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Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular ^{13}C and ^{14}C measurements

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Abstract

The type and flux of organic carbon (OC) delivered from the continents to the sea can both influence, and be influenced by, climate change on regional and global scales. In order to develop a more complete view of OC delivery in the climatically sensitive Arctic region, we measured the stable carbon and radiocarbon isotopic signatures of individual lipid biomarkers and products of kerogen pyrolysis from the surficial sediments of several sites on the Mackenzie Shelf and adjacent slope of the Beaufort Sea. Even carbon numbered fatty acids exhibit a trend of increasing ^{14}C age with increasing chain length, from modern values for the nC_{14}–nC_{18} homologues to several thousand years old for those $\geq nC_{24}$. Such depleted ^{14}C values for longer-chain fatty acids likely reflect supply of vascular plant OC that has been pre-aged on the continents for several millennia prior to delivery to the Beaufort Sea. Their corresponding $\delta^{13}C$ values support a C_3 land plant source. The molecular distributions and ^{14}C and ^{13}C signatures of solvent-extractable alkanes point to at least two sources: higher plant leaf waxes and a ^{14}C-‘dead’ component likely derived from erosion of organic-rich sedimentary rocks exposed within the Mackenzie River drainage basin. The $\delta^{13}C$ and $\Delta^{14}C$ values of *n*-hydrocarbon pyrolysis products from the corresponding demineralized sediments also suggest a mixed supply of ancient kerogen and pre-aged vascular plant-derived precursors to the Beaufort Sea. On a bulk level, the trend in sedimentary OC contents, C/N ratios, and $\delta^{13}C$ values point to an overall decrease in the terrigenous input (mainly from the Mackenzie River) with increasing distance offshore, whereas bulk $\Delta^{14}C$ measurements exhibit no trend suggesting a somewhat constant pre-aged component.

A coupled molecular isotopic mass balance approach based on the lipid $\delta^{13}C$ and $\Delta^{14}C$ signatures is used to construct a budget of terrestrial, marine, and petrogenic OC burial on the shelf. Results indicate that roughly 40–50% of the carbon currently being buried in the Beaufort Sea is derived from the weathering of ancient sedimentary rock. The balance is composed of marine and terrestrial input, supporting the qualitative description of OC sources given by the bulk and molecular patterns above. This suggests that mass balances utilizing the $\delta^{13}C$ and $\Delta^{14}C$ signatures of biomarkers as endmembers can be used to semi-quantitatively deconvolve multiple sources of organic carbon in marine sediments.

Keywords: Petrogenic organic carbon; Radiocarbon dating; Biomarkers; Molecular isotopes; Beaufort Sea; Mackenzie River

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1. Introduction

The flux of organic carbon (OC) to marine sediments includes autochthonous contributions from primary production in overlying waters as well as allochthonous inputs from terrigenous sources such as vascular plants, soils, ancient sedimentary rocks (shales), and anthropogenic contaminants (Hedges et al., 1997). The relative proportion of these carbon pools dictates the composition and burial efficiency of OC in sediments and influences the atmospheric oxidation state on geologic timescales (Berner, 1989; Petsch, 2003). Many studies, therefore, have aimed to quantify these components in rivers and on continental shelves using bulk characteristics such as %OC, C/N ratios, δ^{13}C, and Δ^{14}C (e.g. Megens et al., 2001; Raymond and Bauer, 2001, and references therein) as well as the distributions and stable carbon isotopic compositions of source-specific biomarkers (e.g. Prahl et al., 1994; Yunker et al., 1995; Goñi et al., 1998, 2000; Belika et al., 2002; Yunker et al., 2005). Within this framework, isotopic mass balance calculations used to assess the fractional abundance of modern and ancient OC (Blair et al., 2003, 2004; Goñi et al., 2005) indicate that fully 50% or more of the total carbon preserved in some recent river-dominated shelf sediments is not of recent origin, but instead originates from 'pre-aged' continental reservoirs such as soils (Masiello and Druffel, 2001; Rethemeyer et al., 2004a,b) and wetlands (Trumbore et al., 1999), or 'petrogenic' fossil sources liberated upon sedimentary rock weathering (Di-Giovanni et al., 2002). These pools of reduced carbon are presumably highly refractory and therefore, once mobilized from continental reservoirs, have been hypothesized to escape extensive remineralization in the marine water column and underlying sediments. However, isotopic mass balances utilizing bulk Δ^{14}C and δ^{13}C measurements in sediments cannot independently discriminate between pre-aged terrestrial, petrogenic, and marine OC since the stable and radiocarbon signatures of terrestrial OC often lie in between the latter two ($\Delta^{14}C \sim -1000‰$, $\delta^{13}C = -24‰$ to $-30‰$ and $\Delta^{14}C \sim 0‰$, $\delta^{13}C = -14‰$ to $-20‰$, respectively). In particular, distinguishing and quantifying pre-aged terrestrial OC of vascular plant origin and ancient OC from rock erosion can be particularly difficult because each may be depleted in both ^{14}C and ^{13}C. Nevertheless, distinguishing between vascular plant and shale OC is extremely important since the very different rates at which OC cycles through these reservoirs impacts global biogeochemical cycles (Hedges and Oades, 1997). The isotopic compositions of all three endmembers are thus either assumed (Goñi et al., 2005), inferred from their spatial trends (Blair et al., 2003), or measured on samples taken from the source rock itself (Komada et al., 2004).

This problem may be more directly addressed by measuring both the ^{14}C and ^{13}C content of individual biomarkers specific to each of these endmembers. The source specificity of these compounds avoids the need for assumptions or ancillary sample collections outside of the sediment in which they are contained, and allows for direct determination of signatures which have the potential to vary during delivery to, and subsequent deposition (and re-deposition) over, the seafloor. Such coupled molecular δ^{13}C and Δ^{14}C measurements have been previously used to establish the provenance of natural and anthropogenic compounds in sediments (Eglinton et al., 1997; Pearson and Eglinton, 2000; Pearson et al., 2001), freshwaters, groundwaters, and soils on the continents (Schiff et al., 1997; Agnelli et al., 2002), aerosols (Matsumoto et al., 2001; Eglinton et al., 2002), and the marine water column (Guo et al., 1996). These signatures can also be used to solve a set of simultaneous isotopic mass balance expressions to yield the fractional abundances of the OC sources they represent. Since the provenance of organic matter contained within continental shelf sediments has been traditionally cited as one of the features controlling its ability to survive early diagenesis (Hedges et al., 1997), this approach provides a useful window into the factors controlling the composition and sequestration of organic matter in marine sediments.

The Arctic Ocean contains 20% of the world's continental shelf area (Macdonald et al., 1998) and receives input from many major and minor rivers whose collective drainage area contains half of the global soil carbon inventory (Dixon et al., 1994). The Mackenzie River is the largest fluvial source of both sediment and particulate organic carbon (POC) to the Arctic Ocean at about 125×10^9 kg y^{-1} and 2.1×10^9 kg y^{-1} respectively, with approximately 60% of this POC subsequently buried in the sediments of its delta and the adjacent Mackenzie Shelf (Macdonald et al., 1998, 2004; Rachold et al., 2004). Most of this flux (~90%) is associated with the spring/summer freshet, a period from May through September when ~70% of the annual freshwater discharge (3.3×10^{11} m^3) occurs (Macdonald et al., 1998). The Mackenzie River drainage basin spans the western alpine region of the Cordillera Mountains to the Canadian Shield and includes forests, swamps, grasslands, and permafrost soils interspaced with numerous lakes, smaller streams, and wetlands. The Mackenzie River thus effectively integrates an array of OC sources including those eroding from sedimentary rock, fixed by land plants, sequestered in soils, produced by