1-D photochemical model to predict oxygen isotope anomalies in early Earth atmospheres

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The goal of this project is to reduce uncertainties in the evolution of O_2 levels over Earth history, using a 1-D photochemical model and triple oxygen isotope data.

1. The photochemical model, *Atmos*

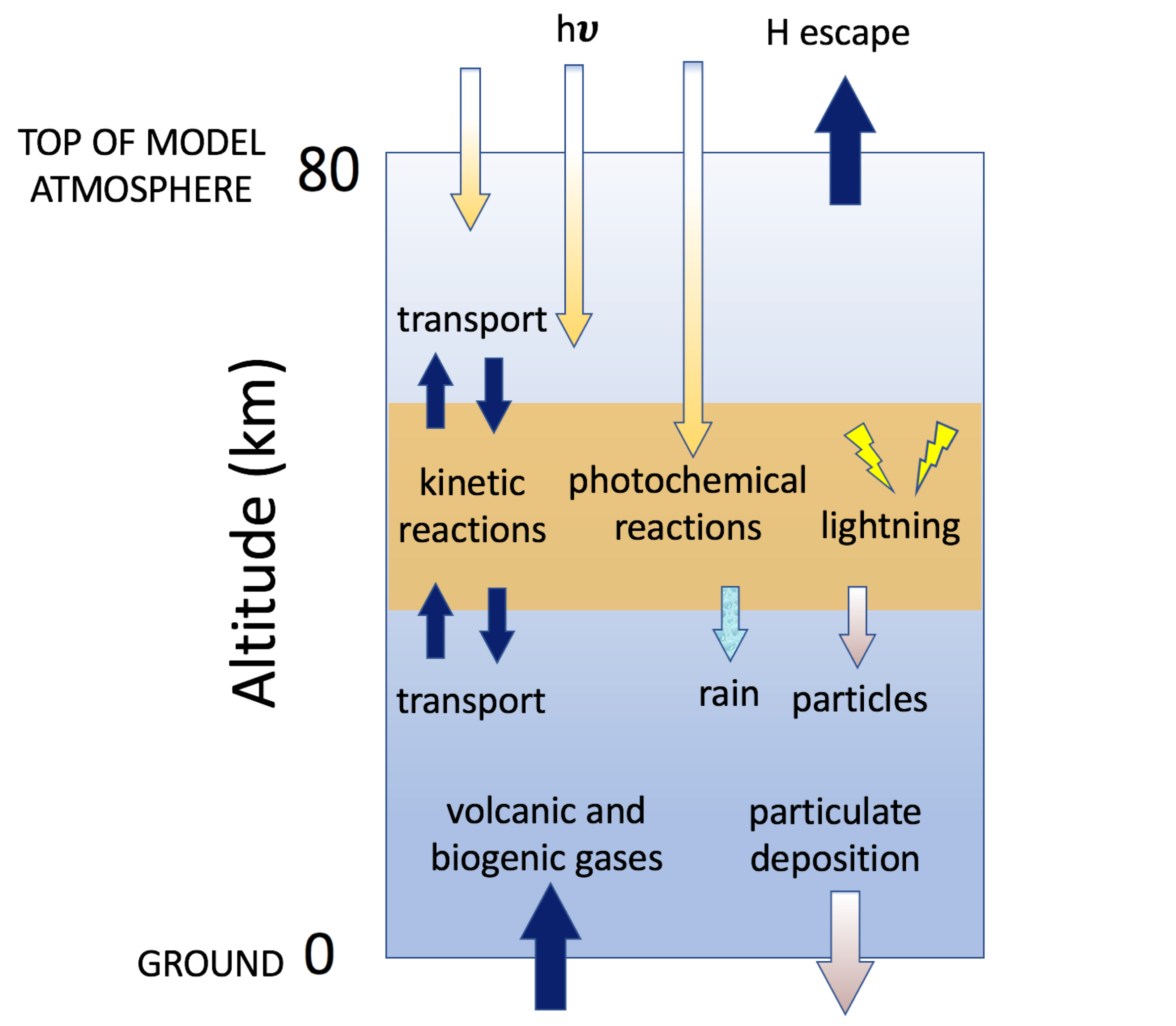

Fig. 1: Schematic of model set-up. Adapted from Claire, personal communication.

We use and develop the 1-D coupled photochemical-climate model *Atmos* (e.g. [1, 2, 3, 4]).

The model calculates production and loss of atmospheric species at each altitude layer, due to chemical reactions and vertical transport (Fig. 1).

Photolysis, lightning, particulate formation & deposition, rain, and influx of gases are included.

Outputs include species mixing ratio profiles.

2. Modelling of oxygen levels suggests two stable states

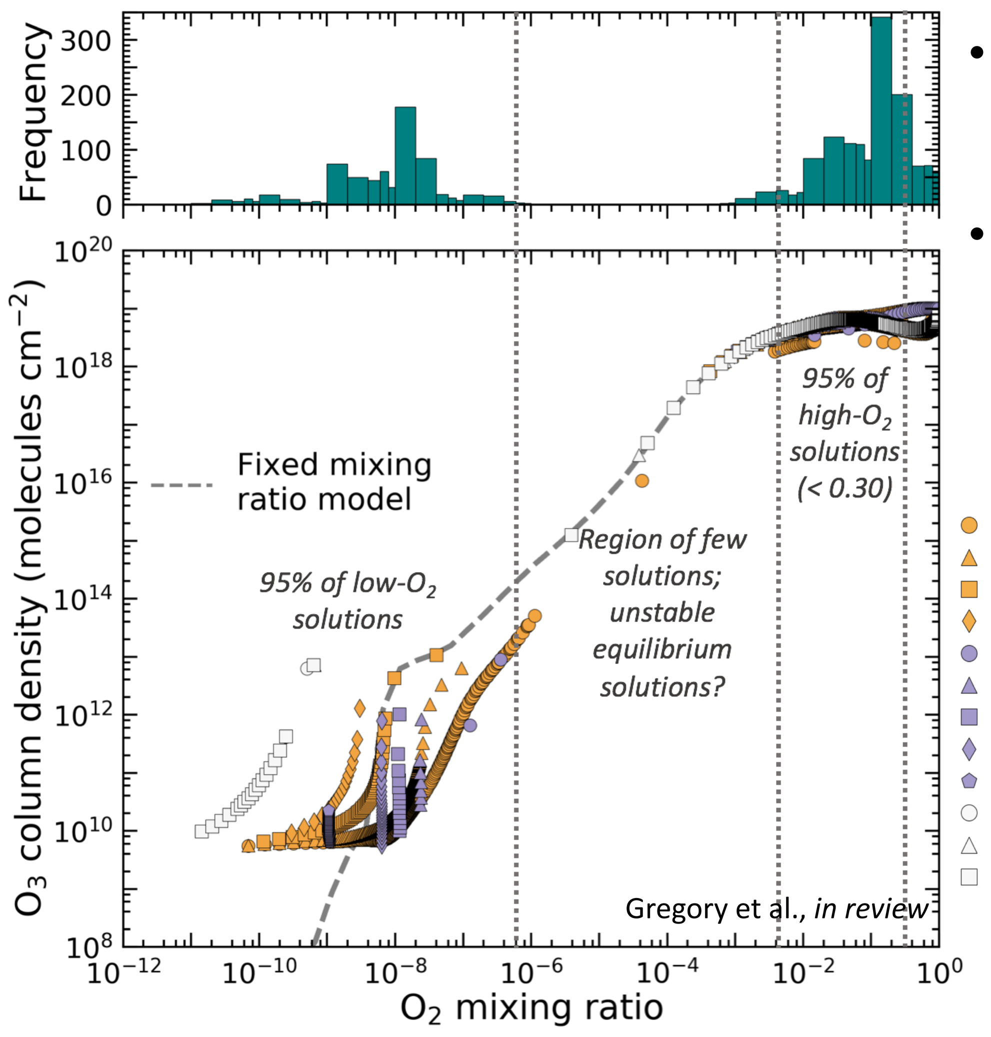

Fig. 2 (above): O_3 column density with O_2 mixing ratio for 2024 model atmospheres (from Gregory et al., in review). For Case 1, we varied O_2 flux and kept CH_4:O_2 flux ratio constant; for Case 2, we varied CH_4:O_2 flux ratio at constant O_2 flux; for Case 3, we included an oxidative weathering flux term for O_2.

- The model *Atmos* is run by varying lower boundary conditions. For O_2, mixing ratio or flux boundary conditions can be chosen.
- Previous fixed mixing ratio-driven models can simulate atmospheres with O_2 ground mixing ratios between $2.1x10^{-6}$ and 0.21[5, 6, 7], but many of these model atmospheres may be unstable equilibrium solutions.
- Models with flux boundary conditions produce few stable solutions for atmospheres with ground-level O_2 mixing ratios between **$6x10^{-7}$ and $2x10^{-3}$** (1% of present atmospheric levels) (Figure 2, Gregory et al., *in review* ([8])).
- This provides a **potential lower limit** on Proterozoic O_2 levels (Figure 3).

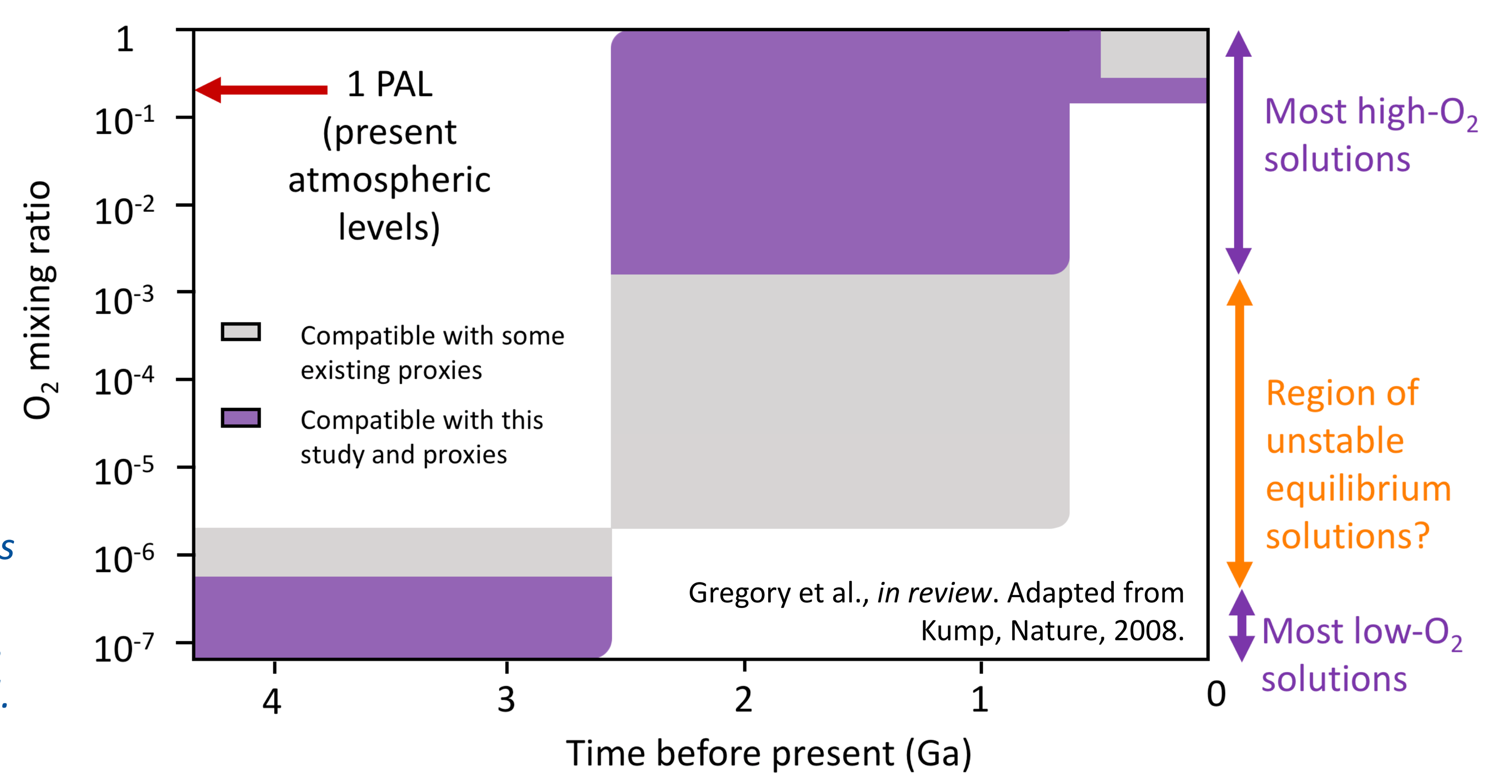

Fig. 3 (right): Potential constraints on oxygen levels over Earth history, from the clustering of model solutions from this study with high-O_2 or trace-O_2 mixing ratios (purple regions)[8]. Adapted from [9].

3. Incorporating triple oxygen isotopes into *Atmos* in order to predict $\Delta^{17}O$

i) Background to atmospheric $\Delta^{17}O$

In the formation of stratospheric ozone:

O_3 gains a **large, positive** $\Delta^{17}O$ value…

… which is propagated to **$O(^1D)$**, **CO_2**, **NO_3^-**, **SO_4^{2-}**, and **H_2O_2** via chemical reactions (e.g. [10]).

Due to mass balance, **O_2** has a **small, negative** $\Delta^{17}O$ value, dependent on pCO_2, pO_2, and primary productivity…

…which can be incorporated into stable **sulphate** and preserved in the geological record.

(where $\Delta^{17}O = \delta^{17}O - 0.528\ \delta^{18}O$)

ii) Developing *Atmos*

We have incorporated the three isotopes of oxygen in order to predict $\Delta^{17}O$ profiles of atmospheric species and $\Delta^{17}O$ values of species reaching the Earth's surface through wet and dry deposition.

iii) Model validation and calibration…

… involves comparison with existing data (e.g. [11, 12, 13]), existing model results (e.g. [14, 15]), and recently-collected salt concentration and oxygen isotope data from Atacama nitrates and sulphates.

Fig. 4: Collecting samples from the Atacama Desert, Chile (Dec 2017). Credit: A. Zerkle.

iv) Research in progress

- Q What is the minimum pO_2 required for a non-zero $\Delta^{17}O$ to be measurable in geological record sulphates?
- Q **What kind of $\Delta^{17}O_{O2}$ values might be expected for the high-O_2 and trace-O_2 atmospheres from the flux-driven modelling results presented above (Figure 3)?**

SUMMARY: We are developing an oxygen isotope model to predict $\Delta^{17}O$ in different species under different conditions, in order to explore our hypothesis of two stable states for oxygen concentrations.

Fig. 5: Maria Elena, Atacama Desert, Chile

References

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