



Editorial

Introduction

Isotopic records of microbially mediated processes

The seed for this special issue was planted at a topical session organized for the 1999 Annual Meeting of the Geological Society of America and sponsored by the Geochemical Society. As organizers of the session, we considered ourselves to be among an already large but rapidly growing group of researchers straddling the interface between biology and geology. This interface spans phenomena occurring at many scales—ranging from microbes and molecules to oceans and continents and from seconds to billions of years—but our vision for the GSA session and indeed for this volume was narrowed to the *Isotopic Records of Microbially Mediated Processes*. Despite the narrowed focus, the range of relevant topics is still vast. We have designed a volume that represents many areas of isotopic research and the coupled biogeochemical cycles.

Those within the emerging field of biogeoscience are dedicated to dissolving boundaries between disciplines. Nevertheless, we have organized the sequence of papers in this volume according to general themes—progressing from detailed characterizations of experimental and natural systems and novel isotope approaches to case studies of modern systems and ancient organic carbon burial. Again, the common thread running through each theme and each paper is the use of stable isotopes as recorders of microbial processes. Isotope relationships in modern systems—when calibrated against experimental and modeling results—provide fingerprints of biogenicity and semi-quantitative estimates of rates of biogeochemical cycling. These fingerprints of life and estimates of rate can persist into the ancient geologic record where solid-phase isotope data—both organic and inorganic—speak to the former presence, pathways, and rates of microbiological activity. Improved understanding of the isotopic effects of such activity also

enhances the feasibility of defining unambiguous isotopic proxies for exploration of life beyond our planet.

In the first group of papers, which are linked by a common focus on experimental approaches and/or carbon isotope records of microbial carbon cycling, Romanek et al. use laboratory cultures to investigate the hydrogen and carbon isotope fractionations related to growth of iron-reducing bacteria. In these experiments, siderite formed only when hydrous ferric oxide was used as the electron acceptor. When lactate was used as the carbon and energy source, isotope partitioning between siderite and CO<sub>2</sub> was consistent with theoretical calculations of equilibrium isotope fractionation. Carbon isotope enrichment factors were substantially lower when H<sub>2</sub>/CO<sub>2</sub> were used as the energy source and yeast extract was used as the source of carbon. The reasons for these differences are explored. Romanek et al. also suggest that bacterial metabolism may facilitate isotope exchange between water and H<sub>2</sub>.

Zhang et al. characterize carbon isotope fractionations during heterotrophic growth of iron-reducing bacteria for use as biomarkers of carbon assimilation pathways in natural environments. In culture experiments, *Geobacter* (GS-15) and *Shewanella* (BrY) display distinct isotope fractionations as expressed in bulk biomass, fatty acids, and carbon (food) resources. These fractionations are attributed to carbon assimilation through tricarboxylic acid (GS-15) and serine (BrY) pathways. Fatty acids and their carbon isotope compositions can be linked to specific bacterial strains, thus providing potential biomarkers for use in the rock record.

Pancost and Sinninghe Damsté have assembled an elegant review and discussion of carbon isotope compositions of prokaryotic lipids in diverse settings.

Because Bacteria contain mostly ester lipids and Archaea ether lipids, relative lipid abundances and their isotopic compositions delineate specific prokaryotic pathways of carbon cycling in modern and ancient depositional settings. The authors review the diagnostic bacterial and archaeal biomarkers and discuss possible mechanisms of carbon assimilation and controls on lipid carbon isotope compositions in different microorganisms. The general principles of carbon assimilation and isotopic fractionations of lipid biomarkers are then highlighted in two case studies. One is an ancient peat deposit, wherein the authors demonstrate the use of hopanoids as tracers of aerobic bacteria and ether-bound isoprenoids as tracers of methanogenic archaea. The other example emphasizes modern cold seeps and reveals diverse Bacteria–Archaea consortia responsible for anaerobic methane oxidation in marine environments.

Brungard et al. describe the stable carbon isotope fractionation associated with biodegradation of a halogenated organic contaminant (*trans*-1,2-Dichloroethylene) through co-metabolism by two different species of methanotrophic bacteria. The authors observe a smaller isotopic fractionation ( $-3.5\text{‰}$ ) for a type I culture than for a type II culture ( $-6.7\text{‰}$ ), indicating that characteristic fractionation patterns exist for different methanotrophic species. Future efforts to quantify the extent of biodegradation of DCE by methanotrophs will benefit from this improved understanding of related isotope effects. The study also offers insight into species diversity and methanotroph populations that may be actively participating in the degradation of halogenated compounds in natural environments.

In the first of a trio of papers best described as novel isotope approaches to the investigation of biological cycling, Roe et al. address Fe isotope fractionation in chromatographic experiments. These experiments show that the magnitude of Fe isotope fractionation increases as more time is allowed for equilibration. The authors interpret this observation as evidence for a significant equilibrium isotope effect in an abiotic system, with the essential implication being that Fe isotope variation in nature cannot be ascribed uniquely to biology.

Beard et al. thoroughly review the range of iron isotope variability observed within diverse geologic materials. All isotopic variability—relative to a well-constrained, homogeneous igneous Fe baseline—is

ascribed to low-temperature processes. And while abiotic isotopic fractionations at low temperatures may explain the range of observed  $\delta^{56}\text{Fe}$  values, the data are also consistent with experimentally measured isotopic fractionations produced by Fe-reducing bacteria. Beard et al. broadly address Fe isotope geochemistry, including new analytical approaches and experimental methods designed to deconstruct the complexities of isotopic exchange. Particular emphasis is placed on biological cycling and the pursuit of isotopic signals that are uniquely biological.

Ellis et al. investigate the use of selenium stable isotope fractionation as an indicator of Se immobilization during reduction. Specifically, the authors have measured Se isotope fractionations during reduction of Se (VI) and Se (IV) oxyanions by natural microbial consortia in sediment slurry experiments mimicking natural conditions. The experiments incorporate a wide range of natural and experimentally modified Se concentrations and sediments from diverse environmental settings. Fractionations did not vary significantly as a function of these variables, suggesting concentration independence for bacterial populations that may be physiologically similar—while following similar reductive pathways—across the spectrum of environmental differences. Ultimately, the experiments provide estimates for Se isotope fractionation in organic-rich wetland environments.

The papers by Lyons et al. and Werne et al. collectively form a comprehensive statement on organic and inorganic sulfur speciation and reaction pathways in the Cariaco Basin, Venezuela, from the last glacial to present. Thematically, these efforts—along with the papers by Mandernack et al. and Aharon and Fu—are each isotope-based case studies of microbial sulfur cycling in a modern marine setting. Lyons et al. incorporate sulfur isotope trends in their argument for a predominance of iron-limited, water-column (syngenetic) pyrite formation over the euxinic interval of the last  $\sim 14,500$  years. When viewed broadly, including comparisons to the modern Black Sea, total-iron-to-aluminum ratios and the degrees of pyritization for the euxinic sediments of the Cariaco reflect the balance between scavenging of Fe during syngenetic pyrite formation and the rates of accumulation of Fe-bearing siliciclastic sediment. The shift from oxic to euxinic marine deposition marking the last glacial-interglacial transition is reflected in a strong secondary pyrite

overprint on the uppermost bioturbated sediments. The Cariaco transition is contrasted with post-glacial  $\delta^{34}\text{S}$  overprints in other restricted, presently euxinic marine basins, such as the Black Sea. Finally, Lyons et al. explore pathways of Mo enrichment in the euxinic sediments of the Cariaco Basin in terms of syngenetic versus diagenetic sequestration, organic richness, and hydrogen sulfide availability.

Werne et al.—although also addressing pyrite relationships in the Holocene/latest Pleistocene euxinic sediments of the Cariaco Basin and confirming the importance of water-column formation—focus on the timing and possible pathways of organic matter sulfuration. Observed and modeled sulfur isotope compositions for organic matter indicate that organic sulfur is derived primarily from pore-water sulfide, with only minor contributions from primary bio-sulfur. Mechanistically, the data do not, however, preclude the possibility that reactive sulfur intermediates, formed by partial oxidation of  $\text{H}_2\text{S}$ , were essential in reactions between sulfur-bearing species and organic matter.

Mandernack et al. interpret their  $\delta^{34}\text{S}$  data for total dissolved sulfide and sulfate and the  $\delta^{18}\text{O}$  of sulfate from water samples spanning the oxic–anoxic interface—as well as deep, permanently anoxic waters—in Framvaren fjord, Norway. Consistent with comparatively high rates of bacterial sulfate reduction in a well-stratified water column, sulfate in deeper anoxic water shows marked  $^{34}\text{S}$  enrichment with depth. Relationships between water-column dissolved species and reduced inorganic S within the Framvaren sediments are interpreted in light of variability in rates of sulfate reduction and the hypothesized relative roles of disproportionation pathways. Finally, observed patterns of  $\delta^{34}\text{S}$  versus  $\delta^{18}\text{O}$  variation for sulfate within the anoxic waters are taken as evidence against oxygen isotope exchange between S-bearing intermediates and water either during bacterial sulfate reduction or sulfide reoxidation. Instead, the isotope pairs are interpreted as full, preserved expressions of the kinetic isotope effects of unidirectional biochemical processes.

Aharon and Fu provide a survey of sulfur and oxygen isotope relationships for coeval sulfate and sulfide in pore waters from cold-seep settings along the oxic slope of the northern Gulf of Mexico, where oil and gas leak to the seafloor through fault conduits. Microbial processes fueled by the hydrocarbons have caused extensive sulfur diagenesis, including unusu-

ally high and variable rates of bacterial sulfate reduction. Fractionation factors for sulfur during bacterial sulfate reduction are estimated assuming both closed- and open-system behavior and are compared to fractionations observed in other natural settings. A mass balance that predicts sulfide loss is discussed in terms of open-system sulfur cycling. Finally,  $\delta^{34}\text{S}$ – $\delta^{18}\text{O}$  relationships for sulfate are interpreted in terms of mixing between seawater sulfate modified by bacterial sulfate reduction and secondary sulfate linked to oxidative  $\text{H}_2\text{S}$  cycling in near-surface environments.

In the final modern-system case study, Aravena et al. demonstrate the utility of stable isotope approaches in a nonmarine setting. Specifically, the authors constrain the origin of methane and dissolved inorganic carbon (DIC) in the Elk Valley Coalfield of British Columbia by tracing the stable isotope composition of hydrogen- and carbon-bearing molecules (methane, DIC, and water) in associated ground waters. The authors ultimately show how the blending of hydrological, physicochemical, and biological information illuminates the origin and transformation of biogenic methane in ways seldom achieved without an integrated perspective.

In the final paper of the volume, Sageman et al. apply the isotopic lessons learned from experimental and natural-system microbial cycling to the interpretation of deep geologic time. In a comparative evaluation of Middle-Upper Devonian, organic-rich shales of the northern Appalachian basin, the authors challenge many of the prevailing paradigms that pervade studies of black shale geochemistry. Among the essential conclusions—based in part on sulfur and carbon isotope relationships—is the assertion that few of the organic-rich units were deposited under a pervasively and persistently anoxic-sulfidic water column and the corollary that water-column stratification was frequently intermittent on short timescales. Sageman et al. further suggest that the “master variable” for organic matter burial is sea level, which modulates the rates of clastic dilution and the relative levels of organic preservation and biological production.

We hope this collection of papers will broaden the reader's perspective on new and refined isotopic approaches to the biogeosciences—as very broadly defined. We thank the participants of the original GSA session for getting the ball rolling and the authors of this volume for their terrific efforts. We are also grateful to Editor Eric Oelkers, the staff of Chemical

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