

Recycling of organic sulphides during early diagenesis – assessing the role of natural vulcanization for the preservation of organic matter

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Although the natural vulcanization of organic matter is now widely accepted as a potential pathway for the preservation of organic matter, the specific environmental conditions for the formation and preservation of organic sulphides are still insufficiently understood. There is still no firm agreement on the relative sequence for the formation of organic and inorganic sedimentary sulphides. Furthermore, it is unclear to what extent sulphidized organic matter can be used as substrate by hydrolytic and fermenting bacteria. Frequently the formation of organic sulphides is considered important only after the pool of reactive iron available for the precipitation of iron sulphides has been consumed. Under these circumstances, natural vulcanization would only be an important preservation pathway for environments with very low clastic and high organic accumulation rates, and would take place at a sediment depth where bacterial hydrolysis rates are slow (Arnosti *et al.*, 1996). Here I present data suggesting that organic sulphide formation is likely a ubiquitous process in all sediments where terminal metabolism includes bacterial sulphate reduction, but that most of the organic sulphides are unstable and play an integral part in the oxidative cycling of sulphide and carbon during early diagenesis.

Methods. Sediments were collected from sulphidic, organic-rich estuarine muds of St. Andrew Bay, Florida to assess the early diagenetic pathways leading to the formation of organic and inorganic sedimentary sulphide species. Abundance and sulphur isotopic composition were determined for dissolved sulphide, dissolved sulphate, elemental sulphur, acid-volatile sulphide, chromium-reducible sulphur, fulvic acid-sulphur, humic acid-sulphur, and residual organic (protokerogen) sulphur using analytical procedures previously described in Brüchert and Pratt (1996). The organic fractions were also analysed for concentrations of carbon, hydrogen, and nitrogen, as well as for their carbon isotopic and molecular composition.

In order to test the rate of formation and relative

degradability of sulphidized organic matter, glucose, polysaccharides, and fresh organic matter from bacterial mats were reacted with a saturated polysulphide solution at neutral pH. Dissolved reaction products were analysed in time series by HPLC and compared to commercially available 5-thioglucose. Solid products were analysed for their bulk chemical composition. Sulphidized and unsulphidized compounds were added as sole organic substrates to mixed, marine, anaerobic bacterial enrichments.

Results. Core profiles in the uppermost 50 cm of recent sediments from St. Andrew Bay, Florida reveal that dissolved sulphides are incorporated into macromolecular organic fractions such as humic and fulvic acids directly at the sediment oxic/anoxic interface. Fulvic acids represent the largest, but transient sink for dissolved sulphide or intermediate oxidized sulphur species such as polysulphides and polythionates. During burial, two thirds of organic-bound sulphides are released into porewaters as polysulphides or as low-molecular weight organic sulphides driving a dynamic cycling of sulphur between sedimentary and porewater species in the uppermost 5 cm of sediment. Only a small fraction of fulvic acid-sulphur is transferred to high-molecular weight compounds such as humic acids and protokerogens. Abundance and isotopic composition of porewater sulphur species indicate limitation of bacterial sulphate reduction by reactive organic matter despite high concentrations of total organic carbon.

The sedimentary organic sulphur pool consists of at least two isotopically distinct pools. Humic acid-sulphur is generally enriched in ^{34}S relative to fulvic acid-sulphur, and both organic sulphur fractions are enriched relative to elemental sulphur and iron sulphides. Isotopic mass balance calculations suggest that organic sulphur is derived from mixing between (1) ^{34}S -depleted sulphur that was recycled from bacterial hydrogen sulphide and (2) ^{34}S -enriched sulphur interpreted as detrital primary

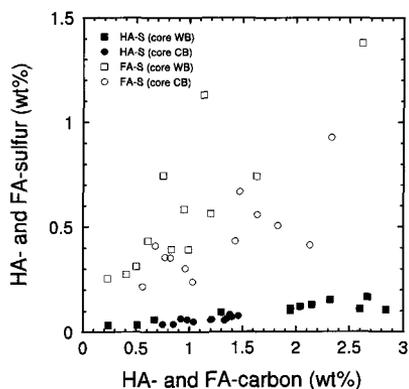


FIG. 1. Relationship between carbon and sulphur in humic and fulvic acids from sediments of St. Andrew Bay, Florida.

biosynthetic sulphur originally assimilated from dissolved sulphate.

Carbon isotopic analysis indicated a characteristic ^{13}C -enrichment of fulvic acids relative to total organic carbon while humic acids are slightly depleted relative to total organic carbon. These data may suggest a greater abundance of labile ^{13}C -enriched carbohydrates and amino acids in the fulvic acid fraction whereas the humic acid fraction contains proportionally larger amounts of phenolic compounds. These conclusions are supported by pyrolysis-GC-MS data which reveal abundant furans and pyrroles in the fulvic acids whereas humic acids are characterized by abundant phenolic compounds.

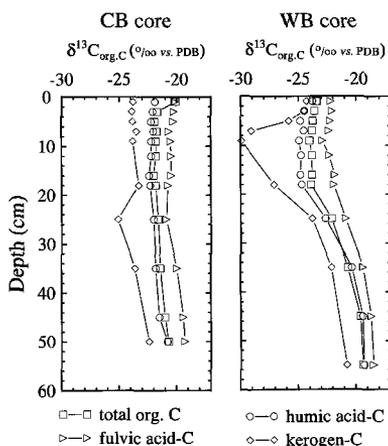


FIG. 3. Carbon isotopic profiles for individual carbon fractions in sediments from St. Andrew Bay, Florida.

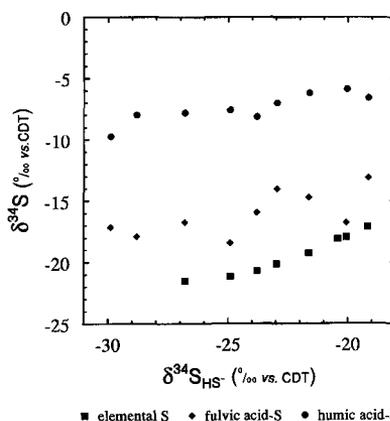


FIG. 2. Sulphur isotopic relationships between fulvic acid-S, humic acid-S, and elemental S indicating the pronounced enrichment in ^{34}S from detrital biosynthetic sulphur in humic acids.

Conclusions. Greater abundances of detrital biosynthetic sulphur in humic acids suggest that the organic sulphur compounds in this operationally defined fraction were already deposited as altered refractory biomolecules, and subsequently incorporated into humic acids. By contrast, the organic matter extracted as fulvic acids represents the dominant organic fraction interacting with bacterial hydrogen sulphide. Bulk, molecular and carbon isotopic differences between humic and fulvic acids suggest a greater functionalization of fulvic acids than humic acids that would be more conducive for substitution or addition reactions involving sulphide or polysulphide. However, both experimental and field data suggest that a large proportion of the intermolecular sulphur bridges are not stable. Instead, polysulphides or low-molecular weight organic sulphides are cleaved from macromolecules. At present, it is not clear whether the release is due to the utilization of organic polysulphides in the oxidative cycling of sulphur, or due to the metabolic consumption of the sulphur-bound organic matter. Consequently, while polymerization reactions of sedimentary organic matter due to sulphide cross-linking may contribute to preservation, it is not possible to assess the quantitative importance of this process to the overall preservation of organic matter.

References

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