

On the origin of kerogen

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It is widely accepted that kerogens in black shale are a necessary precursor to oil generation at oil window temperatures between 75 and 135° C. However, the presence of refractory kerogen-like materials in high P-T cosmic settings (supergiant stars near the galactic center and carbonaceous chondrite meteorites) and terrestrial settings (mantle olivine, green schist facies black shales, hydrothermal metal deposits, and especially serpentinites), and the presence of anomalous metal content in black shale kerogen well above that found in biospheric material (elevated Ni, V, Co, Re, Os, and other PGE's) is highly anomalous to a low temperature biogenic model and requires a reconsideration of its origin as well as that of the derivative oil.

Based on an extensive literature review and our own data, we propose a new model for the origin of kerogen that is consistent with the observations above. It is suggested that most (if not all) Type 1 and Type 2 kerogens are a by-product of serpentinization (serpentine volumes are at least 10 times that of and may potentially exist under all of the planets' sedimentary basins) of two main peridotite types. Type 1 kerogen, which contains elevated nickel relative to vanadium, is probably derived from serpentinization depleted and/or lherzolite harzburgite peridotite in the upper mantle lithosphere, whereas Type 2 kerogen, which contains elevated vanadium and nickel, is derived from enriched aluminium and chrome spinel lherzolite sources. The kerogen-producing reaction occurs in greenschist and blueschist grade serpentinization 'kitchens' where kerogen is formed at highly reduced, hydrogen-nickel rich polymerization/catalytic sites under supercritical conditions.

Produced kerogen is propelled upward in the supercritical water plume until it cools below 400 °C ionizes, densifies, and reacts with hydrogen (from water breakdown) to produce two immiscible product fluids: a reductive hydrogenated, non-ionic petroleum fluid, and an oxidative bicarbonate brine component which can also contain considerable ionized halide and metal components. Only about 20% of the original kerogen material reacts to liquid hydrocarbon; the rest is carried as a refractory residuum by hydrothermal brines to surface seep sites where it is exhalatively deposited as a hydrocarbon-rich chemical sediment (commonly with dolomite and metals from the bicarbonate brine component) at near-vent chemical facies of black shale sequences.

Bulk composition of UHP metasediments and recycling of the sediment component in arc magmas via diapirs

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It is well established that a component is recycled from subducting sediments into arc magmas. This is particularly evident for Th, Be, Nd, Pb and in some cases Sr (e.g. [1, 2]). The 'efficiency' of recycling, e.g. the ratio of sediment input to magmatic output, is not well constrained. However, using sediment input and primitive magma concentrations from PLN and PLCG, or our data, plus estimates for arc magmatic flux, we find 'steady state' recycling rates are close to 100% in all arcs. If so, the residues of this process must be measurably depleted in the recycled component. Alternatively, arc magmatic fluxes have been systematically overestimated, or arc systems are far from steady state.

We have compiled and measured bulk compositions for peraluminous ultra-high pressure (UHP) metamorphic rocks. These show recycled element abundances that are almost universally indistinguishable from average shale $\pm 1\sigma$, except for samples with peak metamorphic temperatures, $T > 1050^\circ\text{C}$, consistent with the hypothesis that trace phases retain most of the Th, Be, Pb, LREE and perhaps Sr in subducting sediments until either (a) large extents of H₂O-fluxed melting or (b) dehydration-melting of phengite (e.g. [3, 4]). Strikingly, even 'fluid-mobile elements' such as U, Ba and K show no measurable depletion in peraluminous UHP rocks relative to average shale $\pm 1\sigma$ when peak $T < 1050^\circ\text{C}$. Samples with peak $T > 1050^\circ\text{C}$ lie at T/P higher than even the hottest estimated subduction zone geotherms.

These observations can be reconciled if subducting sediments, which are compositionally buoyant with respect to overlying peridotite, form diapirs that rise into the mantle wedge where they are heated and undergo large extents of 'super-adiabatic' decompression melting. Dynamical calculations suggest that subducting sediment layers > 200 m thick become unstable and form diapirs beneath most or all arcs worldwide. 'Grosopydite' xenoliths from the mantle could be ancient residues of such a process.

- [1] Plank & Langmuir, *Nature* 1993 [2] PLN, *Chem. Geol.* 1996 PLCG. [3] Plank *et al.* *Nature Geosci.* 2009. [4] Hermann & Rubatto, *Chem. Geol.* 2009.