

# Thermogenic organic matter dissolved in the abyssal ocean

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## Abstract

Formation and decay of thermogenic organic matter are important processes in the geological carbon cycle, but little is known about the fate of combustion-derived and petrogenic compounds in the ocean. We explored the molecular structure of marine dissolved organic matter (DOM) for thermogenic signatures in different water masses of the Southern Ocean. Ultrahigh-resolution mass spectrometry via the Fourier transform-ion cyclotron resonance technique (FT-ICR-MS) revealed the presence of polyaromatic hydrocarbons (PAHs) dissolved in the abyssal ocean. More than 200 different PAHs were discerned, most of them consisting of seven condensed rings with varying numbers of carboxyl, hydroxyl, and aliphatic functional groups. These unambiguously thermogenic compounds were homogeneously distributed in the deep sea, but depleted at the sea surface. Based on the structural information alone, petrogenic and pyrogenic compounds cannot be distinguished. Surface depletion of the PAHs and first estimates for their turnover rate ( $>1.2 \cdot 10^{12}$  mol C per year) point toward a primarily petrogenic source, possibly deep-sea hydrothermal vents, which is thus far speculative because the fluxes of combustion-derived and petrogenic matter to the ocean are not well constrained. We estimate that  $>2.4\%$  of DOM are thermogenic compounds, and their global inventory in the oceans is  $>1.4 \cdot 10^{15}$  mol C, significantly impacting global biogeochemical cycles.

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## 1. Introduction

The oxygen content of the earth's atmosphere and the global cycle of organic carbon are invariably linked (Lasaga and Ohmoto, 2002). Free oxygen in the atmosphere is generated via burial of organic carbon in marine sediments. Sedimentary organic carbon then cycles through the lithosphere. Over geological time scales tectonic and volcanic processes carry petrogenic carbon back to the continents' surface where it is oxidized into CO<sub>2</sub>, consuming atmospheric oxygen. It is this

delicate balance between photosynthesis, organic carbon burial, tectonic forces, volcanism and sedimentary rock weathering that ultimately controls atmospheric composition (Lasaga and Ohmoto, 2002). The time petrogenic organic carbon is protected from oxidation is a crucial parameter. In periods of enhanced tectonic activity, turnover time accelerates and increased amounts of petrogenic organic carbon are oxidized which causes atmospheric oxygen to drop. Decreased oxygen levels, in turn, enhance organic matter preservation in sediments and reduce oxidative rock weathering, providing a negative feedback which is vital for the habitability of earth.

The spatial separation between organic matter burial in the oceans and its oxidation at the continents'

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surface links atmospheric oxygen content to the rock cycle. Volcanic activity occurs equally on the continents and the ocean floor. Some of the most active volcanoes and hydrothermal fields exist along the extensive mid-oceanic ridges and even on the older, tectonized portions of the oceanic crust (Kelley et al., 2002). A global hydrothermal fluid reservoir resides within the uppermost warm oceanic crust (Johnson and Pruis, 2003). The global effect is that a huge amount of water, exceeding the river runoff by an order of magnitude, passes through hydrothermal plumes, equivalent to an ocean water recycling time of  $4\text{--}8 \cdot 10^3$  years (Elderfield and Schultz, 1996; and references therein). Some of the hydrothermal waters can reach temperatures of 350 °C and more, leading to extensive chemical reactions between seawater constituents and rocks (Elderfield and Schultz, 1996). Abundant deposits of hydrothermal petroleum were found in Mid-Atlantic Ridge sediments (Simoneit et al., 2004). The mobilization of soluble organic compounds into hydrothermal fluids is likely (Simoneit et al., 2004), but has gained very little scientific attention (Cowen et al., 2004).

Residues from biomass combustion (“black carbon”) can be highly resistant to further degradation (Seiler and Crutzen, 1980). The abundance of large-scale wildfires that can be triggered by increased volcanism could thus provide an additional negative feedback in the oxygen cycle. However, it is unclear to what degree black carbon persists on geological time scales. It has recently been shown that black carbon in soils can be remobilized into active cycles and transferred into riverine dissolved organic matter (Kim et al., 2004; Mannino and Harvey, 2004).

We hypothesize that a significant fraction of petrogenic or combustion-derived organic matter is remobilized out of marine or terrestrial deposits and finally enters the marine dissolved organic matter pool (DOM). If our hypothesis is true, the chemical signature of thermogenesis should be universally imprinted into the molecular structure of DOM. In particular polyaromatic hydrocarbons (PAHs) with five or more condensed ring systems would unambiguously indicate thermal alteration (e.g. Simoneit, 2002; Kramer et al., 2004). The organic matter that is dissolved in the oceanic water column amounts to  $\sim 700$  Gt of carbon, similar to the quantity of atmospheric CO<sub>2</sub> or living (terrestrial and marine) biota (Siegenthaler and Sarmiento, 1993; Hedges et al., 1997). Up to 90% of the lipophilic DOM fraction has a fossil radiocarbon age and may arise from inputs of pre-aged petrogenic precursors (Loh et al., 2004).

In order to identify a thermogenic molecular signature in marine DOM we used ultrahigh-resolution mass spectrometry. Major advances in molecular fingerprinting and chemical characterization of DOM have recently been achieved by ultrahigh-resolution mass spectrometry via the Fourier transform-ion cyclotron resonance technique (FT-ICR-MS; Kujawinski et al., 2002; Stenson et al., 2002, 2003). The primary strength of the FT-ICR-MS technique is the ability to identify individual molecules in complex natural mixtures without prior separation, e.g. through chromatography. It has been shown by Koch et al. (2005) that FT-ICR-MS is suitable for obtaining detailed compositional information on marine DOM. On the basis of ultrahigh-resolved mass spectrometry data, the authors identified >1500 molecular formulae in marine DOM. Because of the extraordinary mass accuracy of high-field FT-ICR-MS, molecules with the same nominal mass can be distinguished. For instance, N<sub>2</sub>O and CO<sub>2</sub> have the same nominal mass (44 Da), but because of a distinctive mass defect, i.e. different number in protons and neutrons, their actual masses differ slightly (44.001 versus 43.990 Da). This feature can be exploited in order to assign mass differences to specific differences in molecular formulae, and discrete formulae can be determined for each mass detected via FT-ICR-MS. The data presented by Koch et al. (2005) provide molecular insights into the polydisperse and complex mixtures of marine DOM.

The Southern Ocean (Antarctica) is uniquely suited for the purpose of this study because the deep water masses are particularly important for global ocean circulation (Orsi et al., 1999; Mackensen, 2001; and references therein): the Warm Deep Water (WDW) branches from the deep Antarctic circumpolar current and is largely composed of deep water from the Northern Atlantic and even older water masses derived from the Pacific that have traveled all the way through the oceanic conveyor belt, thereby integrating global information. Weddell Sea Deep Water (WSDW) underlies the WDW; it has partly been in contact with the atmosphere and is the water mass that ultimately ventilates the abyssal plains of the three oceans. Antarctic surface water (AASW), on the other hand, is comprised primarily of old (pre-industrial) water masses that have reached the surface from the deep through regional upwelling. Anthropogenic impact is minimal in the Weddell Sea and due to its unique location, aerosol deposition is negligible (e.g. Jickells et al., 2005) and no rivers discharge into it.

The objective of the present study was to elaborate on our hypothesis, the release of thermogenic organic

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