Stable sulphur isotope partitioning in permeable tidal sediments under non-steady-state conditions
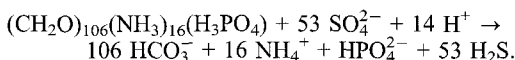
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Degradation of organic matter (OM) in coastal marine sediments to a large part proceeds via anaerobic microbial activity using dissolved sulphate as the final electron acceptor (Jørgensen, 1982) and forming hydrogen sulphide according to the overall reaction:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} + 14\ H^+ \rightarrow$$
$$106\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 53\ H_2S.$$

The rates of dissimilatory sulphate reduction in intertidal sediments may vary considerably and are generally controlled by the availability of dissolved OM and by temperature. The reduced sulphur species ($HS \equiv H_2S + HS^- + S^{2-}$) produced can be lost from the pore waters mainly by precipitation of iron sulphides, re-oxidation and release from the intertidal sediments to surface waters or the atmosphere. Microbial sulphate reduction is associated with a fractionation of the stable sulphur isotopes, where $^{32}SO_4^{2-}$ is preferentially reduced to hydrogen sulphide (e.g. Chambers and Trudinger, 1979). Due to dissolved oxygen in the tidal surface waters and the contact with air during low tide, permeable tidal sediments typically exhibit an oxic surface, and sulphate reduction in the upper 10–20 cm takes place in a more or less open system with respect to dissolved sulphate leading to a constant downcore isotope signature of dissolved sulphate (Fig. 1). However, when the burial of reactive OM (e.g. macro algae, mussels, plankton bloom) locally exceeds the background sedimentation of OM and bacterial activity is enhanced, the anaerobic degradation of organic matter in the sediment may lead to temporarily high amounts of dissolved HS (up to more than 20 mM) which is reflected by the formation of anoxic sediment surfaces ('black spots'), blackened by FeS_x. It was the purpose of the present study to follow the effect of black spot formation on the sulphur isotope partitioning between interstitial waters and sediments under non-steady state conditions.

Methods

The biogeochemical processes involved in the formation of black spots where followed on sediment cores and interstitial waters from sandflats in the backbarrier tidal areas of Baltrum and Spiekeroog Islands (southern North Sea) between May and July 1996. Sediment cores were investigated down to 40 cm depth for total organic and inorganic carbon (TOC; TIC), total nitrogen (TN), total reduced sulphur (TRS), H_2O, $\delta^{13}C(TOC)$, and $\delta^{34}S(TRS)$. Interstitial waters were sampled at 2 cm intervals using pore water lances and pH, alkalinity, DOC, HS, SO_4, $\delta^{34}S(HS; SO_4)$ and $\delta^{18}O(SO_4)$ were measured. The results from black spots are compared to an undisturbed sandflat reference area. Sulphur isotope data are given relative to the V-CDT standard.
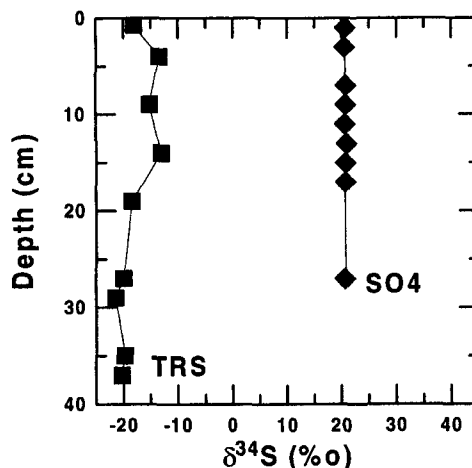

FIG. 1. Downcore variation of isotopic compositions of sulphur species on the reference site (7/1996; Böttcher *et al.*, 1997). Maximum HS concentration was 0.05 mM.
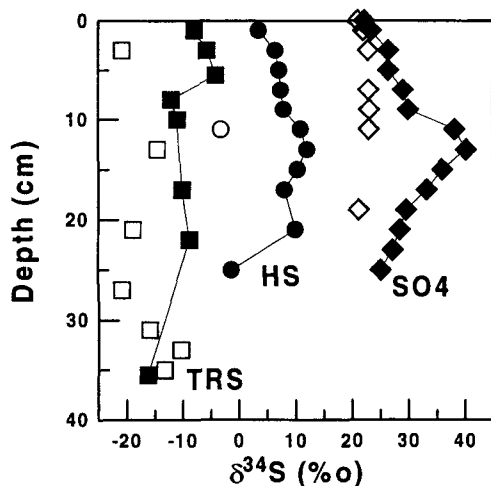
FIG. 2. Downcore variation of isotopic compositions of sulphur species under an anoxic sediment surface. Open and closed symbols mean 2 different sampling dates. Maximum HS concentrations were 16 mM.

Results and discussion

On the reference site, very low TOC concentrations (< 0.1 % dwt.) were measured in the upper part of the sediment increasing below 15 cm, due to an increase of the grain size fraction <63μm (Böttcher *et al.*, 1998). For the OM in the investigated sediments (reference site and black spots) a covariation of the $\delta^{13}C$(TOC) values and the C/N ratios was found indicating a mixture of terrestrial and marine organic matter, influenced by the preferential degradation of more easily decomposable marine OM (Böttcher *et al.*, 1998).

Interstitial waters beneath the black spots were significantly enriched in DOC, when compared to surface waters and the pore waters of the reference area.

On the sandy reference site the downcore sulphate concentration matched the surface water value (about 27 mM), and an overall ^{34}S depletion between −32 and −42‰ was found in TRS compared to coexisting pore water sulphate (Fig. 1). This is within the range observed during microbial sulphate reduction experi-

ments with pure cultures (Chambers and Trudinger, 1979). Similar results were observed for coexisting HS and SO_4 under a large anoxic sediment surface shortly after marine OM was buried (Fig. 2). The TRS fraction, however, was significantly depleted in ^{34}S compared to both HS and SO_4 indicating non-steady state conditions where a previous (un-loaded) situation was still preserved in the TRS fraction, consisting mainly of pyrite which does not exchange sulphur isotopes easily with HS (Böttcher *et al.*, 1997).

Below smaller black spots, however, which are believed to have been loaded with organic matter (macro algae, mussel) a longer time ago, The isotope data of coexisting sulphate and HS indicated isotope fractionation exceeding 60‰. This significantly larger isotope fractionation cannot be explained by microbial sulphate reduction alone. Partial reoxidation of HS may lead to the formation of elemental sulphur, thiosulphate or sulphite which may undergo further oxidation, reduction and disproportionation. Disproportionation of these intermediates is an important pathway in the oxidative part of the sulphur cycle of marine sediments and may be accompanied by significant sulphur isotope effects (Canfield and Thamdrup, 1994; Smock *et al.*, 1997). It is suggested that the complexity of the sulphur cycle as reflected by the dissolved sulphur species on sites with temporarily high concentrations of HS is influenced by the time frame of investigation.

References

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