)(g gas and magma) ⁻¹	mass fraction H ₂ O in magma before degassing
Output	$x_{\text{H}_2\text{O}}$	(mol H ₂ O) (mol magma) ⁻¹	mol fraction of H ₂ O in the magma after degassing
	x_{CO_2}	(mol CO ₂) (mol magma) ⁻¹	mol fraction of CO ₂ in the magma after degassing
	$P_{\text{H}_2\text{O}}$	bar	Partial pressure of H ₂ O
	P_{CO_2}	bar	Partial pressure of CO ₂
	P_{H_2}	bar	Partial pressure of H ₂
	P_{CO}	bar	Partial pressure of CO
	P_{CH_4}	bar	Partial pressure of CH ₄
	α_{gas}	(mol gas)(mol gas and magma) ⁻¹	mol fraction in gas phase

References

Burcat, A., & Ruscic, B. 2005, in (Argonne National Lab.(ANL), Argonne, IL (United States))
Gaillard, F., & Scaillet, B. 2014, Earth and Planetary Science Letters, 403, 307
Iacono-Marziano, G., Morizet, Y., Le Trong, E., & Gaillard, F. 2012, Geochimica et Cosmochimica Acta, 97, 1