



Applying clumped isotopes of O₂ to atmospheric and biogeochemical problems

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I will describe recent measurements of isotopic “clumps” in diatomic molecules, e.g., ¹⁸O¹⁸O in O₂, which are being utilized to constrain atmospheric circulation on glacial-interglacial timescales and biogeochemical cycling in the oceans. While our understanding of these tracers is still evolving, several features of their geochemistry are apparent: (1) the proportional abundance of these isotopic “clumps” is governed by traditional chemical effects as well as combinatorial effects unique to clumped isotopes, and (2) when isotopic exchange reactions are disfavoured, chemical-kinetic and/or reservoir effects, rather than thermodynamic equilibrium, determine their clumped-isotope composition. Combinatorial clumped-isotope signatures imparted during photosynthesis are being developed as endmember signatures of gross primary productivity in the oceans.

In addition, clumped-isotope measurements of O₂ in the atmosphere (i.e., Δ_{36} values) suggest that isotopic clumping in O₂ is continuously being altered by ozone photochemistry in the troposphere and stratosphere. Yet, the contrast in isotope-exchange rates between the stratosphere (where exchange is fast) and the troposphere (where exchange is slow) results in a gradient in Δ_{36} values with altitude, wherein stratospheric intrusions are detectable as elevated Δ_{36} values. Moreover, global chemical-transport model simulations suggest that ozone photochemistry in the troposphere re-orders the O₂ reservoir in the troposphere on annual timescales. The Δ_{36} value at the surface is therefore sensitive to the tropospheric residence time of O₂ with respect to stratosphere-troposphere exchange. Consequently, Δ_{36} values at the surface likely respond to changes in the strength of the global overturning circulation.