

A coupled molecular isotopic approach to trace sources of organic carbon preserved in the sedimentary record

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Organic compounds synthesized by organisms are subject to post-formation biological and physico-chemical processes that alter their chemical composition, and complicate the recognition and quantitation of these materials in downstream organic carbon (OC) reservoirs such as soils and sediments. Moreover, the time-scales over which organic matter is processed prior to burial may vary substantially. As a result of these factors, contemporaneously deposited material may exhibit a range of ages and labilities. For example, vascular plant debris may be directly deposited in aquatic sediments (via eolian transport), or it may enter a protracted soil cycle that both modifies composition and delays delivery. On the other extreme, relict organic carbon eroding from uplifted sedimentary rocks may contribute ancient, highly refractory OC to the depositional environment. Thus, the differing extents of 'pre-conditioning' that organic matter undergoes prior to burial may greatly modify its chemical signature and strongly dictate its reactivity in the sub-surface.

For the above reasons, in seeking to quantify the proportions of organic matter preserved in the sub-surface that stem from different sources it is important to find tracer properties that are largely independent of degradation, and to assign ages to specific source materials. We have applied methodologies to measure the stable carbon isotopic composition and radiocarbon content of individual organic compounds in order to investigate the origin of OC buried in soils and sediments. $\delta^{13}\text{C}$ measurements (Goni and Eglinton, 1996) are used to establish source characteristics, and molecular ^{14}C measurements (Eglinton *et al.*, 1996) are used to

determine apparent ages for assessment of the residence times and cycling rates within (and between) carbon reservoirs. Focus has been placed on the molecular isotopic characteristics of terrestrially-derived organic matter in continental margin sediments. Preliminary measurements of hydrocarbon lipids in surficial marine sediments using this new coupled isotopic approach indicated considerable age variability that could be attributed to specific source inputs (Eglinton *et al.*, 1997). Here, we extend these measurements to other compound classes, including dissociation products of refractory aliphatic and phenolic macromolecules that form a larger proportion of the organic matter preserved in sediments and soils.

Methodology

Bulk carbon isotopic measurements were performed on carbonate-free sediment samples. Lipids constituents were isolated from the sediment via solvent extraction, separated into polarity classes via silica gel chromatography and further purified by urea adduction. The solvent extracted sediment was demineralized using HCl/HF, and the resulting organic matter concentrate was subjected to either chemical (CuO oxidation) or thermal (off-line pyrolysis) degradation. Functionalized products were converted to appropriate derivatives for gas chromatographic separation. Individual components within the purified fractions were characterized by gas chromatography-mass spectrometry (GC-MS) and their $\delta^{13}\text{C}$ compositions determined by isotope ratio monitoring Gas Chromatography-Mass Spectrometry (irm-GC-MS). Individual compounds

were isolated by preparative capillary gas chromatography (PCGC; Eglinton *et al.*, 1996), combusted, and converted for graphite for ^{14}C analysis by Accelerator Mass Spectrometry (AMS; Pearson *et al.*, 1998).

Results

Preliminary bulk and molecular isotopic data have been obtained from near-surface sediments from the Black Sea, Arabian Sea, Santa Monica Basin, Gulf of Mexico and the Washington margin. Depending upon geographic location we have found that terrestrial marker compounds can be either younger or older than the bulk OC ^{14}C age. In the Black Sea, for example, plant wax *n*-alkanes and *n*-alkanols exhibit up to 500 yr younger ages than both TOC and lipids of marine photoautotrophs implying rapid transit of recently biosynthesized terrestrial OC to the depositional setting. In contrast, sediments from the Santa Monica basin show a similar age discrepancy, but in this case the vascular plant markers are correspondingly older than bulk OC. The latter indicates a lag between biosynthesis and deposition. In the Arabian Sea, the plant wax *n*-alkanes are almost 10,000 yr older clearly betraying a relict source (palaeosols and/or fossil carbon; Eglinton *et al.*, 1997). The difference between expected age of the sediment interval studied and the measured bulk OC ^{14}C age provides an indication of the presence of reworked carbon inputs to the sediment. When combined with source specific information on the distribution of ages, the origin(s) of these reworked inputs can thus be identified.

Preliminary ^{14}C measurements of lignin-derived phenols from Lake Washington yield ages that are comparable to bulk OC, consistent with the stronger terrestrial influences on this aquatic system. The ages, when coupled with the relative abundance of specific phenols suggest that the terrestrial OC input derives from 'fresh' (relatively unaltered) vascular plant lignin. Stable isotopic measurements of these products indicate that these terrestrial inputs are predominantly derived from 'C3' vegetation. These results contrast sharply with those for equivalent compounds from the Gulf of Mexico where terrestrial

inputs contain a significant C4 (grassland) component and are highly altered in chemical composition (Goni *et al.*, 1997). The latter may result from processing in soils or during riverine transport. Bulk OC ^{14}C ages of these sediments indicate the presence of an older OC component; it remains to be determined whether this is due to reworked (soil-derived) materials carrying this highly altered land plant signature.

We hypothesize that, in addition to factors such as the chemical composition (recalcitrance) of precursor biochemicals, depositional conditions and mode of particle association, the preservation potential of organic matter is dependent upon the extent to which it has participated in terrestrial and aquatic biogeochemical cycles prior to deposition. The coupled molecular isotopic approach provides valuable insights into the sources and processing history of organic matter in sediments, and the considerable isotopic variability that has been revealed to date highlights the complexity of continental margin sediment systems as repositories of OC.

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