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Tracing the inputs and fate of marine and terrigenous organic matter in Arctic Ocean sediments: A multivariate analysis of lipid biomarkers

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Abstract

An understanding of the carbon cycle within arctic sediments requires discrimination between the terrigenous and marine components of organic carbon, insight into the removal mechanisms for labile carbon during burial and appreciation of shelf-to-basin processes. Using a large data set of multiple molecular organic markers (alkanes, alkanols, sterols, saturated and unsaturated fatty acids, dicarboxylic acids), we apply (1) principal components analysis (PCA) to obtain a robust comparison of biomarker compositions in Arctic Ocean sediments, (2) geometric mean (GM) linear regression of the PCA variables to estimate the relative contributions of labile/marine and stable/terrigenous sources to each biomarker and (3) the slope of the GM regression of each biomarker with TOC to provide a novel measure of the removal rate of each biomarker relative to phytol. The PCA- and TOC-based indices generally increase together: biomarkers with very high TOC-based removal rates such as the saturated and unsaturated *n*-alkanoic acids generally have a high labile/marine content from PCA, while the sterols have low removal rates, but exhibit a range of labile/marine content values and the *n*-alkanes and *n*-alkanols have low values for both. A dominant feature of all PCA models examined is a progressive decrease in the autochthonous/marine biomarkers with each increase in sediment core depth, which points to a universal diagenetic alteration of organic carbon with depth in the cores. The PCA model also displays a shelf to basin trend that is non-diagenetic and implies the ongoing (centuries or more) delivery of long-chain *n*-alkanes, *n*-alcohols and *n*-alkanoic acids in a matrix that is pre-formed and well-preserved within the sediments. Terrigenous biomarker distributions within the PCA model suggest that atmospheric transport of plant waxes in aerosols and the water borne transport of very fine plant macerals likely have significant roles in the export of these vascular plant biomarkers to the basins. Biomarker ratios and profiles of the PCA-based labile/marine content with core depth indicate that the PCA model is more strongly influenced by the biomarker lability than the marine content, while increases in the marine content are largely responsible for the shifts in composition for near-surface core sections.

Keywords: Principal components analysis; Alkanes; Alkanols; Sterols; Fatty acids; Dicarboxylic acids; Organic carbon; Sediment; Beaufort Sea; Chukchi Sea

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1. Introduction

In the dynamic system of the Arctic Ocean, the large seasonal input of terrigenous organic carbon ($\sim 12 \times 10^6$ t/a POC) is dwarfed by marine organic carbon from primary and secondary production ($\sim 250 \times 10^6$ t/a POC; Rachold et al., 2004; Sakshaug, 2004). While the input of terrestrial carbon is controlled largely by physical processes such as river flow, coastal erosion, and ice transport (Macdonald et al., 1998; Stein and Macdonald, 2004a), much of the autochthonous production takes place on the extensive continental shelves in seasonally ice-free regions (polynyas) and marginal seas, and, to a lesser extent, in the ice itself (Wheeler et al., 1996; Gosselin et al., 1997). A portion of the phytoplankton-produced organic matter fuels high levels of secondary production in both the water column and benthos, while a large component of both the primary and secondary carbon is degraded in pelagic, epibenthic, and sediment regimes by bacteria, archaebacteria, and other microbes (Hedges and Keil, 1995; Wakeham et al., 1997b). In such a complex system of multiple marine and terrestrial inputs (Yunker et al., 1995; Fahl and Stein, 1999), the carbon cycle is complicated by organic pools of vastly different recycling times under the influence of strong physical and temporal gradients. Despite the substantial supply of marine organic carbon, sediment composition and organic carbon budgets suggest that much is utilised, with a far larger fraction of terrigenous organic carbon preserved in Arctic Ocean sediments compared to marine organic carbon (Stein and Macdonald, 2004a).

Terrigenous and marine molecular organic biomarkers can serve as proxies to provide insight into how aquatic systems process, metabolise and sequester carbon in both the water column and sediments over decadal to geological time scales and are extremely useful in resolving the complexity of systems with multiple organic carbon sources (Hedges et al., 1997; Meyers, 1997; Wakeham et al., 1997b; Belicka et al., 2004). Here a major goal is to utilise organic biomarkers to track the fate of organic material from arctic primary and secondary production in the context of the large and variable background of terrigenous inputs to the Arctic Ocean. The Arctic is also a region where these biomarkers can provide important insights into the current primary productivity regime and its potential alterations in response to climate forcing. Without such studies, we are not going to able to anticipate the response of the Arctic Ocean to global climate change (Macdonald, 1996; Gobeil et al., 2001; Belicka et al., 2004).

In temperate and tropical regions the terrestrial component of TOC normally decreases both with distance offshore and distance from major rivers (Westerhausen et al., 1993; Prahl et al., 1994; Hedges and Keil, 1995; Meyers, 1997). In contrast, in the Arctic the incorporation of resuspended sediments into sea ice through frazil and anchor ice production during winter and the subsequent transport of this sea ice offshore facilitates the direct delivery of terrigenous carbon from the shelves to the basins (Rachold et al., 2004, and references therein). The significance of this process does vary dramatically between regions, however, due to large differences in the supply of POC and DOC delivered by individual rivers and the efficiency of sediment entrainment by ice on specific shelves (Rachold et al., 2004). The Arctic Ocean terrestrial biomarker composition also could vary between major rivers and/or the different arctic shelves due to differences in the composition of the vegetation: e.g., spruce (*Picea* spp.) dominates in the northern boreal forests of North America while larch (*Larix* spp.) dominates in Siberia (Dyke et al., 1997). Consequently, the terrestrial component of the TOC would not necessarily be expected to be homogenous throughout the Arctic Ocean, or to decrease with distance offshore as rapidly in the Arctic as in temperate or tropical regions (e.g., Prahl et al., 1994).

Marine primary production occurs throughout the Arctic Ocean (Wheeler et al., 1996; Gosselin et al., 1997). However, the pronounced seasonality and episodic nature of this production can produce large variations in the biomarker composition (Yunker et al., 1994, 1995) through, for example, species or growth-stage changes in the dominant phytoplankton or zooplankton or the extent of zooplankton grazing (Graeve et al., 1994; Albers et al., 1996; Volkman et al., 1998). Furthermore, enhanced coupling of primary production with the benthos is likely through rapid sinking of ungrazed ice algae mats that are released in large clumps particularly when ice melts (Goñi et al., 2000). This process can facilitate the direct delivery of fresh marine carbon to the sediments (largely bypassing the water-column degradation experienced by smaller particulate) and would be expected to contribute additional variation to the marine