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Frontiers of stable isotope geoscience

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ABSTRACT

Isotope geochemistry is in the midst of a remarkable period of innovation and discovery; the last decade (or so) has seen the emergence of 'nontraditional' stable isotopes of metals (i.e., variations in isotopic compositions of Mg, Fe, Cu, etc.), a great expansion of mass-independent isotope geochemistry, the invention of clumped isotope geochemistry, and new capabilities for measurements of position-specific isotope effects in organic compounds. These advances stem from the emergence of multi-collector plasma mass spectrometry, innovations in gas source mass spectrometry, infrared absorption spectroscopy, and nuclear magnetic resonance techniques. These new observations demand new connections between isotope geochemistry and the chemical physics that underlie isotopic variations, including experimental study and modeling of vibrational isotope effects, photochemical isotope effects, and various nuclear volume and magnetic effects. Importantly, such collaborations also have something to offer chemists and physicists because the novel observations of emerging branches of stable isotope geochemistry hold the potential to reveal new insights into the nature of chemical bonds and reactions. This review looks broadly across the frontiers of new methods and discoveries of stable isotope geochemistry and the fundamental chemical–physics problems they pose, focusing in particular on the most pressing problems in: kinetic isotope effects in complex systems; mass independent isotope geochemistry (both the strong effects in photochemical reactions and the subtle variations of more conventional reactions); clumped isotope geochemistry; and the position-specific isotopic anatomies of organic molecules.

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1. Introduction

The nuclear, physical and biological chemistry of isotopes has profoundly influenced the geosciences; these fields underpin the calibration of geological time scales (e.g., Patterson et al., 1955; Bowring and Schmidz, 2003), reconstructions of past climates (e.g., Epstein et al., 1951; Zachos et al., 2001), 'tracer' studies in the hydrosphere and atmosphere (e.g., Dansgaard, 1964; Jouzel et al., 1997), and numerous other geological and geochemical tools. This discipline is in the midst of a sustained burst of innovation and discovery as dramatic as any period since its foundation in the 1940's and 50's. New analytical techniques for isotope geochemistry have increased the scope of the discipline, adding to both the list of elements that can be analyzed and the properties of isotope distribution that can be interrogated, including mass laws of fractionations, position-specific isotope effects and isotopic ordering or 'clumping'. These methodological innovations have led to a variety of discoveries that are playing central roles in the study of earth history and processes. But, many of these discoveries involve phenomena beyond our basic understanding of the chemistry of isotopes.

Recent decades have also seen noteworthy advances in ab initio and molecular dynamic models of the structures and energetics of chemical compounds (e.g., Becke, 1993). These advances have enabled the first-principles modeling of molecular structures and isotope effects on molecular properties and dynamics for complex materials with unprecedented levels of accuracy (Car and Parrinello, 1985; Panagiotopoulos, 1987; Laio and Parrinello, 2002), including solute–solvent interactions and phase interfaces, (e.g., Kolmodin et al., 2002; Sharif et al., 2006) — the sorts of materials most relevant to many earth science problems (Varma and Rempe, 2006; Bourg and Sposito, 2011; Stack et al., 2012). These methods are capable of illuminating the chemical physics of isotope fractionations (Dreisner et al., 2000; Hill et al., 2010; Rustad et al., 2010) and have been widely applied to classic problems in traditional stable isotope geochemistry (e.g., the carbon isotope fractionation associated with photosynthetic carbon fixation; Tcherkez et al., 2006). But this work has not yet been brought to bear on most of the new observations coming from novel branches of stable isotope geochemistry.

Thus, isotope geochemistry and the chemical physics of isotopes are both in an unusual period of their development — each has separately made substantial progress on their own, but would benefit by turning their attention on common sets of new goals. Some of the greatest past discoveries and advances in understanding of the isotope geosciences have come from such collaborations — for example, the invention of quantitative paleoclimate reconstructions was based on isotope effects on vibrational energies of chemical bonds (Urey, 1947); the discoveries of metabolic and other biological isotopic fractionations (e.g., Dole and Jenks, 1944) led to new insights into biochemical kinetics and new biogeochemical tools (e.g., Farquhar et al., 1989); discoveries of mass-anomalous isotope effects in nature (i.e., departures from canonical mass laws followed by common fractionation mechanisms; Clayton et al., 1973; Mauersberger, 1987), led to fundamental research in isotope effects in photochemistry and other gas phase reactions dominated by electronic transitions (e.g., Thiemens and Heidenreich, 1983; Mauersberger et al., 1999; Thiemens et al., 2012) and fundamental chemical–kinetic theory (e.g., Gao and Marcus, 2001), which in turn has led to further discoveries regarding the history of the Earth's atmosphere (Farquhar et al., 2000a). From a geoscientist's point of view, the