Sulfurization of humic acids during early diagenesis in surface sediments of a tropical upwelling system

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The early diagenesis of sulfur and the potential impact on sulfurization of humic acids (HAs) was followed in several short sediment cores from the continental shelf under the influence of a tropical upwelling system (Cabo Frio, Brazil). Besides contents and elemental stoichiometries of organic matter (OM), HAs, and the kerogen fractions, their stable isotope composition of carbon, nitrogen and sulfur was followed and compared, for instance, with the composition of sedimentary pyrite. Based on 210Pb and 14C dating, the investigated parts of the sediments span a range up to 2 ka cal BP.

The stable carbon and nitrogen isotope compositions of OM indicate a dominant marine source with no significant contributions from anthropogenic N sources, as also found in the HA fraction. It is found, that the atomic C/N ratios of HAs increased with depth with a corresponding shift towards negative in the stable sulfur isotope ratios. The sulfur isotope ratios cover a range between -8 and +5 ‰, being significantly enriched in the lighter isotope compared to sea and pore water sulfate (about +21‰), but depleted with respect to co-existing pyrite (between -27 and -42‰). Sulfur isotope latter do not correlate with the S/C ratios, but indicate an increasing contribution of diagenetic sulfur with depth, which is estimated based on a stable sulfur isotope mass balance approach.

Anoxygenic Cyanobacterial Mats in Middle Island Sinkhole, Lake Huron: An Analogue of the Precambrian

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Cyanobacteria are well recognized as the innovators of oxygenic photosynthesis and as critical agents of Earth's oxygenation. Although most of the evolutionary history of cyanobacteria was characterized by low-O_2 and/or redox-stratified environments, little is known about cyanobacteria that operate under these conditions or the potential signatures that they might leave in the geologic record. The Middle Island Sinkhole (MIS) in Lake Huron (USA) provides a valuable analogue of such Precambrian cyanobacterial mat systems. Groundwater rich in sulfur and low in O_2 fosters benthic cyanobacterial mats that thrive under persistent low-O_2, sulfidic conditions. Just beneath the mats is a thin calcite-rich layer of carbonate followed by organic-rich sediments with sulfate-reducing and methanogenic communities [1].

MIS mats are capable of both oxygenic and anoxygenic photosynthesis and have genes for sulfide oxidation (sulfide quinone oxidoreductase) [2]. However, genes for the biosynthesis of hopanoids, a commonly used biomarker of cyanobacteria, are absent [2]. Metatranscriptomic data points to the prevalence of viral predation, transposases, and the production of accessory pigments for light harvesting. To further evaluate potential geologic signatures of anoxygenic cyanobacterial mat systems, we are now characterizing the stable carbon and nitrogen isotope composition of the organic fraction of mats and sediments as well as mineralogy and carbon isotope content of carbonates.

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