

# SULPHUR GEOCHEMISTRY IN ORGANIC-RICH RECENT SEDIMENT (MAKIRINA BAY, CROATIA)

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## Abstract

The concentration and speciation of sedimentary sulphur, as well as sulphate and sulphide in pore water in the organic-rich sediment of Makirina Bay were studied. The most abundant sedimentary S species is disulphide (predominantly pyrite) comprising up to 85% of total S, and in some horizons organosulphur compounds ( $S_{org}$ ), whereas sulphate is much lower. Isotopic signatures of sedimentary sulphide and  $S_{org}$  indicate that sulphate reduction is the governing process in the S-geochemistry, along with syngenetic pyrite and  $S_{org}$  formation.

**Keywords:** sediments, sulphur, speciation

## Introduction

Pyrite and  $S_{org}$  compounds are major end-products of the S cycle in anoxic sediments. The reaction rates of  $S_{org}$  are slower than those of pyrite formation. Delayed  $S_{org}$  formation is suggested by enrichment of bulk organic sulphur in  $^{34}S$  relative to co-existing pyrite [1]. Active incorporation of dissolved sulphide into the humic fraction was observed in salt marsh sediments, representing over 50% of sedimentary sulphur in some cases, and pointing to simultaneous early diagenetic formation of  $S_{org}$  and pyrite [2].

Makirina Bay is a small, shallow (0.2-1 m deep) lagoon in Central Dalmatia, Croatia, 17 km N of Sibenik, with a small freshwater tributary in the south. In medieval times, salt was produced in the southern part of the bay. The water depth in the investigated area is between 0.2 and 0.8 m. The carbonate bottom of the bay is covered by a thick lens-shaped layer of clayey silt (up to 3 m), mostly covered by seagrass and algae.

## Materials and methods

Sediment cores were collected at three sampling sites approximately 100 m distance from each other, with increasing freshwater influence toward the south. They were immediately transferred to the laboratory and sectioned in a glove bag filled with nitrogen. Pore water was extracted under a pressure of 0.4 MPa through a 0.45  $\mu$ m membrane filter. Water samples for sulphide analysis were mixed with an equal volume of 6% Zn-acetate. Dissolved sulphate was determined turbidimetrically, while dissolved sulphide was determined colorimetrically. The precision of both methods was  $\pm 2\%$ . Total S and organic C concentrations in the sediment were determined using an IR-212 LECO Organic Carbon Determinator and an SC-132 LECO Sulfur Determinator. The accuracy ( $\pm 3\%$ ) was determined by replicate measurements. Sedimentary sulphate, Cr-reducible sulphide (disulphide) and  $S_{org}$  were extracted as described previously [3]. Isotopic analyses of sulphide were performed on a Europa 20-20 continuous-flow isotope ratio mass spectrometer with a precision of  $\pm 0.2\%$ , while sulphate and  $S_{org}$  were analysed on a dual-inlet IRMS (modified MI-1305) with a precision better than  $\pm 0.15\%$ . Results are reported as parts per thousand (‰) deviation from Canyon Diablo Troilite (CDT) reference standard.

## Results and discussion

Sub-sampling of the sediment cores revealed a high heterogeneity with pocket-like structures of different grain-size and colour, reflected in scattered depth profiles of all observed species, especially in the central part of the bay. In the pore water, the sulphate concentration decreased rapidly from 35 mM in the supernatant down to 20 mM at a depth of 1 cm, indicating intensive sulphate reduction immediately below the sediment/water interface. The low sulphide concentration ( $>0.1$  mM) is attributed to the simultaneous precipitation of Fe-sulphide and incorporation of  $S^{2-}$  into organic S [4]. Concentrations of sedimentary organic carbon and total sulphur ranged between 2.5-5% and 0.1-2%, respectively. They were higher in the central part of the bay, decreasing toward the south due to the increasing freshwater influence. Except in the uppermost sediment layer, disulphide (mostly in the form of pyrite) was the predominant S species, reaching up to 1.1 wt.% or 85% of total S (Fig. 1).  $S_{org}$  was between 0.03 and 0.8 wt.% (2-50% of the total S), while sulphate ranged between 0.03 and 0.35 wt.% (13-33%).  $S_{org}$  was generally below 10% of total S; however, it increased with depth and in some lower horizons even exceeded disulphide, indicating that formation of  $S_{org}$  is an important sink for dissolved sulphide. Intensive sulphate reduction in the uppermost sed-

iment segment just below the sediment/water interface is most probably driven by the oxidation of upwelling methane, which is produced in the sediment [5]. The low  $\delta^{34}S$  of disulphide (between  $-33$  and  $-29\%$  CDT) suggest that bacterial sulphate reduction is the governing process in the sulphur geochemistry of the sediment.  $S_{org}$  is depleted in  $^{34}S$  compared to marine sulphate as well ( $\delta^{34}S$  between  $-4$  and  $-2\%$ ), indicating that  $S_{org}$  is formed from dissolved sulphide, which is derived from sulphate reduction. No correlation between disulphide and organic C was observed in the sediment, which would be typical of "normal" marine sediments with diagenetic pyrite formation [6]. Furthermore, disulphide and  $S_{org}$  depth profiles are mirror-images, indicating that both are formed syngenetically, maybe even in competitive processes.

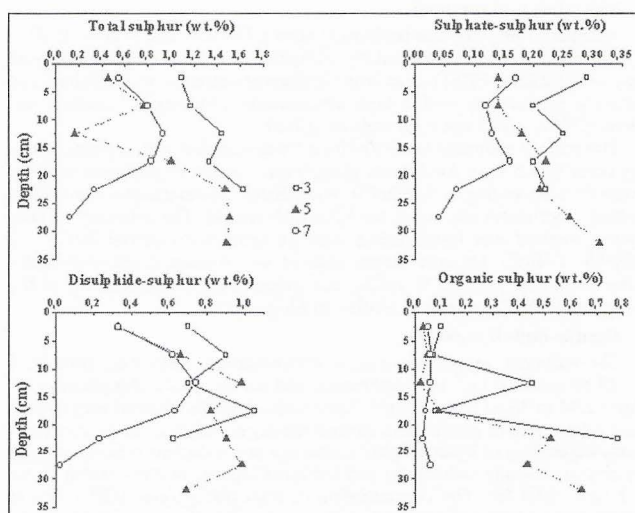


Figure 1: Depth distribution of sulphur concentration in the sediment; freshwater influence increases from 1 to 3

## References

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