

The triple isotopes of oxygen in planetary upper atmospheres

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Introduction: The triple isotopes of O have been well studied in Earth's atmosphere below ~60 km. Mass-independent O₃ formation [1] creates ¹⁷O enrichment that is passed to other atmospheric species [2] including stratospheric CO₂ [3], and by mass balance yields a depletion in ¹⁷O in O₂. This creates a potential measure of atmospheric CO₂ abundance in subaerially-formed sulfate over time [4].

How do O isotopes behave in the upper atmosphere? The upper atmosphere, or thermosphere, is the region where molecular diffusion dominates over eddy diffusion (~100 km for Earth). The thermosphere also includes the escape region, the exobase, at ~500 km. A substantial loss of atmosphere over geologic time can alter the isotopic composition of the bulk atmosphere and volatile reservoirs. We show here that O isotopes behave fundamentally differently in the thermosphere.

Methods: We used both diffusion theory [5] and a 1-D photochemical model [6] of Earth's thermosphere to investigate the isotopes of O. The thermosphere composition is dominated by O₂, N₂ and NO, transitioning into primarily O above 200 km. We included masses 16, 17, and 18 for O-containing species. The model has all necessary photochemical reactions and ion species. Our diffusion theory calculations include eddy and molecular diffusion, and use approximate number density profiles for O, O₂ and other species.

Results/Conclusions: Both our photochemical and diffusion theory models show that O isotopes in the thermosphere follow a 0.500 fractionation law instead of the typical 0.528 law. The 0.500 law derives from the individual diffusive profiles followed by atmospheric species above 100 km, which is a result of gravity [7]. We are presently evaluating the implications of this fractionation law for escape of O for Earth and Mars.

References: [1] Thiemens & Heidenreich (1983), *Science* 219, 1073-1075. [2] Lyons (2001), *Geophys. Res. Lett.* 28, 3231-3234. [3] Yung et al. (1991), *Geophys. Res. Lett.* 18, 260-263. [4] Bao et al. (2008), *Nature* 453, 504-506. [5] Banks and Kockarts (1973), *Aeronomy* Ch. 15, 32-63. [6] Tsai et al. (2017), *ApJS*, 228, 2. [7] Brinjikji and Lyons (2020), *Rev. Mineral. & Geochem.* 86, Ch. 6, 197-216.