Unravelling the atmospheres of rocky planets with real gas equations of state and solubility

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Introduction and Motivation

- Formation of rocky planets involved stages of melting through radioactive decay and planetary impacts, generating atmospheres
- Moreover, a new class of planet, sub-Neptunes, observable by James Webb Space Telescope (e.g., Madhusudhan et al. 2023) are likely to have a magma-atmosphere or water-atmosphere interface
- In order to better i) understand the generation of atmospheres around rocky Solar System bodies and ii) interpret observations of atmospheric spectra of rocky- and sub-Neptune exoplanets, we develop a new code, *Atmodeller*, of the solubilities of major gases (H-C-O-N-S-Cl) in silicate magmas, their equilibrium speciation and non-ideality, as well as their condensation from the gas phase.

Methods

- *Atmodeller* runs in Python 3.10+, has object-oriented design, full logging, benchmarked with FactSage, ~100 tests
- Users able to select elements of interest (H, C, S, etc.)
- Can specify either partial pressures of discrete gas species (e.g., O_2, H_2) or total mass of elements.
- Number of independent chemical reactions required to solve system determined automatically by Gaussian elimination
- Planetary mass, radius, fraction of melt, and temperature selected independently
- Solubility laws implemented from a variety of temperatures, melt compositions and fO_2 (see Table 1, below)
- Non-ideal gas equations of state using Compensated Redlich-Kwong (Holland and Powell, 1991; 1998) and Virial coefficients (Shi and Saxena, 1992)

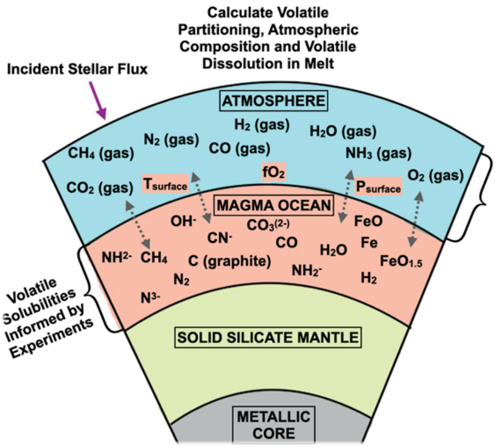


Fig. 1. Schematic illustration of the processes covered in *Atmodeller*. The code self-consistently treats mass balance, chemical equilibria, solubility, condensation and non-ideal gas equations of state to calculate the composition of the atmosphere in equilibrium with the magma oceans for a range of temperatures, planetary masses and melt fractions.

Species	Composition*	Reference	Experimental Calibration[†] Pressure (kbar)	Temperature (K)	fO_2 rel. IW (log10 units)
H_2	Basalt, Andesite	Hirschmann et al. (2012, Table 2)	7-30	1673	0
H_2	Silicate glass (obsidian)	Gaillard et al. (2003, Table 4)	0.001-0.265	1073	-3.6 to 0.6
He	Basalt (tholeiitic)	Jambon et al. (1986)	0.001	1523-1873	8
H_2O	Basalt	Dixon et al. (1995, Fig. 4)	0.2-0.7	1473	4.2 to 5.5
H_2O	Peridotite	Sossi et al. (2023)	0.001	2173	-1.9 to 6.0
H_2O	Basalt	Wilson & Head III (1981) and Hamilton et al. (1964)	1-6	1373	2.2, 3.8, 9.5
H_2O	Lunar basalt, Ano.-Dio.	Newcombe et al. (2017, Fig. 5)	0.001	1623	-3.0 to 4.8
CO	Basalt, Rhyolite	Yoshioka et al. (2019)	2-30	1473-1773	0.5 to 4.0
CO	Basalt	Armstrong et al. (2015, Eq. 10)	10-12	1673	-3.65 to 1.46
CO_2	Basalt	Dixon et al. (1995, Eq. 6)	0.21-0.98	1473	4.2 to 5.5
CH_4	Basalt (Fe-free)	Ardia et al. (2013, Eq. 7a and 8)	7-30	1673-1723	-9.50 to -1.36
N_2	Basalt (tholeiitic)	Libourel et al. (2003, Eq. 23)	0.001	1673-1698	-8.3 to 8.7
N_2	Basalt	Dasgupta et al. (2022)	0.001-82	1323-2600	-8.3 to 8.7
N_2	Basalt	Bernadou et al. (2021)	0.8-10	1473-1573	-4.7 to 4.9
S_2[‡]	Basalt, Andesite	Boulliung & Wood (2022, 2023)	0.001	1473-1773	-0.14 to 10.8
S_2	Mafic silicate melts	Namur et al. (2016, Eq. 10)	0.001-40	1473-2023	-9.4 to -1.5
Cl_2	Basalt, Ano.-Dio.-For.	Thomas & Wood (2021, Fig. 4)	15	1673	2.05

Tab. 1. Compilation of experimental work used to derive solubility laws in atmodeller. Most are fit to an equation of the general form:

$$X_i = \alpha f_i^{\beta}$$

where X is the mole fraction and f is the fugacity of species i, α is the solubility constant and β the stoichiometric coefficient.

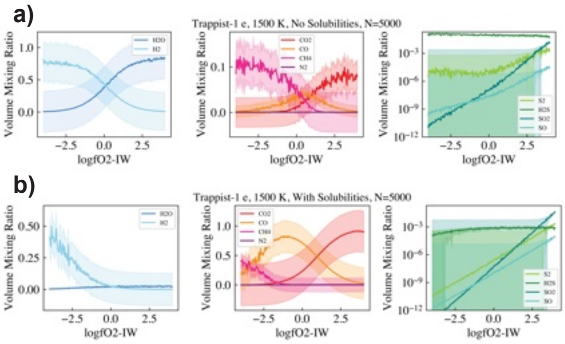


Fig. 2. Results of Monte Carlo simulations (n = 5000) of atmospheres around a TRAPPIST-1e/Earth-like planet at 1500 K with a range of H/C ratios (0.1 - 10), ocean masses of H (1 - 10) and fO_2 (-4 to +4 relative to the iron-wüstite, IW, buffer) for **a)** no solubilities and **b)** solubilities for all species included.

Results

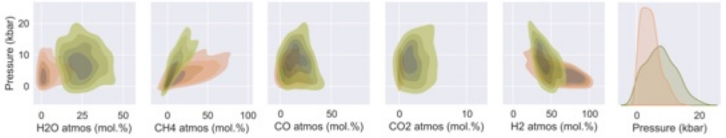
Terrestrial planets

- Solubilities of major gas species decrease in the order $H_2O < CO_2 < H_2 < CO$
- Atmospheres produced from bulk silicate Earth-like compositions are C-rich at high temperatures (cf. Bower et al. 2022; Sossi et al. 2023), or H_2-rich at very low fO_2 (<IW-3; Fig. 3)
- Higher pressures/low temperatures favour formation of associated gas species (NH_3, CH_4)

Sub-Neptunes

- May be characterised by H_2, H_2O, CO or CH_4 as major species, depending on fO_2 and C/H ratio (Fig. 4)
- Accounting for real gas behaviour reduces total pressure of atmospheres (<14 kbar) compared to ideal cases (<21 kbar)
- Results from increase in fugacity coefficients (φ) of all gases with increasing pressure
- H_2O more abundant as increase in φ is lower relative to H_2

a) Ideal



b) Real

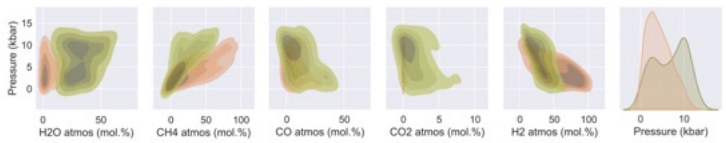


Fig. 3. Results of Monte Carlo simulations (n = 1000) of atmospheres in the C-O-H system around a K2-18b/sub-Neptune-like planet for melt fraction = 0.1 of total mass at 2000 K with C/H ratios (0.05 - 3.25), ocean masses of H (1 - 3500) and fO_2 (-5 to 0 relative to the IW buffer) for **a)** ideal gases and **b)** real gas equations of state.

Implications

- Terrestrial planets may store much (>99 %) water in their interiors
- Non-detections of atmospheres around TRAPPIST-1 planets (e.g., Greene et al. 2023) do not necessarily mean they are dry or do not support liquid oceans
- SO_2 can become a major component of terrestrial planet atmospheres and could be diagnostic of oxidised, Earth-like planets
- Sub-Neptune atmospheres have lower total pressures than predicted from ideal gas EoS, but have higher H_2O mixing ratios
- Significant amounts of H_2 and H_2O could be dissolved in their interiors, thereby affecting their mass/radius characteristics
- Provides a means of testing the Hycean worlds paradigm (e.g., Madhusudhan et al. 2023; Shorttle et al. 2024; Wogan et al. 2024).

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