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Importance of isotope measurements in marine organic geochemistry

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ABSTRACT

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We present here some specific areas of research, prefaced by brief and selected reviews, that address the cycling of organic matter in the marine environment. These are areas in which isotopic signatures will provide vital answers or clues.

INTRODUCTION

The largest exchangeable organic carbon reservoir on Earth is in the form of dissolved organic matter (DOM) in seawater. Less than 10% of this DOM has been characterized either with regard to organic compound classes or specific organic molecules. Moreover, little is known about the sources of marine DOM. For instance, it remains a mystery whether or not an appreciable part of this DOM is of terrestrial origin, and if so, whether it is significantly altered with time. Isotopic signatures ($\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$) have proven powerful tracers in helping establish the sources and sinks of DOM and living and detrital particulate organic matter (POM) in the oceans, and in assisting in determining the extent and direction of transformation processes between the soluble and particulate phases. In conjunction with chemical data (i.e. total DOM, oxygen, nutrients, total CO_2, alkalinity and salinity), isotopic measurements are essential for assessment of the processes controlling organic matter distributions in the oceans.

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STABLE CARBON ISOTOPES (δ^{13}C)

Recent carbon and nitrogen isotopic measurements have revealed information about the sources of organic matter and the transformation processes that occur in the oceanic water column. Studies of δ^{13}C have been used to distinguish between terrestrial (-30 to $-25‰$) and marine (-23 to $-15‰$) sources of POM. However, various factors complicate this method:

(1) the dependence of δ^{13}C on $CO_{2(aq)}$ concentrations in the water (Rau et al., 1989b);

(2) kinetic effects on δ^{13}C of organisms that grow slowly (i.e. at the base of the euphotic zone) (Bishop et al., 1977);

(3) fractionation that occurs in some regimes during diagenesis/remineralization (McNichol et al., 1991);

(4) biomagnification of ^{13}C in the food web, which causes the enrichment of ^{13}C in higher trophic level organisms, and possibly in their excretion products (McConnaughey and McRoy, 1979);

(5) the wide range of δ^{13}C values in source biocarbon, ranging from $-10‰$ in macroscopic algae to $-28‰$ in some phytoplanktons. The reader is referred to a comprehensive review by Fry and Sherr (1984) of δ^{13}C measurements as indicators of carbon flow in aquatic environments.

Studies of organic δ^{13}C in nearshore sediments have been useful for determining relative quantities of marine-derived vs. terrestrially derived organic carbon (see, for instance, Gearing et al. (1977)). The δ^{13}C signature of UV-oxidizable DOC is suggestive of a marine origin for oceanic DOM (Williams and Gordon, 1970; Williams and Druffel, 1987). This agrees with the results of Meyers-Schulte and Hedges (1986), who used lignin-derived phenols as molecular-level probes of DOM to demonstrate that only about 10% of DOM in open ocean water had its origin from terrestrial sources. Mantoura and Woodward (1983), however, projected a mainly terrestrial origin for DOM in the ocean based on the conservative behavior of DOM in an estuary in the UK. Unequivocal attribution of so much terrestrial or marine components to marine DOM is qualitative at best using δ^{13}C signatures, as there are large overlaps between the δ^{13}C values of terrestrial and marine end-members.

Thus, it is clear that δ^{13}C alone cannot unambiguously answer the questions that confront us. Instead, tracers with different input functions must be used in conjunction with δ^{13}C to determine sources and sinks of organic matter and the transformation processes that they undergo in the water column and in the sediment. Two such tracers are radiocarbon (^{14}C) and ^{15}N.

RADIOCARBON (Δ^{14}C)

Radiocarbon is derived from two sources: natural cosmogenic production in the stratosphere, and bomb production during the late 1950s and early

1960s. In the dissolved inorganic carbon (DIC) pool, bomb radiocarbon is restricted mainly to the upper 1000 m of the water column in non-polar oceans, the exception being North Atlantic Deep Water laden with bomb ^{14}C that has penetrated as far south as 30°N. Organic matter produced in seawater during photosynthesis contains high levels of ^{14}C (Δ^{14}C $= +50$ to $+150$‰) that are retained because of the long half-life (5730 years) of ^{14}C. Thus, surface-derived material found in the deep sea and in the sediments contains bomb ^{14}C. Lower levels of ^{14}C (Δ^{14}C $\leqslant -50$‰) indicate pre-bomb levels, suggesting that there has been minimal turnover of carbon in the past 35 years. Thus, ^{14}C is useful as both a long- and short-term tracer because of the natural and bomb-produced components, respectively.

Hedges et al. (1986) measured radiocarbon levels in suspended particulate organic matter and dissolved humic and fulvic acids transported by the Amazon River and found bomb radiocarbon in all fractions analyzed. This indicates rapid turnover for riverine organic matter, where different values for the coexisting fractions reflect varying degrees of retention by soils in the drainage basin.

On the other hand, marine dissolved organic carbon (DOC) contains very low radiocarbon activities. In the deep North Pacific, Δ^{14}C values are relatively constant at -520‰ (Williams and Druffel, 1987), whereas the surface values are -150‰. The similarity between the surface-to-deep gradients in the DO^{14}C and the DI^{14}C activities suggests that bomb radiocarbon has penetrated each of these pools to similar depths of about 1000 m in the North Pacific by 1987. The very old ^{14}C activities of the deep DOC (6000 years B.P.) indicate that at least a portion of the UV-oxidizable organic matter has been cycling within the oceans on time-scales several times that of the oceanic mixing time. With the discovery by Sugimura and Suzuki (1988) that there is an 'extra' fraction of DOC in seawater that is undetected by conventional oxidative methods, the question arises: 'What is the ^{14}C age of this "extra" DOC?' Problems in answering this question include obtaining sufficient oxidative-CO_2 (50–100 μg C) for accelerator mass spectrometry (AMS) ^{14}C measurements.

We also must use ^{14}C to date individual compound classes (for instance, lipids, and total hydrolyzable amino acids and carbohydrates) within the dissolved and particulate organic carbon pools, to understand the origins of the various organic constituents within these reservoirs. If these components are surface derived they will contain post-bomb levels of ^{14}C; if their ^{14}C activities are low, however, production of these compounds at depths greater than 1000 m will be inferred.

Another intriguing observation is the gradual reduction with depth of ^{14}C activities in sinking and suspended POC (Druffel and Williams, 1990) and in the organisms that feed on POC (Williams and Linick, 1975; Pearcy and Stuiver, 1983; Williams et al., 1987). As the turnover time of suspended POC

(5–10 years; Bacon and Anderson, 1982) is much shorter than the lifetime of bomb ^{14}C in the oceans (35 years), it is difficult to envision a purely surface-derived source for deep-sea POC. Instead, there must be a deep-derived source of carbon to the POC pool, perhaps mediated by heterotrophic bacterial activity and/or the result of adsorption of DOC onto POC.

The potential to measure the ^{14}C content in micrograms of carbon is a most exciting development. Dissolved, colloidal and particulate organic phases in seawater, sediment pore-water, river water and precipitation, as well as bio-carbon derived from micro- and macroorganisms can now be fractionated into individual compound classes and even into individual molecular compounds, which in turn may be age-dated by AMS. Such data will help resolve such questions as:

(1) How rapidly has bomb ^{14}C been incorporated into deep-sea organic carbon pools?

(2) How important are coagulation and dissolution processes with respect to suspended, sinking and soluble organic phases in the water column?

(3) How much does the total amount of DOM in the deep oceans change with time, if at all, as reflected in the ^{14}C content of humic substances and/or the UV-oxidizable fraction of DOM?

(4) Is the colloidal fraction older or younger than the truly dissolved organic matter, and are there differences between the ^{14}C content of the organic compound classes in these two fractions vis-à-vis the suspended and sinking particles?

(5) Can dietary carbon sources for deep-sea organisms be differentiated via ^{14}C changes in muscle and visceral organs?

(6) What are the ^{14}C contents of heterotrophic bacteria — do they reflect pathways of specific organic energy sources?

(7) Can the flux of dissolved organic matter into seawater from sediments be evaluated by using Δ^{14}C in conjunction with δ^{13}C and δ^{15}N isotopic signatures?

NITROGEN ISOTOPES (δ^{15}N)

Nitrogen isotope ratios (δ^{15}N) are used to trace sources and transformation processes of marine organic matter. In a study of δ^{15}N in sedimentary nitrogen phases in the Santa Barbara Basin, Sweeney and Kaplan (1980a) concluded that most of the dissolved N in pore-waters was derived from planktonic organic matter degraded by bacterial activity and that more than 25% of the total N in the sediments was terrestrially derived. Peters et al. (1978) observed a linear correlation between δ^{13}C and δ^{15}N measured in organic matter separated from nearshore sediments of the Northeast Pacific, and attributed this correlation to the mixing of terrestrial and marine 'end-members' of refractory organic matter.

Altabet (1988) observed a difference in the $\delta^{15}N$ of suspended and sinking POM, and concluded that the net transformation of suspended into sinking particles in the North Atlantic was the result of active processes such as macrozooplankton feeding, as opposed to passive physical effects. Rau et al. (1989a) used $\delta^{15}N$ and $\delta^{13}C$ of mesopelagic shrimps to illustrate inter-species feeding differences, despite considerable overlap in the reported depth distribution of each species.

In addition to assessing terrestrial inputs and food chain trophodynamics, the measurement of $\delta^{15}N$ in the total DOM and individual compound classes of the DOM should be an important tracer, with ^{14}C, in determining the origin of DOM. Do $\delta^{15}N$ values for DOM reflect those in the corresponding suspended and sinking POM or are they more closely related to $\delta^{15}N$ values of surface micro- and/or macroplanktonic organisms or to the surface DOM? There are no measurements of $\delta^{15}N$ in DOM as yet, and these determinations should be a high priority.

There is great potential for understanding the fate of organic matter in the oceans using the multiple isotope tracer approach. Whereas ^{14}C integrates the depths in the water column from where the organic matter was derived, the number of trophic levels and the degree of fractionation that has occurred are obtained from the $\delta^{15}N$ and $\delta^{13}C$ signatures, respectively.

OTHER ISOTOPES

Other isotopes are useful 'clocks' of processes in the upper ocean. For example, Lal et al. (1988) used ^{33}P and ^{32}P activities measured in DOM and POM to demonstrate that these tracers are suitable for determining phosphorus pathways through the pelagic food chain and for determining the flux of phosphorus through the thermocline, averaged over a period of about 1–2 months. Recently, ^{31}P, the stable isotope of P, has been used to characterize organic P compound classes in marine sediments by ^{31}P NMR (nuclear magnetic resonance) spectroscopy (Ingall and Ruttenberg, 1990). This measurement appears to be valuable for detecting trace amounts of anthropogenic organic phosphorus compounds (e.g. pesticides).

Stable sulfur isotope ratios ($^{34}S/^{32}S$ and $\delta^{34}S$) are an additional isotopic tracer for organic matter sources, especially in delineating terrestrial vs. marine origins. For example, Peterson and Howarth (1987) have used $\delta^{34}S$ values of upland plants, *Spartina*, and plankton to assess the energy sources for macroconsumers in the Sapelo Island salt-marsh estuaries. Sweeney and Kaplan (1980b) found that $\delta^{34}S$ values reflect both sewage and biogenic (marine bacterial-derived) components in nearshore sediments and suspended detritus from nearshore municipal outfalls on the San Pedro shelf. Organic $\delta^{34}S$ values in suspended and sinking particles could be important in oxic–anoxic transition zones for determining the extent of bacterial transformation

of organic matter at these interfaces by reflecting the bacterial incorporation
of sulfur derived from sulfate reduction.

CONCLUSIONS

We consider important areas of future research involving $\delta^{13}C$, $\delta^{15}N$ and
$\Delta^{14}C$ (and, to a lesser degree, $\delta^{34}S$, ^{31}P, ^{32}P and ^{33}P) to include:

(1) measurement of these isotopic signatures in particulate, colloidal and
soluble organic phases, both the bulk fractions and in specific compound
classes and discrete compounds within these fractions;

(2) comparison of these same measurements with identical ones on terres-
trial organic phases in rivers and within seawater–river-water mixing zones;
and

(3) measurement of $\delta^{13}C$, $\delta^{15}N$ and $\Delta^{14}C$ in bacteria, plankton and higher
organisms whose identities, feeding depths and trophic levels are known.

Such measurements will improve resolution of, if not solve, the confusion
now posed by scattered and incomplete data sets in the determination of the
origins and transformations, and oxidation and preservation of organic
matter in the oceans.

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