



Theoretical Amino Acid-Specific Radiocarbon Content in the Environment: Hypotheses to Be Tested and Opportunities to Be Taken

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Tracing of biogeochemical pathways using molecular approaches has advanced our basic understanding of the carbon cycle and life's legacy in the sedimentary record. To this end, compound-specific radiocarbon analysis has been instrumental in shedding light on the turnover, age, and sources of a range of biomarkers embedded within complex environmental matrices. However, despite their foundational importance for life and their omnipresence throughout geologic space and time, the biogeochemical cycling of amino acids remains largely unexplored. Here, we discuss the potential of using amino acid-specific radiocarbon to deepen our knowledge of the biogeochemistry of food webs and sedimentary organic carbon.

Keywords: amino acid, radiocarbon, ecology, food web, organic matter-mineral interactions, peptide, compound specific isotope analysis, protein

INTRODUCTION

The “building blocks of life” constitute a common foundation which all life on Earth shares and depends on (Miller and Urey, 1959; Kitadai and Maruyama, 2018) and amino acids are one of the largest pools of characterizable organic matter found in sedimentary environments (Trask, 1936; Degens, 1970; Lee et al., 1983; Wakeham et al., 1997; Hedges et al., 2001). In contrast to other biomarkers where source specificity is a key attribute for understanding sedimentary and biogeochemical cycling pathways [e.g., lignin from the terrestrial biosphere (Hedges and Parker, 1976), lipids from the marine biosphere (Volkman et al., 1980)], amino acids are arguably among the least specific “biomarkers” as the molecules themselves are omnipresent in all life forms and occur across most of geologic space and time (Abelson, 1954; Erdman et al., 1956; Degens and Bajor, 1960; Hare, 1969). Embracing this property of environmental omnipresence, previous workers, as summarized by Kvenvolden (1975), have provided insights on the utility of amino acids (and their degradation products) as molecular clocks, (paleo)thermometers, and diagenesis proxies. Since then, appreciable progress on compound-specific isotope measurements has been made. Here, we share our perspectives on how amino acid-specific radiocarbon

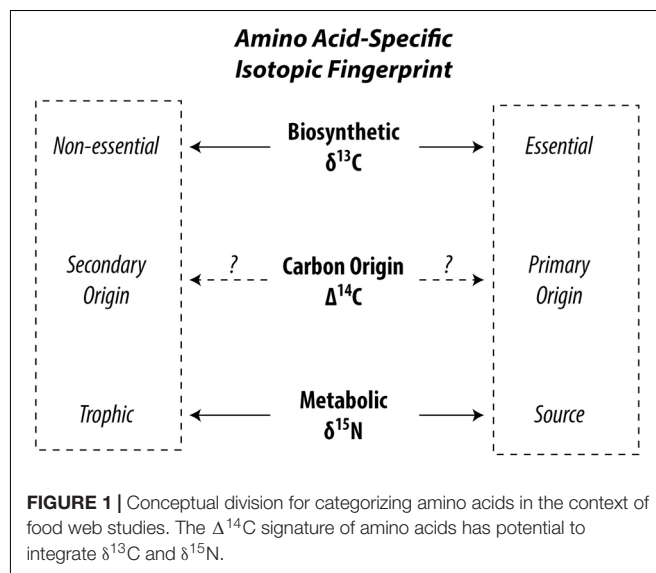
content can theoretically provide insights into a variety of biogeochemical studies.

BIOGEOCHEMISTRY OF AMINO ACIDS IN FOOD WEBS

Although amino acids are part of the living fabric of all organisms, not all amino acids can be synthesized by all organisms leading to facultative or mandatory dietary acquisition of certain amino acids. This circumstance leads to different pathways of carbon and nitrogen propagating through the food web up to higher trophic positions. $\Delta^{14}\text{C}$ is successfully used to trace carbon pathways in bulk biomass (Williams et al., 1987; Ishikawa et al., 2013), a point we will get back to later. Analytical developments first opened stable carbon and nitrogen isotopic compositions of amino acids ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) to exploration and our current state of knowledge rests on what these isotopes have revealed. The isotopic composition of amino acids within organisms reflect the isotopic composition of carbon and nitrogen sources in the food web with superimposed effects of metabolic processes (Hare et al., 1991; Carstens et al., 2013). “Trophic” amino acids fractionate heavily against ^{15}N due to preferential deamination or transamination during metabolism, enriching the ^{15}N in the remaining trophic amino acids (Macko et al., 1986; Goto et al., 2018). In contrast, “source” amino acids show no or a lesser extent of ^{15}N fractionation, because their amino group is preserved during metabolism (Chikaraishi et al., 2009). This allows amino acid nitrogen isotopic compositions to be used as excellent proxies for determination of trophic position of organisms in recent and paleo studies (Ohkouchi et al., 2017) and provides useful information for identifying ecological niches of organisms in food webs (Ishikawa, 2018). The “trophic” and “source” categories are controlled by catabolism of amino acids, such as deamination (Chikaraishi et al., 2015), whereas the “essential” and “non-essential” categories are controlled by anabolism such as biosynthesis (McMahon et al., 2010). Metabolic energy is produced in the former and consumed in the latter (Bender, 2012). In autotrophs, the $\delta^{13}\text{C}$ profile of “essential” amino acids are influenced by biosynthetic processes specific to phylogeny because diverse precursors, intermediates, and reactions produce a different pattern of ^{13}C fractionation among amino acids (Larsen et al., 2009). Using normalized $\delta^{13}\text{C}$ of several essential amino acids, Larsen et al. (2009) found that plants, fungi, and bacteria can be discriminated from each other in multivariate space. Higher organisms such as vertebrates are unable to biosynthesize essential amino acids, which are exclusively derived from their diets. This is reflected in the findings of McMahon et al. (2010) which show that $\delta^{13}\text{C}$ of essential amino acids in fish are consistent with those of their diet, whereas $\delta^{13}\text{C}$ of non-essential amino acids deviate, suggesting that non-essential amino acids are at least partly biosynthesized by higher organisms using different compound and carbon skeleton precursors, which can be exploited to trace dietary sources at higher trophic positions such as for zooplankton and fish (Larsen et al., 2013; McMahon et al., 2016). Therefore, the stable carbon isotopic

compositions of amino acids, especially of essential amino acids, are used as a fingerprint of primary producers. Stable carbon and nitrogen isotopic investigations of amino acids in organisms have currently led literature to two contrasting dichotomies, i.e., “trophic” vs. “source” and “essential” vs. “non-essential” (Figure 1). While there are wide overlaps between the source and essential categories and for trophic and non-essential categories, a few amino acids behave out of line. Additionally, the carbon pools from which the carbon atoms of the amino acids stem remain loosely constrained. Catalyzed by recent advances in accelerator mass spectrometry enabling the routine analysis of small-scale radiocarbon measurements (McIntyre et al., 2017), methods have been developed to investigate amino acid-specific radiocarbon in soft tissue of organisms opening a new frontier in research possibilities (Ishikawa et al., 2018).

In this context, natural abundance $\Delta^{14}\text{C}$ appears a promising tool to help disentangle complex amino acid metabolic pathways and offer new leads in resolving the differences between these competing dichotomies (Figure 1). Unlike $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, isotopic fractionation for $\Delta^{14}\text{C}$ is internally canceled out by definition (Stuiver and Polach, 1977). Therefore, metabolic effects should be canceled out with $\Delta^{14}\text{C}$ and its value should reflect that of their carbon origin(s), such as dissolved inorganic carbon (Broecker and Walton, 1959; Guillemette et al., 2017) or organic materials (Petsch et al., 2001). Most amino acids in the biosphere can be expected to bear a “modern” signature (Wang et al., 1996, 1998; Hwang et al., 2005). However, carbon originating from the atmosphere, dissolved inorganic and organic carbon, surface sediments, methane, and kerogen (often) show contrasting radiocarbon fingerprints. If an ecosystem intersects two or more of these domains, the radiocarbon gradient should be exploitable. To date, efforts have focused on radiocarbon dating of amino acids (particularly hydroxyproline) found in bone collagen for archeological applications (McCullagh et al., 2010). For the “building blocks of life,” there is nearly no data on amino acid radiocarbon in flora and fauna and there is



clearly incentive to shed light on this area of basic research (c.f. Bour et al., 2016).

BIOGEOCHEMISTRY OF SEDIMENTARY AMINO ACIDS

The importance of organic matter-mineral interactions in soils began to emerge in the mid-20th Century (Beutelspacher, 1955) and their importance for the stabilization of organic matter in marine sediments became recognized in the 1990s (Keil et al., 1994b; Mayer, 1994; Kennedy et al., 2002). These processes influence contrasting degrees of loss-and-replacement of terrestrial with marine organic matter along land-ocean transitions (Keil et al., 1997; Blattmann et al., 2018, 2019).

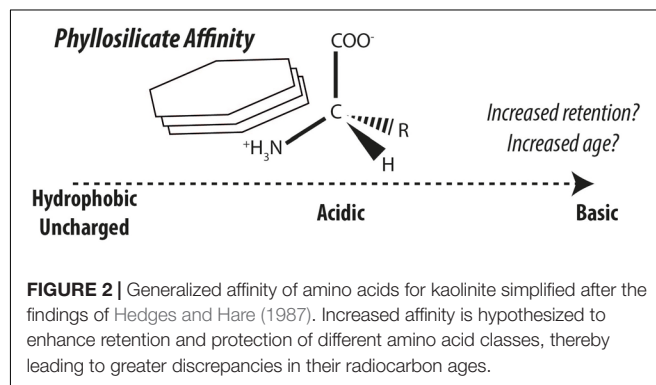
Nitrogenous compounds are classically considered biogeochemically labile and therefore are efficiently remineralized (Vernadsky, 1930). In the case of amino acids, their sustained existence is unlikely due to their intrinsic lability (Kirchman, 1990; Pantoja and Lee, 2003) leaving stabilization by mineral surfaces as the likeliest explanation (Keil et al., 1994a; Hedges et al., 2001). The modes of interactions between organic matter and minerals include ligand exchange, ion exchange, cation bridging, van der Waals forces, hydrogen bonding, hydrophobic interactions, and combinations thereof (Beutelspacher, 1955; Keil and Mayer, 2014). The stabilization of amino acids and their polymers have been hypothesized and identified as important in the formation of recalcitrant organic nitrogen (e.g. Müller, 1977; Henrichs and Sugai, 1993; Keil et al., 1994a; Hedges et al., 2001; Estes et al., 2019). Different amino acids and structurally related compounds exhibit very different sorption affinities for phyllosilicate mineral surfaces (Hedges, 1978; Hedges and Hare, 1987). Sorption experiments have demonstrated the strong participation of basic amino acids by way of electrostatic interactions in forming phyllosilicate-amino acid/protein complexes (Ensminger and Gieseking, 1941; Hedges, 1978; Hedges and Hare, 1987; Cowie and Hedges, 1992). This effect appears mirrored in nature with the high abundance of basic amino acids found in continental margin sediments (Keil et al., 1998). Amino acids and proteins associated with phyllosilicates and natural sediments have revealed sometimes erratic and irreversible desorption behavior (Henrichs and Sugai, 1993; Wang and Lee, 1993; Montluçon and Lee, 2001; Ding and Henrichs, 2002), which may ultimately influence their bioavailability (Pinck and Allison, 1951). Amino acids are likely more representative of bulk sedimentary organic matter than most other compounds, yet their ubiquity limits their value in quantitatively assessing contributions from sedimentary organic matter sources. On a molecular level, sedimentary amino acids are subject to differential microbial processing and loss-and-replacement of terrestrial with marine amino acids as revealed by stable carbon isotopes (Keil and Fogel, 2001) and therefore source apportionments recorded by individual amino acids are overlain by a variety of effects.

Amino acids stabilized by mineral surfaces are expected to exhibit very slow turnover rates and or would resist loss-and-replacement during land-ocean transit, giving rise to

depleted radiocarbon fingerprints borne by mineral-stabilized amino acids. It is thus hypothesized, that radiocarbon isotopic compositions of individual amino acids can provide a biomarker tool to measure the effect of organic matter-mineral interactions in natural sedimentary environments (Figure 2; see also ideas by Keil et al., 1998). One of the greatest uncertainties in studying the stabilization effects of minerals on organic matter in nature is the longstanding and ongoing discussion whether organic matter is stabilized by minerals or if organic matter is intrinsically stable due to its structural characteristics or by other factors (compare Hedges et al., 2001; Eusterhues et al., 2005; Schmidt et al., 2011; Keil and Mayer, 2014; Kleber et al., 2015). To this end, amino acid-specific radiocarbon can offer new perspectives in this ongoing debate. Method developments have also opened up this frontier of amino acid-specific radiocarbon in sediments to exploration (Blattmann et al., 2020).

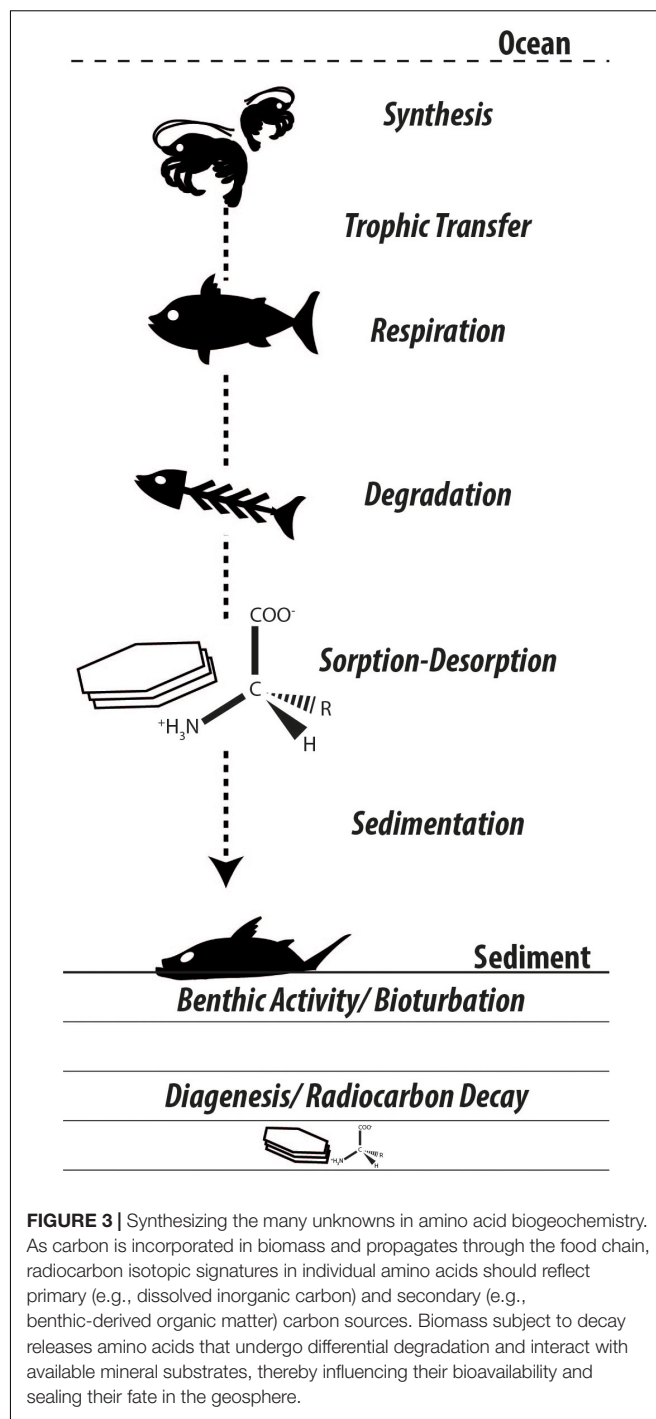
IS ENANTIOMER-SPECIFIC RADIOCARBON THE NEXT FRONTIER?

With methods for amino acid-specific radiocarbon now developed for biological (Ishikawa et al., 2018) and earthen (Blattmann et al., 2020) samples, we share our thoughts on the merits of what we see as a promising next analytical frontier. Radiocarbon isotopic composition of individual compounds reflects a combination of influences stemming from aging, mixing, reservoir effects, etc. By isolating the effect of radioactive decay, constraints on the time since synthesis are attainable (Libby et al., 1949). In addition to this radioactive clock common to all organic compounds, amino acids distinguish themselves by having enantiomers (i.e., mirror image molecular structure like our left and right hands). In the biosphere, the L-form dominates, with certain organisms containing D-amino acids including bacteria (Corrigan, 1969; Lam et al., 2009), plants (Neuberger, 1948), freshwater and marine algae (Yokoyama et al., 2003), and higher organisms including insects and mammals (Neuberger, 1948; Corrigan, 1969). In a process called racemization, L-amino acids switch into D-configuration and vice versa. Racemization is a time and temperature dependent process and is also influenced by humidity, pH, and a host of matrix effects (see review by Bada, 1985). Over time, increasing



amounts of D-amino acids are present in living tissue with slow turnover (e.g., dentin and eye lenses) such as for whales (Olsen and Sunde, 2002) and humans (Masters et al., 1977). This trend continues in organic remains such as in wood (Lee et al., 1976), bones (Bada et al., 1973, 1989), and in biospheric remains in the form of dissolved organic matter (Yamaguchi and McCarthy, 2018), subfossil foraminifera (Harada and Handa, 1995), and sedimentary organic matter (Bada et al., 1970; Kvenvolden et al., 1970; Bada and Schroeder, 1975; Bada and Man, 1980). Over time (within 15 million years), a steady state is approached where all amino acid enantiomers are present in a racemic mixture (i.e., D/L ratios equal to 1), which is mostly the case in kerogen (Kvenvolden, 1975) and extraterrestrial amino acids (Engel and Nagy, 1982). In addition to racemization producing D-amino acids, D-amino acids are actively removed from soils by way of enzymatic activity (racemase) by microbes (Zhang and Sun, 2014), further constraining environmental amino acid enantiomeric ratios. However, despite these complications, with constraints on temperature history (e.g., organism and sediment temperature), amino acid enantiomers harbor rich information on age constraints (or vice versa), with less precision than radiocarbon, but extending back further in time (see also reviews by Kvenvolden, 1975 and Kaufman and Miller, 1992).

Going a step beyond amino acid-specific radiocarbon, development of a method for enantiomer-specific radiocarbon could be pursued. The technical feasibility of such an approach was recently made plausible, where underivatized individual amino acids, which were previously isolated from sediments, were chromatographically separated into their L and D forms (Blattmann, 2018). If collected, such isolates can provide insight into the radiocarbon population distributions of a single compound on a coarsest of levels. Other efforts to constrain the complex age distributions of organic matter using compound-specific radiocarbon (using fatty acids) have recently come to fruition using time series inversion approaches deconvolving pools of organic matter with different turnovers (French et al., 2018; Vonk et al., 2019). However, even without performing inversions, enantiomer-specific radiocarbon can provide direct insight into the radiocarbon population distributions of individual amino acids. In a simplest end member of cases involving conservative mixing, contributions of biospheric L-amino acids can be teased apart from petrogenic sources, which exhibit D/L ratios equal to 1. In such a case, the age of biospheric L-amino acids can be assessed by mass balance as petrogenic amino acids would equally contribute to the radiocarbon fingerprint of L- and D-amino acids, while biospheric sources would exclusively contribute to the L-amino acid pool (c.f. Silber et al., 1994). In open systems involving dynamic changes such as contributions of D-amino acids stemming from peptidoglycan from bacteria (c.f. Pelz et al., 1998; Glaser and Amelung, 2002; Veuger et al., 2005), an enantiomer-specific approach can provide insight into microbial pathways of carbon flow embedded in the tapestry of radiocarbon ages contained within dissolved and sedimentary organic matter (e.g., incorporation of carbon derived from young, labile organic



matter into bacterial biomass). Additionally, for calibrations of archeological and geochronological time using amino acid enantiomer ratios (e.g., Bada et al., 1984; Kosnik et al., 2013; Simonson et al., 2013), the integrity of purportedly closed systems such as within biominerals can be tested with enantiomer-specific radiocarbon, which can provide insight into radiocarbon disequilibria between enantiomers thereby unveiling open system behavior. The possibility of performing

enantiomer-specific radiocarbon for amino acids is unique among most other compounds and the hypothesized benefits for understanding biogeochemical cycles for ecological as well as environmental applications look promising.

SYNTHESIS AND OUTLOOK

Following the biospheric pathways along which amino acids are synthesized, propagate through food webs, and decay with a very small fraction finding its way into the geosphere, many questions arise regarding the origin and fate of carbon in these biosphere internal and biosphere-geosphere exchanges (Figure 3). Following their purposes in the biosphere, amino acids face extensive degradation and diagenetic changes, yet remain among the largest characterizable fractions of organic matter preserved in the geologic record (Trask, 1936; Erdman et al., 1956; Wakeham et al., 1997). Amino acid-specific radiocarbon appears a promising tool to confront a range of ecological, sedimentological, and biogeochemical challenges. The authors will report on their progress in future contributions.

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AUTHOR CONTRIBUTIONS

Both authors equally contributed and wrote this manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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