

Organic sulfur as part of the sulfur cycle from early diagenesis through catagenesis

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During the diagenetic stage the sulfur –organic matter (S-OM) chemical environment is dominated by the aquatic media. The pH variations of the interstitial water and the redox potential prevailing control the various sulfur species hence their chemical activity. Some of the more polar organic matter being hydrophilic is exposed to the reduced active sulfides (e.g. S_x^{-2} , HS⁻, RS⁻) that are very active nucleophiles. In the last four years we have extended the research to decipher the mechanisms controlling these reactions. The more hydrophobic organic matter can be exposed to similar reactions in the presence of phase transfer catalysts (PTC). However, under these conditions the actual environment for the reaction is the organic phase. Since the diagenetic stage is considered to pertain to ambient to mild increased temperatures range all laboratory simulations indicate equilibration controlled mechanisms for both sulfur introduction into the (OM) as well as nucleophilicity controlled exchange. The only kinetic controlled reactions were either due to thermal stress or easily removed (substituted) groups most of which are rare in young sedimentary OM. We consider for these transformations the sulfate as un-reactive sulfur specie.

The catagenetic stages are controlled primarily by elevated temperatures however for the present discussion it is imperative also to note the non aquatic sedimentary environment. Some of the more labile sulfur species even being part of the organic matrix (Type II kerogen) can be released. Such is the case for polysulfides moieties that can expel hydrogen sulfide as well as elemental sulfur both of which can be chemically active at these temperatures. It is therefore that the catagenetic stages are dominated by free radical sulfur species and hence can lead to both isotopic mixing and molecular thermal transformations. The sulfur in sulfate becomes active due to thermal stress as well as some molecules containing sulfur that lower activation energy for the thermal sulfate reduction (TSR). At these chemical modifications if the system is closed or open we will find different products distribution. Sulfur speciation in OM preservation in sediments as well as better mechanistic approach for its important role in both diagenesis and catagenesis leading to generation of petroleum is worth a refreshed look.

Characteristics of dissolved organic matter in the hydrothermal fluids and the associated water samples obtained from arc-backarc systems

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Dissolved organic matter (D OM) is expected to play an important role of global carbon cycle as one of carbon reservoirs; however, the behavior of DOM is still unclear. Although the seawater contains around a hundred $\mu\text{mol/kg}$ of DOC (dissolved organic carbon), it is insufficiently understood that the hydrothermal activity at seafloor work as organic carbon source or sink against to the ocean reservoir [1]. Fluid and plume water samples have been collected from the five hydrothermal fields around Japan, which developed on the arc and backarc tectonic setting. One of them, Suiyo seamount is a sediment-starved hydrothermal system, while the others, Wakamiko crater, Minamiensei Knoll, Iheya North, and Hatoma knoll are sediment-hosted system. The samples were collected during the dive studies using ROV/HyperDolphin and DSV/Shinkai6500 of JAMSTEC in 2007 and measured concentrations of DOC and volatile fatty acids (acetate and formate).

The concentrations of DOC in the high-temperature fluid samples from the sediment-hosted systems tend to rich in DOC relative to those from sediment-starved system and some of those samples from the sediment-hosted systems show higher concentrations than that of the ambient seawater. On the other hand, the low-temperature shimmering fluids (up to 10°C) show higher concentrations of DOC. These results suggest that hydrothermal circulation process work exclusively as sink of DOC, while ascending hydrothermal fluid through organic rich sediment take some organic matter from the sediment. In addition, the high-temperature fluid samples from sediment-hosted systems tend to rich in the volatile fatty acids.

[1] Rang *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 3830-3842.