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Sulfur speciation in the upper Black Sea sediments

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ABSTRACT

We report solid phase sulfur speciation of six cores from sediments underlying oxic, suboxic and anoxic-sulfidic waters of the Black Sea. Our dataset includes the five sulfur species [pyrite-sulfur, acid volatile sulfides (AVS), zerovalent sulfur (S(0)), organic polysulfides (RS_x), humic sulfur] together with reactive iron and manganese, as quantified by dithionite extraction, and total organic carbon. Pyrite – sulfur was the major phase in all cores [200-400 µmol (g dry wt)$^{-1}$] except for the suboxic core. However, zerovalent sulfur and humic sulfur also reached very significant levels: up to about 109 and 80 µmol (g dry wt)$^{-1}$, respectively. Humic sulfur enrichment was observed in the surface fluff layers of the eastern central basin sediments where Unit-1 type depositional conditions prevail. Elemental sulfur accumulated as a result of porewater sulfide oxidation by reactive iron oxides in turbidities from the anoxic basin margin and western central basin sediments. The accumulation of elemental sulfur to a level close to that of pyrite-S in any part of central Black Sea sediments has never been reported before and our finding indicates deep basin turbidites prevent the build-up of dissolved sulfide in the sediment. This process also contributes to diagenetic pyrite formation whereas in the non-turbiditic parts of the deep basin water column formed (syngenetic) pyrite dominates the sulfur inventory. In slope sediments under suboxic waters, organic sulfur (humic sulfur + organic polysulfides) account for 33-42% of total solid phase S, indicating that the suboxic conditions favor organosulfur formation. Our study shows that the interactions between depositional patterns (Unit 1 vs. turbidite), redox state of overlying waters (oxic-suboxic-sulfidic) and organic matter content determine sulfur speciation and enable the accumulation of elemental sulfur and organic sulfur species close to a level of pyrite-S.

1. Introduction

The marine sedimentary sulfur cycle is a complex web of biogeochemical interactions driven by the generation of dissolved sulfide by the actions of sulfate reducing prokaryotes (Jørgensen, 1982). The usual fate of sulfide in normal marine sediments (that lie under oxygenated waters) is either reoxidation to a number of sulfur species, such as $S_2O_3^{2-}$, S_x^{2-}, S(0), SO_4^{2-} or reacting with metals, mostly minerals of Fe, to give FeS and then ultimately pyrite – FeS_2, the latter being the stable end product. If the sediment is relatively Fe-poor and rich in organic matter, both dissolved sulfide and sulfur intermediates can react with organic matter to give organic sulfur (Vairavamurthy and Mopper, 1987; Francois, 1987a,b; Kohnen et al., 1989; Luther and Church, 1992). Especially in the sediments that lie under permanently anoxic and sulfidic (euxinic) waters, abiotic reoxidation becomes less important and the sulfur system is governed by the competitive balance between reactions of sulfide with reactive Fe minerals or with reactive organic matter. Upper Black Sea sediments provide possibilities to study the entire marine sedimentary sulfur cycle because oxic, suboxic, and anoxic/sulfidic conditions permanently exist in this marine system.

The Black Sea sediments have been of interest for many decades for their unique depositional history (Ross et al., 1970; Mitropolsky et al., 1982). Ross et al. (1970) identified the three depositional patterns in the uppermost several meters of the anoxic basin sediments: Unit 1, comprising about the uppermost 30 cm of the sediment column, is rich in coccolith derived carbonates and has relatively low levels of organic carbon. This layer has light micro-laminated layers of high carbonate with intervening darker, organic rich layers. Below this layer is Unit 2, about 40 cm thick and with high levels of organic carbon (up to 20%) and low carbonate content. Below these layers are Unit 3 sediments, very low in organic C (<1%). Unit 1, which can be sampled with box or multicorers and therefore are most intensely studied among these three types, has been investigated with respect to reactive iron enrichment and pyrite formation in a number of studies (Volkov, 1964; Volkov and Fomina, 1974; Rozanov et al. 1974; Berner 1974; Lyons 1991; Lyons and Berner 1992; Canfield et al., 1996; Hurtgen et al., 1999; Wijsman et al. 2001a; Anderson and Raiswell, 2004). These authors generally observed pyrite enrichment

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of the deep basin Unit 1 sediments. The approach to estimate the level of this enrichment has been the use of the parameter "degree of pyritization" (DOP), which is defined as pyrite Fe / (pyrite Fe + reactive Fe) (Berner, 1970). DOP values larger than 0.75 were found to be typical of deep basin, and indicative of anoxic and sulfidic (euxinic) deposition conditions (Raiswell and Berner, 1985; Canfield et al., 1996).

The mechanism for the enrichment of deep basin sediments in pyrite is thought to be mainly due to water column formation (mostly at the top of sulfidic zone) and subsequent accumulation in the sediment (Muramoto et al., 1991; Lyons, 1997); a conclusion mostly based on sulfur isotope data. In most of the studies mentioned so far, turbidites were also found within the deep basin, interrupting the Unit 1 sequence and a homogeneous nature was ascribed to these turbidite layers (Lyons, 1991). Lyons and Berner (1992) found that total reduced sulfide (they measured this through boiling Cr reduction – Canfield et al., 1986) in the solid phase was still high in the turbiditic part of their cores despite their low organic C content. These investigators suggested this was indicative of pyrite formation within the turbidite mud; however, the exact sulfur composition of the turbidite muds remained unexplored. A more complete study with respect to sulfur speciation was that of Wijsman et al. (2001a,b), who measured the three inorganic S species (pyrite, AVS and elemental S) for northwestern shelf sediments along with a slope and deep basin core in the western basin. Their deep basin core was Unit 1 like (rich in pyrite, low in reactive Fe) and they clearly demonstrated AVS enrichment in various shelf depositional/organic loading settings.

Detailed solid phase sulfur speciation studies were conducted on the sediments of salt marshes (Ferdelman et al., 1991), anoxic estuarine muds (Brüchert, 1998), continental margin of South America (Vairavamurthy et al., 1995; Zopfi et al., 2008), sediments lying under anoxic brines of the Eastern Mediterranean (Henneke et al., 1997) and Oman margin, Arabian Sea (Passier et al., 1997). Most of these studies reported solid phase S (0), organic polysulfides and humic S (in addition to commonly measured pyrite and AVS) and demonstrated how the relative abundance of sulfur species may change drastically under differing sedimentation patterns, organic matter load and redox dynamics. As Black Sea sulfur studies have focused on pyrite formation and calibration of DOP-based proxies in Unit 1, the other sulfur species have been neglected. Since the Unit 1 sequence is not common to all of the anoxic basin and its margin due to turbiditic deposition, different sulfur speciation patterns may emerge within the basin and its margin (i.e. from pyrite dominated to S (0)-AVS rich or organic S dominated). Moreover, slope sediments lying below suboxic Black Sea waters may be rich in sulfur intermediates, such as organic polysulfides, which tend to be stable under non-reducing conditions (Boulegue et al., 1982) and were shown to exist in high amounts in salt marshes (Ferdelman et al., 1991) and anoxic brine sediments (Henneke et al, 1997).

In this paper we report and discuss cm-resolution vertical profiles of inorganic [pyrite-S, AVS and elemental S (or zerovalent sulfur-S_8)] and organic solid phase sulfur species (organic polysulfides and humic sulfur). These data are from the same cores as the study of Konovalov et al. (2007), who studied the Black Sea sediments with solid state voltammetric microelectrodes for mm-scale vertical profiles of dissolved H_2S, Mn and Fe (II) in the upper 20-30 cm. That study demonstrated how variable porewater chemistry can be across the basin. Our cores, as described by Konovalov et al. (2007) in detail, are from oxic shelf, suboxic slope and anoxic basin sediments, and within the anoxic basin cores both turbiditic and Unit-1 type sections exist. We support our sulfur data with measurements of reactive Fe and Mn phases and organic C/organic N and present the solid phase data along with the porewater profiles (reproduced from Konovalov et al (2007) except for two stations). Our goals are to (1) evaluate the effect of water column redox state (oxic-suboxic-anoxic) and deposition pattern (turbidite vs. Unit 1) on the speciation of sulfur in the solid phase of surface sediments and (2) to assess the relative importance of organic sulfur phases (humic sulfur + organic polysulfides) versus inorganic sulfur in the Black Sea sediments.

2. Sampling and Experimental Methods

2.1. Sampling, in situ microelectrode profiling and sample storage

Sediment samples were retrieved with a multicorer during the 2003 R/V Knorr Black Sea expedition which lasted from April 10 to May 10. Upon retrieval, voltammetric microelectrode profiling was performed as described by Konovalov et al. (2007). Briefly, this technique allows mm scale determination of porewater redox species such as HS^-/H_2S, Fe(II)/Fe(III), Mn(II), FeS and O_2 (Brendel and Luther, 1995; Luther et al., 1998, 2008). Some of these data will be reproduced along with the solid phase data throughout this paper. Of many stations occupied during this cruise, 6 stations were further sampled for on-shore solid phase analysis. Basic data on the location of these stations are given in Table 1 and Fig. 1. Of these 6 stations, 19, 23, 07 and 30 were located in the anoxic basin, site 12 was located in the southwestern continental slope under suboxic waters and 29 was a shelf core. Upon completion of microelectrode profiling, cores were sliced in 1 cm depths in a glove bag filled with ultra-high purity argon. Then, each section was put in 50 mL falcon tubes and frozen at -20 °C. Only for the station 12 core, which was 36 cm in length, not every cm was sliced but six sections were chosen based on microelectrode profiles (0-1, 4-5, 8-9, 14-15, 20-21 and 30-31 cm). On the shore, test tubes were weighed, centrifuged, porewater was decanted and test tube was weighed again. This transfer was performed in a glove bag under argon. These weights along with the dry/wet ratio of the remaining sample were used in the computation of porosity. Determination of dry/wet weight conversions was accomplished by subsampling about 0.5 g wet sediment in a glass beaker (which was weighed previously) and letting it dry in 105 °C oven until reaching constant weight (this usually took 2 days). After centrifugation and decanting of the porewater, the dry weight fraction of the remaining sediment was usually between 0.45-0.55. For each core section analyzed, another one was dried as above to determine this ratio.

For each of the analyses described below, a wet subsample is taken from the 50 mL test tube containing the 1 cm slice and processed accordingly.

2.2. Solid phase sulfur species

Sediments were analyzed for five sulfur species (AVS, pyrite, elemental sulfur, organic polysulfides and humic sulfur). As shown by Henneke et al. (1997), the sum of the concentrations of these five species gives a reliable estimate for total sulfur concentration.

2.2.1. Sequential Analysis of AVS and Pyrite-S

Acid volatile sulfides (AVS) and pyrite-sulfur were sequentially determined on a wet subsample by acidification of the sample

Table 1
Stations of the R/V Knorr 2003 Black Sea expedition that were sampled for this work.

Station	Leg	Area	Latitude (North)	Longitude (East)	Water Depth (m)
07	8	Eastern Central	42 47.9961	37 30.3789	2187
19	8	East-anoxic basin margin	41 29.4197	40 45.4203	1764
23	8	Eastern central	42 00.76	39 30.57	2033
29	8	Shelf	42 10.83	34 23.63	111
30	8	Western central	42 32.16	30 54.48	2182
12	9	Southwestern slope (suboxic)	41 23.74	29 21.097	161