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Some perspectives on isotope biosignatures for early life

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Abstract

The idea of using stable isotope compositions of light elements, particularly of carbon, as a sign of biological activities (biosignatures), both present and past, dates back to the dawn of stable isotope geochemistry in the 1940s. In the wake of the discovery of large variations in $^{13}C/^{12}C$ ratios among various carbon-bearing materials including plants and fossil fuels, the contentious debate ensued between Kalervo Rankama and Harmon Craig in the early 1950s whether the origin of graphitic carbon in ancient rocks (biogenic vs. abiogenic) can be uniquely identified by its isotopic compositions. During the last half-century, great progress has been made in understanding biogeochemical processes in modern and ancient terrestrial environments. Rapid developments in the last decade of novel analytical techniques and the birth of new geoscience fields such as geomicrobiology and astrobiology has prompted resurgence in the application not only of conventional light stable isotopes, but also of those of metal and other intermediate elements. However, recent debates on the origin of graphitic carbons from Early Archean rocks from Australia and Greenland are very much reminiscent of the Rankama–Craig debate half a century ago. Here, an attempt is made to review briefly the history of isotope biosignatures and to critically assess current criteria for early life. A number of possible abiotic pathways exist that lead to the synthesis of various organic and reduced carbon compounds (alkanes, PAH, amino acids, lipids, graphitic carbon, etc.) depleted in ^{13}C due to large kinetic isotope effects (up to ca. −60‰). It also seems very likely that the mantle contains indigenous carbons (graphite, diamond, dissolved carbons, carbide) with low $\delta^{13}C$ values (−20‰ to −30‰), which have previously been considered recycled sedimentary organic carbons or surface contamination. This analysis prompts us to reassess our current and future strategies for identifying early and extraterrestrial life using isotope biosignatures.

Keywords: Isotopes; Biosignatures; Organic compounds; Graphite; Archean

1. Introduction

With the advent of modern mass spectrometers in the late 1930s, it became possible to measure routinely small natural variations of stable isotope compositions of various light elements. Nier and Gulbransen (1939) and Murphy and Nier (1941) were

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the first to determine rather large (ca. 30‰) natural variations in $^{13}C/^{12}C$ ratios among various terrestrial and extraterrestrial materials (meteorites, limestones, plants, oil, and others).[1] The observation that modern plants and fossil organic matter (oil, coal) are both depleted in ^{13}C by a similar magnitude (20‰) compared to inorganic carbonates led them to suggest that the fossil organic matter is of biogenic origin. Recognizing the primary importance of carbon in plant metabolism, Wickman (1952) and Craig (1953a, 1954a) conducted the first systematic surveys of $^{13}C/^{12}C$ ratios of various plant samples from different locales. Their studies not only confirmed that all plants are significantly depleted in ^{13}C relative to inorganic CO_2 and carbonates, but also revealed that plants from different environments (marine, terrestrial, and desert) exhibit varying degrees of ^{13}C depletions. A laboratory experiment conducted by Baertschi (1953) demonstrated that CO_2 assimilation and photosynthesis caused a ^{13}C depletion by about 26‰, and Craig (1954a) presented the first quantitative model for a biological carbon isotope fractionation process in plants. It was later discovered by Bender (1968) that the then newly discovered C4 photosynthetic pathway in desert grasses had caused the ^{13}C enrichments observed by Wickman (1952) and Craig (1953a), compared to far more abundant C3 pathways in plants. In fact, the different degrees of ^{13}C discrimination between the C3 and C4 pathways have been used as a diagnostic tool for distinguishing the two types of plants. The reader is referred to Ehleringer and Vogel (1993) for a brief history of isotopic studies on plants.

[1] Until the mid-1950s, many investigators, including Nier and Gulbransen (1939) and Murphy and Nier (1941), determined absolute $^{12}C/^{13}C$ ratios for carbon isotopes of natural compounds. Craig (1953a) introduced PDB as a primary interlaboratory standard and determined relative differences of $^{13}C/^{12}C$ ratios in δ-values (‰) against PDB (PDB scale). It is not straightforward to convert the reported absolute ratios to values on the PDB scale due to systematic errors associated with absolute ratio measurements at each laboratory. For example, $^{12}C/^{13}C$ ratios reported for PDB in the 1950s vary from 88.68 to 88.99 (Craig, 1953a, 1954a, 1957): the most recent value is 89.45 (Coplen et al., 2002). This error leads to an uncertainty up to 3‰ on the PBD scale, which is not significant to discussion in this article. Uncertainty in the conversion of δ-values between the PBD and V-PDB scales is very small. In this article, $\delta^{13}C$ values are discussed on the PDB and V-PBD scales interchangeably.

2. Isotope biosignatures for early life

2.1. Then—the early 1950s

No sooner were fossil organic matter and modern photosynthetic plants found equally depleted in ^{13}C than the carbon isotopic ratios of fossil organic matter were suggested as a criterion for inferring biological origin (Wickman, 1941). Back then, the oldest purported fossil was peculiar cell-shaped small sacs in the form of graphite, *Corycium enigmaticum* Sederholm, occurring in 1.5 Ga phyllites on the shore of the Tampere Region in Finland. With Al Nier's help, Rankama (1948) determined $^{13}C/^{12}C$ ratios of these purported fossils and concluded their biogenic origin on the basis that their measured carbon isotope values ($^{12}C/^{13}C > 90.5$ or $\delta^{13}C <$ approximately -20‰ PDB[1]) overlap those of biogenic materials (plants, animals, oil) (Rankama, 1948, p. 390);

"...C^{12}/C^{13} determinations furnish definite proof of this and also final proof of the organic nature of the Corycium... the oldest ever recorded with definite certainty"

Rankama (1954a) further extended the notion of carbon isotope biosignatures to 2.55 Ga sedimentary rocks of the Rice Lake Group from Canadian Shield. In the absence of any fossil-like materials in the sediments, the carbon isotope ratios of carbonaceous slates was used as a sole evidence for biogenic origin (Rankama, 1954b, p. 150);

"In the absence of contradictory geologic evidence, one is safe to conclude that finely disseminated carbon.....are of biogenic origin if their isotopic constitution lies within the biogenic origin"

Rankama's claim of carbon isotope evidence for the oldest fossil of *C. enigmaticum* met immediate criticism on both geological and biological grounds (Straaten, 1949; Hutchinson, 1949). He responded to their comments by a paper titled "*Corycium resuscitum*: A discussion" (Rankama, 1950). However, the fiercest criticism of Rankama's assertion that the carbon isotope compositions of ancient graphite can be used as clear-cut biosignatures came from Harmon Craig. In his paper titled "*Corycium defunctum*: The non-indicative properties of isotopes and review articles" (Craig, 1953b) and in later