

Sulfurization of organic matter in recent estuarine sediments (Authie Bay, N France)

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Abstract: Biogeochemical cycling of sulfur in estuarine sediments was studied in Authie Bay, N France, based on Distribution and stable isotope composition of sedimentary S species. The accumulation of biosynthetic and diagenetic organic S was not related to the fluxes of organic matter, but critically depended on the competitive processes of pyrite formation and sulfurization of organic substrates.

Key words: sediment, sulfur, isotope, humic acid, fulvic acid

INTRODUCTION

The enrichment of organic matter with sulfur (S) during earliest stages of diagenesis has been amply documented in marine sediments, while the importance of such reactions in freshwater environments is not very much appreciated (BRÜCHERT, 1998, URBAN ET AL., 1999). However, recent studies of lacustrine and soil-derived humic and fulvic acids showed, that their S-containing functional groups play an important role in binding and immobilization of metals (HUTCHINSON ET AL., 2001). In estuarine humic and fulvic acids, S is present predominantly in oxidized forms as sulfate or sulfoxide rather than in reduced forms (e.g. in oxidation states close to 0) (BILLON ET AL., 2002). Laboratory experiments showed, however, that polysulfides are principal sulfurizing agents for organic matter in environments with pH close to neutral (AMRANI AND AISENSTRAT, 2004).

The aim of the present study was to investigate the timing of sulfurization of humic and fulvic acids in estuarine environment along the salinity gradient in a relatively pristine environment of the Authie Bay (N France). Distribution and stable isotope composition ($d^{34}S$) of dissolved and sedimentary S species were analyzed in three sediment cores collected along the last 5 km of the Authie River flow, with salinity ranging from 0 to 23. Dissolved sulfide and sulfate, as well as sedimentary S forms: acid volatile sulfide (AVS, consisting predominantly of amorphous FeS, greigite and mackinivite), CRS (pyrite and elemental S), elemental S, and S bound to humic (HAS) and fulvic acids (FAS) were extracted using sequential extraction procedures described in the literature (BRÜCHERT, 1998, BILLON ET AL., 2002, HENNEKE ET AL., 1997). Stable isotope composition of extracted species was determined

using a continuous flow IRMS (Europa 20-20). Concentrations of organic carbon and total nitrogen, as well as reactive Fe (as degree of pyritization) were also analyzed.

RESULTS AND DISCUSSION

The total S concentration generally decreased with depth and was the highest in the marine environment. The distribution of individual S species in the sediment varied as well. With increasing marine influence, inorganic S forms (AVS, CRS and elemental S) became prevailing over organosulfur compounds. No correlation between sedimentary organic C and organic S was observed, indicating that the accumulation of biosynthetic and diagenetic organic S was not related to the fluxes of organic matter, but critically depended on the competitive processes of pyrite formation and sulfurization of organic substrates. Fe^{2+} is supposed to be an effective sink for

H_2S , however, in the Authie Bay the formation of FAS and HAS was generally independent on the availability of reactive Fe. At the same time, the formation of FAS and HAS above the AVS and CRS in the freshwater or mixed environments indicates that the predominant reactants for organosulfurs are partially reduced S ionic species, such as polysulfides, rather than sulfide.

The stable isotope composition of sedimentary S species is shown in Figure 1. Dissolved sulfate was the most ^{34}S -enriched species and its $\delta^{34}\text{S}$ value increased with depth, however, the enrichment varied from site to site. Among the sedimentary S species, CRS generally exhibited the most negative $\delta^{34}\text{S}$ values. $\delta^{34}\text{S}$ values of HAS and FAS were generally not correlated with their concentration and lied between those of dissolved sulfate and sulfides, confirming the assumption that dissolved sulfide was not directly bonded to the organic substrate. Using a simple mix-

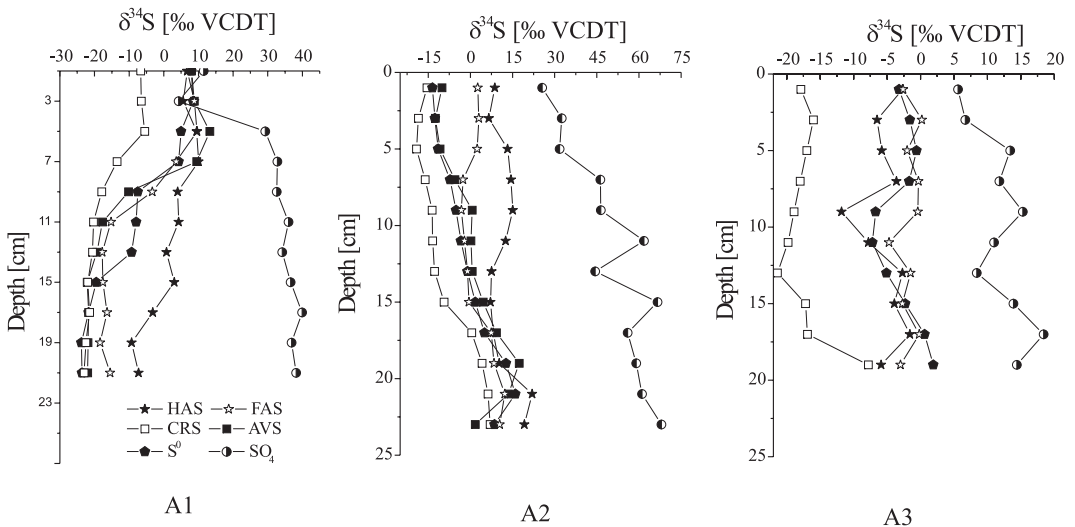


Figure 1. Stable isotope compositions of dissolved and sedimentary S species in the sediments of Authie Bay; A1 - Authie Aval (marine environment); A2 - Port de la Madelon (marine with strong freshwater influence); A3 - Authie Amont (freshwater).

ing equation for determination of sources of S in the organic matter, it was estimated that around 70 % of organosulfurs are of biosynthetic origin, while the rest is diagenetic. The $\delta^{34}\text{S}$ of fluxes of added diagenetic S to the organic substrates were estimated to be between -12 and $+8$ ‰, i.e. values that are lower than those of dissolved sulfate, showing that the sulfur incorporated into the organic matter was subject to sulfate reduction and most probably also to recycling of reduced S in the sediment.

CONCLUSIONS

The occurrence of organosulfur compounds in the uppermost sediment layer and their

enrichment in ^{34}S relative to AVS and CRS suggest their biosynthetic origin, but also a considerable contribution of diagenetic sulfurization of humic and fulvic acids in the earliest stages of diagenesis. Based on S isotope composition of HAS and FAS, the main sulfurizing agents are supposed to be partially reduced and/or recycled dissolved S species rather than sulfide or sulfate.

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