What Remains?
Molecular and spectroscopic analysis of non-hydrolyzable St. Lawrence

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Sediments are the ultimate long-term sink for organic carbon (OC) on Earth, thus playing an important role in the global cycles of O_2 and CO_2. Estuaries and river deltas are major conduits for terrestrial organic matter (OM) into marine systems, where it is mixed with locally produced OM and is eventually deposited and buried in the sediment bed. About 45% of global OC burial occurs along these river deltas and estuaries [1], therefore it is of interest to follow OM deposition and preservation in these terrestrial to marine transition zones. We chemically fractionated bulk OM from a series of sediments from the St. Lawrence Estuary and Gulf into distinct reactivity classes. We define three such OM fractions based on pioneering work by Hedges and Keil (1995) who classified OM based on chemical reactivities: labile (degradable at similar rate under oxic and anoxic conditions), non-hydrolyzable (degraded primarily under oxic conditions), and refractory (preserved on long time scales independently of redox conditions). Here we present data on the spectroscopic (HR-MAS ^{1}H/^{13}C NMR) characterization of the non-hydrolyzable fraction because of its importance in the long-term burial of OC below the seafloor. We used mild oxidation methods (RuO_4) followed by chromatographic and compound-specific isotope analysis (δ^{13}C CSIA) of the oxidation products. Combining results from the bulk and molecular analytical techniques provides insights into the composition and cycling of non-hydrolyzable OM in transitional system, from which OM preservation can be better understood.

[1] Hedges (1995) *Marine Chemistry* **49**,81-115

Diamond growth from organic carbon suggested by coupled δ^{18}O-δ^{13}C variations in diamonds and garnet inclusions

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The sources of carbon in the mantle and the mechanisms of its transport and precipitation as diamond are poorly understood. Diamond itself contains only a limited amount of geochemical information, primarily in the form of carbon isotope ratios and nitrogen abundances, and therefore a substantial effort has focussed on relating syngenetic mineral inclusions to their diamond hosts. For example, it is well known that, on a worldwide scale, diamonds with eclogitic inclusions have a distinct δ^{13}C distribution when compared to more abundant diamonds with peridotitic inclusions. Eclogitic diamonds have a distribution that extends from mantle-like δ^{13}C values (ca. -5‰), to very light carbon (<-20‰), whereas peridotitic diamonds have a distribution that clusters close to -5‰, without the long tail. The relatively low δ^{13}C values have been explained by either the subduction of organic carbon [1], the presence of heterogeneous primordial carbon reservoirs in the mantle [2], or high-temperature fractionation [3].

Here we report high-precision SIMS δ^{18}O measurements ($2\sigma < \pm 0.4‰$) of eclogitic garnet inclusions in diamonds from three distinct deposits, Damtshaa (near the Orapa mine) in Botswana; Argyle in Australia; and ultradeep inclusions from Jagersfontein, South Africa. The measured δ^{18}O values are highly variable, and the distributions of each locality are clearly distinct. Damtshaa garnet inclusions range from +4.8‰ to +8.8‰ (n=15) and have a broadly similar distribution to δ^{18}O values of eclogite xenoliths. Argyle garnet-inclusions range from +5.9‰ to +10.8‰ (n=29), and are skewed towards ^{18}O-rich isotopic compositions. Ultradeep, majoritic garnet inclusions from Jagersfontein have a narrow range between +8.6‰ and +10.0‰ (n=11).

All three localities are distinct from each other in their univariate δ^{18}O and bivariate δ^{18}O-δ^{13}C distributions. Damtshaa has negatively correlated δ^{18}O-δ^{13}C, Argyle has a distribution that is offset from "mantle-like" ^{18}O-^{13}C distributions, and Jagersfontein has low-variance δ^{18}O-δ^{13}C, but at anomalously high-δ^{18}O and low-δ^{13}C. Importantly, none have the distribution expected from independent knowledge about δ^{18}O values of cratonic eclogites and the sampling distribution of δ^{13}C values in eclogitic diamonds. The association of crustal-like δ^{18}O values with low δ^{13}C values suggests that the carbon responsible for the low δ^{13}C values is subducted organic material.

[1] Sobolev & Sobolev (1980) *Dokl Akad Nauk SSSR* **250**, 683-685.
[2] Deines (1980) *GCA* **44**, 943-961.
[3] Javoy *et al*. (1986) *Chem Geol* **57**, 41-62.