

Introduction to “In search of isotope biosignatures”

Since its foundation in the 1940s–1950s, one of the main objectives of isotope geochemistry of light elements (H, C, N, O, and S) has been to identify and quantify biogeochemical processes in modern and ancient environments, including extraterrestrial samples. This has been particularly true for carbon isotopes because of the essential role that the element carbon plays in the biological cycle of a myriad of organic and biological compounds in nature. Using a modern mass spectrometer, Nier and Gulbransen (1939) and Murphy and Nier (1941), for the first time, determined large natural variations in $^{12}\text{C}/^{13}\text{C}$ ratios among various terrestrial and extraterrestrial materials. Soon, Frank Wickman and others followed to conduct systematic measurements of $^{12}\text{C}/^{13}\text{C}$ ratios of various terrestrial compounds (graphite, carbonates, sediments, petroleum, natural gases, metamorphic rocks, etc.). The notion of carbon isotope biosignatures in the ancient rock record was already proposed and tested in the 1940s. It was at this time when Harmon Craig published his now-classic paper titled, “*The Geochemistry of the Stable Carbon Isotopes*” [*Geochimica Cosmochimica Acta* 3, 53–92 (1953)]. This paper is truly a landmark paper in the history of isotope geochemistry, including several hundreds of carbon isotope analyses of virtually all carbon-bearing materials. It is remarkable that today, even after more than half a century, many salient features in the general distribution of stable carbon isotopes of terrestrial materials established by Craig (1953) remain largely intact. Thanks to these early pioneers (Nier, Wickman, and Craig), including Libby for his discovery of radioactive ^{14}C , a great deal of knowledge was already amassed on carbon isotope geochemistry by the early 1950s (see Rankama’s 1954

book, *Isotope Geology*, for more details). Studies of other isotopic systematics, sulfur isotopes in particular, followed developmental paths similar to that of carbon isotopes in terms of applications to biogeochemical cycles. Since then, it became almost impossible to conduct quantitative studies on biogeochemical processes without utilizing the stable isotope techniques of light elements.

The past decade has witnessed perhaps the most exciting and revolutionary developments in the field of isotope geochemistry since its foundation more than half a century ago. Rapid developments of novel analytical techniques (continuous-flow mass spectrometry for compound-specific isotopic analyses of organic/biological molecules, accelerator mass spectrometry for compound-specific ^{14}C analyses, and secondary ion mass spectrometry for in situ microanalysis) made it possible to investigate isotope distributions at molecular and micrometer scales. Multi-collector ICP mass spectrometry opened up a new, exciting branch of stable isotope geochemistry for intermediate elements (Fe, Cu, Mo, Zn, etc.) (Johnson et al., 2004). These technologies are finding increasing applications in emerging and rapidly developing new fields of geosciences such as environmental geochemistry, geomicrobiology, astrobiology, and molecular biogeochemistry, which all deal with biogeochemical processes in somewhat different environments.

It was against this backdrop that a special session, titled “*In Search of Isotope Biosignatures*,” was organized at the 13th Goldschmidt Conference, Kurashiki, Japan, September 7–12, 2003. When we started organizing this special session, we were well aware of the historical significance of 2003, which

marked the golden anniversary of Harmon Craig's 1953 landmark paper on the geochemistry of carbon isotopes. This interdisciplinary symposium called for innovative studies and applications of both conventional and metal stable isotopes toward this ever-elusive goal for the past half century—isotopic biosignatures. The symposium was well attended by a number of isotope geochemists and other geoscientists from across the world with lively discussion on the topics of isotope biosignatures. This special issue of *Chemical Geology* is a collection of 12 manuscripts that were all presented in this and other symposiums with closely related topics at the conference. Reflecting the depth and diversity of the papers presented at the symposium, articles in this special issue cover a wide range of topics from atmospheric to terrestrial to marine environments and from modern to ancient settings, utilizing both light (C, N, Si, and S) and heavy (Fe) stable and radioactive (^{14}C) isotope systematics. Mohammadzadeh et al. developed and applied a novel technique of liquid chromatography and continuous-flow mass spectrometry for compound-specific isotope analysis of dissolved organic carbons from a municipal landfill. The role of rice paddy in the geochemical cycle of greenhouse gases, CO_2 and CH_4 , was systematically investigated for temporal and spatial variations (Han et al.) and under elevated pCO_2 conditions (Cheng et al.). Ding et al. reported perhaps the largest natural variations in $^{30}\text{Si}/^{28}\text{Si}$ ratios among different parts of rice plants from China. A 200-year sedimentary record from a lagoon provided information on natural and anthropogenic changes in coastal environments in western Japan (Yamamuro and Kanai). A powerful combination of stable and radioactive carbon isotope ratios of bulk organic matter from coastal marine sediments (Nagao et al.) and of individual lipid biomarkers from Pacific sediments (Uchida et al.) provided clues to complex sources, transportation, and biogeochemical cycles of organic matter in coastal and open marine environments. Carbon and nitrogen isotopic compositions of fossil bones revealed dietary history of wild boar (Minagawa et al.) and Neolithic human (Ogrinc and Budja). Yamamoto et al. studied genetic relationship of organic compounds (hopanoic and 28-norhopanoic acid) from Neogene marine sediments of Japan and the United States. Yamaguchi et al. analyzed Fe-isotopes of Archean–Paleoproterozoic sedimentary

rocks from South Africa and discussed the biogeochemical evolution of early atmosphere and oceans. Horita reflected on historical development and the current status of carbon isotope biosignatures from ancient rocks.

It is a tall order to cover the subject of isotope biosignatures in a single journal issue or even by a book. However, it is hoped that a collection of the articles in this special issue provide a glimpse of the idea how diverse and powerful isotope geochemistry has become to address the topics of primary importance in geochemistry and beyond. Now we have entered the second half century in the study of isotope biosignatures, and we can certainly expect more exciting discoveries and developments to come in the future.

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Juske Horita
*Chemical Sciences Division,
 Oak Ridge National Laboratory,
 Oak Ridge, TN 37831-6110, USA
 E-mail address: horitaj@ornl.gov.*
 Corresponding author.

Alan Matthews
*Institute of Earth Science,
 Hebrew University of Jerusalem,
 Jerusalem 91904, Israel*