Goldschmidt Medal Abstract

The diversity of isotopic ordering in small molecules

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As recent analytical advances have enabled us to explore isotopic ordering in geochemical systems more broadly, the diversity of clumped isotope signatures and their applications is becoming apparent: Equilibrium clumped-isotope signatures can be used not only as geothermometers but also geospeedometers [1, 2]; kinetic clumped-isotope effects can be predicted from first principles and verified by laboratory measurements, opening the door to a class of isotopic reaction fingerprints that can complement isotopic reservoir fingerprints [3, 4]; combinatorial "declumping" reflects intramolecular isotopic heterogeneity, and can in principle be used to extract information about geochemical reservoirs and reaction pathways [5]. Yet the field is still young, and many of its most significant contributions lie ahead.

Perhaps the most interesting aspect of clumped-isotope approaches is their ability to distinguish process-level effects from reservoir effects. Contrasts in chemistry between different reservoirs (e.g., stratospheric vs. tropospheric ozone photochemistry) can be exploited within a reaction-transport framework to extract rates of reservoir mixing, material residence times, and flux budgets, potentially even from the geologic record. I will describe recent developments in the clumped-isotope geochemistry of O_2 and N_2, the basic principles gained from examining clumped-isotope systematics of these small molecules, and emerging applications in atmospheric and biogeochemical research within this context.

[1] Eiler (2011) *Quat. Sci. Rev.* **30**, 3575-3588. [2] Passey & Henkes (2012) *Earth Planet. Sci. Lett.* **351-352**, 223-236. [3] Joelsson et al. (2014) *Chem. Phys. Lett.* **605-606**, 152-157. [4] Schmidt & Johnson (2015) *Geophys. Res. Lett.* **42**, 3546-3552. [5] Yeung (2016) *Geochim. Cosmochim. Acta* **172**, 22-38.