Early diagenetic processes in northwestern Black Sea sediments
Wijsman, Johannes Wijnandus Maria

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CHAPTER 5

Sulfur and iron speciation in surface sediments along the northwestern margin of the Black Sea

Jeroen W. M. Wijsman, Jack J. Middelburg, Peter M. J. Herman, Michael E. Böttcher, Carlo H. R. Heip
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Introduction

River deltas and continental shelf areas play an important role in the global cycles of sulfur and iron and are important sites for the formation and burial of authigenic iron sulfides (Berner, 1982; Jørgensen, 1982; Lin and Morse, 1991). This is due to high rates of organic matter fluxes to the sediments in combination with the input of reactive iron through rivers (e.g. Lin and Morse, 1991). With increasing load of reactive organic matter to the sediment, the relative importance of sulfate reduction usually increases (Canfield, 1989a; Thamdrup and Canfield, 1996 and chapter 4 of this thesis). Sulfate reduction is, therefore, the major mineralization pathway in sediments of productive coastal marine systems, accounting for 10 – 90 % of the total organic matter degradation (Jørgensen, 1977; Jørgensen, 1982; Henrichs and Reeburgh, 1987; Canfield et al., 1993a; Thamdrup and Canfield, 1996; Kostka et al. 1999).

Dissolved hydrogen sulfide that is produced during bacterial dissimilatory sulfate reduction may quickly react with sedimentary reactive iron compounds to form iron monosulfide, FeS, (Rickard, 1995), which can further react with dissolved sulfide, elemental sulfur or polysulfides (Berner, 1970; Luther, 1991; Rickard, 1997a) to form pyrite (FeS$_2$). This immobilization of free sulfide within the sediment has major consequences for the cycling of iron and sulfur. Transport processes and turnover rates are significantly reduced by the formation of solid-phase iron sulfides. Moreover, the formation of iron sulfides and the subsequent burial in the sediment has been recognized as the dominant pathway for the permanent removal of sulfur and iron (Berner, 1982; Berner and Raiswell, 1983). Since hydrogen sulfide ($H_2S \equiv H_2S_{(aq)} + HS^- + S^2-$) dissolved in the pore waters is toxic for many macrofaunal species (e.g. Bagarinao, 1992), the fixation of $H_2S$ through the formation of metal sulfides is also an important detoxifying mechanism for the macrofauna community.
In the absence of sufficient sedimentary reactive iron, \( H_2S \) can diffuse into underlying sediments or the water column (Passier et al., 1999), can be chemically or microbially reoxidized to sulfur intermediates (elemental sulfur, thiosulfate, sulfite) or sulfate (Fossing and Jørgensen, 1990; Zhang and Millero, 1993) or react with organic matter (e.g. Sinninghe and De Leeuw, 1990). Additionally, bioturbating organisms can transport iron sulfide minerals from the reduced to the oxidized part of the sediments, where they are subsequently re-oxidized (Berner and Westrich, 1985; Aller, 1988; Aller and Rude, 1988). Thus benthic organisms might have a positive effect on the recycling of sulfur and iron within the sediments by their bioturbating and bio-irrigating activities. Oxygen has a direct effect on sulfur and iron cycling through re-oxidation, but also an indirect effect by its influence on the biomixing and bio-irrigating activity of the macrofauna that, in turn, depend on oxygen to respire.

It has been shown that a significant part of \( H_2S \), which is produced in the sediments, is not permanently buried but reoxidized (Jørgensen, 1977). Besides diagenetic pyrite formation in the sediment, syngenetic precipitation in the anoxic water column has been shown to significantly contribute to sedimentary pyrite in the Black Sea (Fry et al., 1991; Muramoto et al., 1991; Raiswell and Canfield, 1998; Neretin et al., 2000).

The overall effect of early diagenetic reactions is not only reflected in the depth distributions of various dissolved and particulate sulfur and iron compounds within the sediment (e.g. Jørgensen, 1983), but also in the stable isotopic composition of metal sulfides, in particular pyrite (e.g. Goldhaber and Kaplan, 1974). The bacterial dissimilatory reduction of sulfate is associated with a significant discrimination of the stable sulfur isotopes \(^{34}S\) and \(^{32}S\), leading to an enrichment of the lighter isotope in the \( H_2S \) produced (e.g. Chambers and Trudinger, 1979). Since no significant further isotope discrimination occurs upon iron sulfide formation (Price and Shieh, 1979; Böttcher et al., 1998b), the overall isotopic composition of the metabolic product \( H_2S \) should be preserved in the pyrite fraction. Therefore, the sulfur isotope ratios of sedimentary sulfur species in marine sediments have been found to be extremely useful in the characterization of biogeochemical processes in the coupled sulfur – carbon – iron cycles during early diagenesis (e.g. Goldhaber and Kaplan, 1974; Raiswell, 1997; Böttcher et al. 1998a; Passier et al., 1999; Böttcher et al., 2000). Most previous studies on the sulfur isotope geochemistry of Black Sea sediments were related to the water column or sediments deposited below the chemocline (Sweeney and Kaplan, 1980; Fry et al., 1991; Muramoto et al., 1991; Calvert et al., 1996; Lyons, 1997, Neretin et al., 1998; Neretin et al., 2000). Pyrite which is found in the water column and the surface sediments in the anoxic part is extremely depleted by up to -62 ‰ compared to coexisting sulfate (e.g. Fry et al., 1991; Lyons, 1997; Neretin et al., 1998). However, experiments with sulfate-reducing bacteria isolated from the Black Sea water column yielded an isotope fractionation of only about -30 ‰ (Fry et al., 1991). This discrepancy has been attributed to contributions from the oxidative part of the sulfur cycle (Canfield and Thamdrup, 1994) but is still a matter of debate (Fry et al., 1991; Neretin et al., 2000).

In the present study, we present data on the distribution of iron sulfur speciation and the sulfur isotopic composition of pyrite in surface sediments of the northwestern Black Sea along a transect from the coastal area, just in front of the river deltas, down to the anoxic deep-sea. It was the aim to provide additional information on the influence of depositional environments on the formation of and sulfur isotope partitioning into early diagenetic pyrite.
Study area

The Black Sea is the world’s largest anoxic basin with a permanent reservoir of hydrogen sulfide in the water column at depths > 100 m (Sweeney and Kaplan, 1980; Sorokin, 1983; Codispoti et al., 1991). It has been an object of intensive study concerning the cycling of iron and sulfur (e.g. Berner and Raiswell, 1983; Berner, 1984; Calvert and Karlin, 1991; Middelburg et al., 1991; Lyons and Berner, 1992; Lyons, 1997; Wilkin et al., 1997 and chapter 6 of this thesis). The Black Sea is often seen as the modern equivalent of ancient euxinic basins with pyrite formation and sulfide oxidation processes existing in the upper part of the sulfidic water column of the deep-sea (Goldhaber and Kaplan, 1974; Calvert and Karlin, 1991; Jørgensen et al., 1991; Luther et al., 1991). Consequently, most previous studies concerning the iron and sulfur cycling in the Black Sea focused on the deep-sea.

Three major rivers (Danube, Dniester and Dnieper), accounting for 76% of the total river input into the whole Black Sea (Tolmazin, 1985b; Mee, 1992; Fabry et al., 1993) discharge their water on the northwestern shelf which represents only 17% of the total Black Sea area (Tolmazin, 1985b; Wijsman et al., 1999). The effect of these rivers on one side and the anoxic deep-sea on the other side introduce strong gradients across the northwestern shelf that could potentially affect the cycling of iron and sulfur within these sediments. The rivers discharge large amounts of nutrients and organic matter to the shelf. Consequently the benthic mineralization rates in the area just in front of the river mouths are much higher compared to the offshore areas (Wijsman et al., 1999). Large rivers such as the Danube are also a major source of reactive iron to continental shelf sediments (Martin and Windom, 1991; Guieu et al., 1998). In the Black Sea, this reactive iron is re-allocated from the shelf to the deep-sea sediments due to the pyrite formation in the water column of the deep-sea (Chapter 6 of this thesis). The oxygen concentration of the near-bottom water on the northwestern shelf is also variable. Due to upwelling/downwelling, internal waves and seasonal and long-term changes in mean circulation (Shaffer, 1986; Dimitrov et al., 1987; Lyons et al., 1993), the oxic/anoxic interface migrates over the shelf edge. As a consequence the bottom water oxygen concentration in the area near the oxic/anoxic interface fluctuates between fully oxic and anoxic. Moreover, oxygen depletions could occur in the shallow coastal waters as a result of high degradation rates in the sediment after a phytoplankton bloom in combination with a temperature stratification of the water column (Zaitsev, 1993).

Material and Methods

Sampling locations

Sediment was collected from nine stations in the northwestern part of the Black Sea in May 1997 (Figure 5.1; Table 5.1). Stations 2, 9, 10, 24 and 22, respectively, were positioned on a transect ranging from high organic loading in the shallow coastal waters to low organic loading in the permanently anoxic deep-sea. The coastal station 13 was located in front of the mouth of the river Dniester. Station 16 was situated in the northern part of the central shelf and is supposed to be directly influenced by (the discharge of) the Danube river (Wijsman et al., 1999), while station
Figure 5.1. Locations of the sampling stations in the northwestern part of the Black Sea

Table 5.1. Characteristics of sampling stations in the northwestern part of the Black Sea

<table>
<thead>
<tr>
<th>Stn</th>
<th>Area</th>
<th>Location Latitude</th>
<th>Location Longitude</th>
<th>Depth (m)</th>
<th>Oxygen (µM)</th>
<th>Temp (°C)</th>
<th>Org. C (%)</th>
<th>Total S (µmol g⁻¹)</th>
<th>Total Fe (µmol g⁻¹)</th>
<th>SCOC (mmol O₂ m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Delta</td>
<td>46°03'N 30°29'E</td>
<td>13</td>
<td>350</td>
<td>8.4</td>
<td>0.64</td>
<td>72</td>
<td>202</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Delta</td>
<td>45°12'N 29°51'E</td>
<td>26</td>
<td>207</td>
<td>6.5</td>
<td>2.15</td>
<td>244</td>
<td>807</td>
<td>37.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Central shelf</td>
<td>43°45'N 28°48'E</td>
<td>52</td>
<td>285</td>
<td>6.8</td>
<td>0.84</td>
<td>70</td>
<td>205</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Central shelf</td>
<td>45°10'N 31°03'E</td>
<td>54</td>
<td>314†</td>
<td>5.5†</td>
<td>2.78</td>
<td>46</td>
<td>123</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Central shelf</td>
<td>44°34'N 29°46'E</td>
<td>57</td>
<td>243</td>
<td>6.6</td>
<td>1.71</td>
<td>194</td>
<td>504</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Central shelf</td>
<td>44°18'N 30°05'E</td>
<td>72</td>
<td>284</td>
<td>6.6</td>
<td>2.93</td>
<td>115</td>
<td>200</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Shelf edge</td>
<td>44°29'N 31°00'E</td>
<td>120</td>
<td>126†</td>
<td>7.7</td>
<td>2.53</td>
<td>200</td>
<td>486</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Shelf edge</td>
<td>44°00'N 30°29'E</td>
<td>137</td>
<td>190†</td>
<td>7.5</td>
<td>1.56</td>
<td>164</td>
<td>368</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Deep-sea</td>
<td>43°18'N 31°02'E</td>
<td>1494</td>
<td>0</td>
<td>9</td>
<td>4.64</td>
<td>488</td>
<td>298</td>
<td>n.d§</td>
<td></td>
</tr>
</tbody>
</table>

* Upper 16 cm of the sediment
† Measured in the bottom water from the box-corer
§ Not determined

6 in the southern part of the central shelf is less influenced by the Danube river. Stations 19 and 24 were positioned at the shelf-edge, near the interface between oxic and anoxic bottom water. Station 22 was located in the anoxic deep-sea at a depth of 1494 m. Sediment was sampled at all stations using a Reineck box-corer (60 × 30 × 30 cm).
Pore water collection and analysis

Sediment cores were sub-sampled from the box-corer using Plexiglas core tubes (10.3 cm i.d., 50 cm length) and closed with rubber stoppers. The cores were transferred into a $N_2$ gas filled glove box ($O_2$ concentration < 500 ppm) through an air lock at the bottom of the box and sectioned in various intervals (0–0.5, 0.5–1, 1–2, 2–3, 3–4, 4–5, 5–7, 7–9, 9–11, 14–16, 19–21, 24–26 and 29–31 cm). Pore water was obtained by squeezing over a 0.45 µm filter using manually operated Teflon squeezers at a maximum pressure of 1 bar $N_2$ gas inside the glove box. A sub-sample of 1 ml pore water was collected and preserved in anoxic $Zn(Ac)_2$ (50 µl; 1M) for $H_2S$ determination (Cline, 1969) and stored frozen until analysis. Another sub-sample of 3 ml was acidified with $H_2SO_4$ (100 µl; 7 N) and analyzed within one month for total dissolved iron concentration using a graphite furnace atomic absorption spectrometer with Zeeman background correction. Some complexed Fe(III) may contribute to the measured concentration of total dissolved iron. $SO_4^{2-}$ concentration was measured spectrophotometrically in the remainder of the pore water using an autoanalyzer.

Solid phase analysis

The solid residues that remained after squeezing were put into diffusion-free bags and stored frozen for solid phase iron and sulfur analysis. All further processing of these solid residue samples were performed in a Coy anaerobic chamber (Coy Laboratory Products, Ann Arbor, Michigan) to prevent oxidation. The anaerobic chamber was filled with a mixture of $H_2$ gas (5 %) and $N_2$ gas (95 %). Any traces of oxygen were consequently removed by reaction with $H_2$ gas on a palladium catalyst. The oxygen concentration in the chamber was always less than 0.5 ppm.

Acid volatile sulfides (AVS), which include iron monosulfides ($FeS$) and dissolved hydrogen sulfide, were extracted from 0.5 g homogenized wet sediment samples by means of cold acid distillation (Fossing and Jørgensen, 1989) for 2 hours in deoxygenated $HCl$ (10 ml, 6 N). The liberated sulfide was stripped from the solution with $N_2$ gas and trapped in 10 ml deoxygenated $Zn(Ac)_2$ (0.1 M). At the end of the distillation, the $ZnS$ concentration in the traps was measured using the methylene blue method (Cline, 1969).

For pyrite determination 2–3 g wet sediment was dried 3 days in a hood at 40°C to oxidize the AVS to elemental sulfur (Henneke et al., 1991; Passier et al., 1999) and ground by pestle and mortar. The elemental sulfur produced by AVS oxidation, together with the elemental sulfur originally present in the sediment were removed by double extraction with acetone (Passier et al., 1996). Pyrite was determined using the Cr(II) reduction method (Zhabina and Volkov, 1978; Canfield et al., 1986; Fossing and Jørgensen, 1989). About 10 mg of the dry, acetone-extracted sediment was digested in 16 ml of 1 M $Cr^{2+}$ in 0.5 N $HCl$ and 8 ml 12 N anoxic $HCl$. Hydrogen sulfide that evolved was quantified as for AVS. Additionally for pyrite sulfur isotope analysis ($\delta^{34}S_{pyrite}$), about 0.2 g acetone extracted sediment was exposed to a cold chromium reduction. The evolved hydrogen sulfide was trapped in $Zn(Ac)_2$ and subsequently converted to $Ag_2S$ by addition of a slight excess of $AgNO_3$. The $Ag_2S$ was collected on 0.45 µm filters, carefully washed and dried. The sulfur isotopic compositions was measured by means of combustion isotope–ratio–monitoring mass spectrometry (C–irmMS) using a Carlo Erba elemental analyzer connected to a Finnigan MAT 252 gas isotope mass spectrometer via a Finnigan Conflo II split
interface (Böttcher et al., 1998b). $^{34}\text{S}/^{32}\text{S}$ ratios are expressed in the $\delta$–notation relative to the Vienna Canyon Diablo Troilite (V–CDT) standard.

Sub-samples of 1 g wet sediment were extracted for elemental sulfur ($S_0$) determination. First, the samples were rinsed with anoxic sodium chloride (0.5 M) to remove the residual pore water sulfate. Then elemental sulfur was extracted twice with deoxygenated methanol. The methanol mixture was analyzed for elemental sulfur by means of reverse-phase HPLC (Henneke et al., 1997). Total sulfur content of the sediment was determined on dried and homogenized samples with a Carlo Erba NA 1500 elemental analyzer using vanadium pentoxide as catalyst to ensure complete oxidation.

Dithionite extractable iron (FeD) was determined by adding 0.5 to 1 g wet sediment to 10 ml dithionite (sodium dithionite 50 g l$^{-1}$ in 0.2 M sodium citrate / 0.35 M acetic acid; $pH = 4.8$) in 20 ml glass vials (Kostka and Luther, 1994). Samples were vortex mixed and placed on a rotary shaker for two hours. After extraction, the samples were filtered over a 0.45 µm filter and stored for 1 day to oxidize the dithionite and sulfite (Canfield et al., 1993b). The extracted iron was determined by the injection of 50 µl solution into 5 ml reducing HEPES (12 g HEPES plus 20 ml hydroxylamine (10 g / 100 ml) per l, $pH = 7.0$). After 30 minutes 300 µl Ferrozine (5 g l$^{-1}$) was added and iron was determined spectrophotometrically after a minimum of 3 hours for complete color development (Stookey, 1970; Canfield et al., 1993b). Dithionite was expected to extract both poorly and well-crystallized iron oxides (except magnetite), AVS, iron-containing carbonates and iron adsorbed onto sediment particles (Canfield, 1988, Canfield et al., 1993b). Additionally there may be a small contribution of iron from silicate minerals. Porosity of the solid residue was calculated from water contents (weight loss on drying 105 °C) assuming a sediment dry density of 2.55 g cm$^{-3}$.

Sediment community oxygen consumption (SCOC)

Oxygen fluxes across the sediment water interface were measured by shipboard core incubations. Two Plexiglas core tubes (10.3 cm i.d.; 30 cm length) were sub-sampled from the box-corer and sealed with a lid containing a YSI 5739 oxygen electrode and a Teflon coated magnetic stirrer. The cores were incubated in the dark in a thermo stated bath at in situ temperature for 4 to 8 hrs. SCOC was calculated by linear regression of the oxygen concentration of the overlying water versus incubation time. A more detailed description of the flux chamber measurements is given by Wijsman et al. (1999).

Results

Sulfur and iron species inventory

Depth-integrated data for the various sulfur fractions (AVS, pyrite, sulfate and others) and dithionite extractable iron (FeD) are presented in figure 5.2. The stations are ordered with respect to a decreasing SCOC (Table 5.1), which is an indicator for the depth-integrated rate of carbon mineralization in sediments (Heip et al., 1995). For each station, the data are integrated over the upper 16 cm of the sediment column,
Figure 5.2. Distribution of various sulfur species (stacked bars) and dithionite extractable iron (line graph) integrated over the upper 16 cm of the sediment. Others represent total sulfur minus AVS, pyrite and pore water sulfur (SO$_4^{2-}$ and H$_2$S), and include elemental sulfur. Stations are ordered with a decreasing organic matter loading as implied by the sediment community oxygen consumption which is the maximum depth for which data are available for all stations. Pyrite sulfur was the major sulfur phase at all stations accounting on average for 67% of the total sulfur pool. Highest contents were found at the central shelf station 9 (11.6 mole S m$^{-2}$), the stations 19 and 24 near the oxic anoxic interface (11.6 and 12.1 mole S m$^{-2}$, respectively) and at the deep-sea station 22 (11.5 mole S m$^{-2}$). AVS contents were highest in the active stations (2 and 13) in front of the rivers Danube and Dniester (5.3 and 2.1 mole S m$^{-2}$, respectively) and decreased offshore. This is in agreement with previous observations of high AVS concentrations in sediments with high deposition rates (Middelburg, 1991; Kostka and Luther, 1994; Gagnon et al., 1995; Lyons, 1997). Pore water SO$_4^{2-}$ ranged from 1.1 mole S m$^{-2}$ at station 13 to 2.5 mole S m$^{-2}$ at station 22, which is partly due to differences in porosity. The low SO$_4^{2-}$ concentrations at the coastal stations 2 and 13 are caused by the low salinity in this area and sulfate reduction within the sediment. The sulfur fraction indicated by ‘Others’ is calculated by difference from the total sulfur content and pyrite, AVS and SO$_4^{2-}$. Due to analytical uncertainty and propagation of errors this resulted in negative concentrations at stations 6 and 16 (-0.26 and -0.04 mole S m$^{-2}$, respectively). The fraction of elemental sulfur was always less than 1.5% of the total sulfur content and was assigned to ‘Others’. Dithionite extractable iron (FeD) includes oxidized forms of iron that are available for iron reduction and iron in the form of AVS. FeD was highest in the coastal stations (2, 13 and 6) and decreased offshore. Remarkably high
FeD concentrations were found at stations 19, which was located near the oxic/anoxic interface.

### Down core distribution of sulfur and iron species

The pore water profiles of the active river delta sediments (Stations 2 and 13) showed a clear decrease in $SO_4^{2-}$ from 15 mM near the sediment-water interface to 10 and 2 mM at 25 cm depth, respectively (Figure 5.3). At both stations, the decline was strongest at depths more than 10 cm. This decrease in $SO_4^{2-}$ concentration with depth in the sediment suggests relatively high rates of sulfate reduction at these stations (Klump and Martens, 1989). In spite of these high sulfate reduction rates no free sulfide was observed in the pore water. This is probably caused by the presence of excess reactive iron in these sediments that is able to react with free sulfide to form iron sulfides (Chapter 6 of this thesis). The concentrations of AVS in these delta sediments were relatively high (up to 153 and 54 µmole S g$^{-1}$ for stations 2 and 13, respectively). The AVS remained high at greater depth in the sediment and were not converted into pyrite. Due to oxidation, the AVS concentrations near the sediment-water interface were very low at both stations. Relatively high amounts of pyrite were observed near the sediment-water interface of both stations. At these coastal stations with a relatively high biomass of deposit feeders (Wijsman et al., 1999) pyrite can be transported from the deeper sediment layers to the sediment-water interface. Since pyrite is less vulnerable to oxidation than AVS, it will not be completely oxidized. A remarkable feature in the pyrite profiles at stations 2 and 13 was the abrupt decrease at

![Figure 5.3](image-url)

**Figure 5.3.** Concentration versus depth profiles of AVS, pyrite, $S^0$, dissolved iron ($Fe_{(aq)}$), $SO_4^{2-}$, $\Sigma H_2S$ and dithionite extractable iron (FeD) for stations 2 and 13 located in front of river deltas.
depths of 15 and 20 cm, respectively. Since it is not likely that pyrite is oxidized at these depths, we suggest this decrease reflects a non-steady state deposition. Moreover, the dissolved iron and FeD profiles show that reactive iron oxides were still present at these sediment depths.

The straight profiles of sulfate that were observed at the central shelf stations (Figure 5.4) indicate that the net sulfate reduction (i.e. sulfate reduction - sulfide oxidation) was low compared to the delta stations. Also sulfide was below the detection limit (< 1 µM). The profiles of $S^0$, AVS and pyrite display classical patterns for coastal sediments. The AVS profiles are characterized by a subsurface peak at a depth of 2 to 5 cm, which is the depth where FeS is formed through the reaction of sulfide with reactive iron. In the more oxidized conditions near the sediment-water interface AVS is consumed by oxidation which is reflected by a peak in $S^0$. At greater depth in the sediments, FeS reacts further to pyrite. As a result the pyrite concentration increased asymptotically from a depth of about 2 to 5 cm. The strong decrease of dithionite extractable iron in the upper part of the sediment suggests a high activity of iron reduction at this depth. However, this is not reflected in a clear peak in dissolved iron. Dissolved iron produced by iron reduction was likely removed by secondary reactions such as iron sulfide formation and iron oxidation.

The profiles of dithionite extractable iron were very different between the two stations located near the oxic/anoxic interface (Figure 5.5). Station 19 (120 m) showed a distinct peak in FeD at the sediment-water interface of more than 300 µmole Fe g$^{-1}$, while this peak was absent at the slightly deeper station 24 (137 m). Apparently dissolved iron that is produced by iron reduction was efficiently oxidized at or near the sediment-water interface of station 19, while at station 24 iron was probably lost from the sediments by diffusion into the water column. The uniform distribution of sulfate concentration with sediment depth and the absence of free sulfide in the pore water suggest that the net effect of sulfate reduction was relatively limited in this area. This is confirmed by the low respiration rates at these stations (Table 5.1). The pyrite profiles corresponded to the profiles observed at the central shelf stations, with an asymptotic increase from < 15 µmole S g$^{-1}$ in the upper 5 cm to a maximum value of 200 to 300 µmole S g$^{-1}$ at depths of more than 10 cm. AVS concentrations at these stations were very low (< 3 µmole S g$^{-1}$) and increased with depth in the sediment. The peak in elemental sulfur near the sediment-water interface reflected oxidation of reduced sulfur.

At the deep-sea station 22 H$_2$S was observed in the pore water (Figure 5.6). The decreased concentration near the sediment-water interface is probably an artifact due to oxidation during sampling. The majority of this H$_2$S was probably not produced locally by sedimentary sulfate reduction since there was no sulfate gradient. The sulfide likely originates from the sulfidic water column. In the euxinic Black Sea, pyrite is formed in the upper part of the water column through the reaction of reactive iron with sulfide (Goldhaber and Kaplan, 1974; Leventhal, 1983; Calvert and Karlin, 1991). As a result all reactive iron is converted to AVS and pyrite before reaching the sediments. Consequently the dithionite-extractable iron at station 22 was entirely composed of iron sulfides. Although the majority of the iron sulfides reach the sediment in the form of pyrite, there is also a small fraction of FeS reaching the sediment or formed in the sediments. During burial in the sediment this FeS is converted to pyrite.
Figure 5.4. Concentration versus depth profiles of AVS, pyrite, $S^0$, dissolved iron ($Fe_{(aq)}$), $SO_4^{2-}$, $\Sigma H_2S$ and dithionite extractable iron (FeD) for stations 6, 9, 10 and 16 located in central part of the continental shelf.
Figure 5.5. Concentration versus depth profiles of AVS, pyrite, $S^0$, dissolved iron ($Fe_{(aq)}$), $SO_4^{2-}$, $\Sigma H_2S$ and dithionite extractable iron (FeD) for stations 19 and 24 located in at the shelf-edge, near the interface between oxic and anoxic bottom water. Mind the different scales for FeD.

Figure 5.6. Concentration versus depth profiles of AVS, pyrite, $S^0$, dissolved iron ($Fe_{(aq)}$), $SO_4^{2-}$, $\Sigma H_2S$ and dithionite extractable iron (FeD) for the deep-sea station 22.
CHAPTER 5

Sulfur isotopic composition of sedimentary pyrite

Since only minor isotope fractionation seems to occur during the reaction of $H_2S$ with iron compounds to form pyrite (Price and Shieh, 1979), the isotopic composition of pyrite at a certain depth in the sediment can be used as a proxy for the $\delta^{34}S$ of $H_2S$. Heaviest $\delta^{34}S$ values (-13.7 ‰; $\sigma = 4.6 ‰$) were observed at station 2 in front of the Danube delta (Figure 5.7). Assuming an isotopic composition for dissolved sulfate of about +19 ‰ (Sweeney and Kaplan, 1980) for the near bottom water at the continental shelf, this corresponds to an apparent isotopic fractionation of about -32 ‰. At the central shelf stations (9 and 10) the $\delta^{34}S$ values of pyrite were much lower (-46.3 ‰ to -38.5 ‰), resulting in apparent isotope fractionation between -57 ‰ and -65 ‰. At station 9, pyrite became slightly enriched in $^{34}S$ towards the sediment water interface. The isotope values in the upper 10 cm of station 24, located near the interface between oxic and anoxic bottom waters, correspond to those observed in the central shelf stations. At greater depth pyrite became rapidly heavier up to -5.8 ‰ at 25 cm depth. The $\delta^{34}S$ values at the deep-sea station 22 ranged from -37.0 to -38.9 ‰. This is similar to previous data reported for Unit 1 sediments in the Black Sea (Table 5.2) and corresponds to $\delta^{34}S$ values between of -35 to -40 ‰ that are reported for $H_2S$ near the chemocline (Fry et al., 1991; Lyons, 1997) or in the deeper part of the anoxic water column (Neretin et al., 1998), as well as pore water $H_2S$ from deep-sea sediments (Neretin et al., 2000). The isotopic composition of pyrite corresponds to an apparent isotopic enrichment factor of about -57 ‰.

Discussion

Down core distribution of iron and sulfur species

The presence of large rivers discharging high amounts of suspended solids and nutrients (Popa, 1993) cause clear gradients in sedimentation, organic loading and iron input into the sediments of the northwestern continental shelf. This is also reflected in the depth distribution of the various sulfur and iron fractions in the sediments. The delta area, with sedimentation rates of about 1 cm yr$^{-1}$ (Wijsman et al., 1999) is characterized by relatively high rates of benthic mineralization (Table 5.1). As a result of high sulfate reduction rates, the sulfate concentration decreases with depth in the sediment at both delta stations (2 and 13). The break in sulfate profiles that is observed at a depth of 10 cm at both stations could mark the maximum depth of bio-irrigation in these sediments (Goldhaber et al., 1977). However, we suggest that this break is caused by enhanced rates of sulfate reduction at depths greater than 10 cm. This is supported by the relatively high concentrations of AVS at these depths, which are apparently not (yet) converted to pyrite. According to Boesen and Postma (1988) and Middelburg (1991) preservation of $FeS$ in modern sediments could be attributed to a lack of elemental sulfur, polysulfides or hydrogen sulfide that are necessary to transform $FeS$ to $FeS_2$. However, this does not seem to be the case at these stations, where elemental sulfur is observed over the whole measured depth range. Besides the presence of elemental sulfur, polysulfides or hydrogen sulfide, the transformation of $FeS$ to pyrite requires time (Middelburg, 1991). According to Berner (1970) the process occurs on a timescale of years. Apparently pyrite formation in these active sediment layers is not completed yet, which is also reflected in the
abrupt decrease in the pyrite concentrations at 15 cm (Station 2) and 20 cm (Station 13). We suggest that there is an active layer present at a depth of 10 to 20 cm at both delta stations with high rates of sulfate reduction and high concentrations of reactive iron oxides. These sediments have recently been covered with less active sediment with higher pyrite concentration.

In comparison to the Delta stations, the central shelf stations are characterized by lower carbon loading to the sediment, as is reflected in the SCOC (Table 5.1). The depth profiles of the various sulfur and iron fractions show classical patterns that could largely be described by the use of a steady state diagenetic model (Chapter 4 of this thesis). There are exponential decreases in FeD with depth in the upper part of the sediment, subsurface peaks in AVS at depths of 2 to 5 cm, asymptotic increases in pyrite and peaks in $S_0$ at sediment water interfaces due to oxidation. These sulfur and iron profiles were consistent among the stations, but the total amount varies between the stations. The maximal concentrations of AVS at stations 6 and 9 that are located closer to the coast are higher (23.3 µmole S g$^{-1}$ and 17.7 µmole S g$^{-1}$, respectively) than the more offshore stations 10 and 16 (0.6 µmole S g$^{-1}$ and 1.2 µmole S g$^{-1}$, respectively). This difference could partly be explained by differences in carbon loading, but also factors such as the availability of reactive iron and mixing processes by bioturbating and bio-irrigating benthic organisms in the sediment could cause this.
Table 5.2. Compilation of δ\(^{34}\)S data (‰) for sulfur species from the water column, sediment traps and surface sediments of the Black Sea

<table>
<thead>
<tr>
<th>Station</th>
<th>Water depth (m)</th>
<th>Depth</th>
<th>Sulfate</th>
<th>δ(^{34})S (‰)</th>
<th>ΣH(_2)S</th>
<th>S(^{(-+polysulfide)})</th>
<th>S(^{O_{3}^{2-}}) (+SO(_{3}^{2-}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water column</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St.6 396</td>
<td>&gt;324 m</td>
<td></td>
<td></td>
<td>-39.5 to -40.3</td>
<td>-39.7</td>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St.7 1176</td>
<td>&gt;472 m</td>
<td></td>
<td></td>
<td>-38.7 to -39.9</td>
<td>-39.7</td>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1136 2000</td>
<td>0–200 m</td>
<td></td>
<td>+18.5 (σ=0.3)</td>
<td>-39.6 (σ=0.7)</td>
<td>-31.3 to -39.3</td>
<td>-38.5</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>St.8 2045</td>
<td>&gt;475 m</td>
<td></td>
<td>+19.4 (σ=0.7)</td>
<td>-39.4 to -40.1</td>
<td>(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1135 2050</td>
<td>0–200 m</td>
<td></td>
<td>+18.4 (σ=0.2)</td>
<td>-40.1 (σ=0.6)</td>
<td>-38.5</td>
<td>(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BS2–1 2128</td>
<td>0–300 m</td>
<td></td>
<td>+19.6 (σ=0.5)</td>
<td>-40.1 (σ=0.6)</td>
<td>-38.5</td>
<td>(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BS2–2 2130</td>
<td>0–300 m</td>
<td></td>
<td>-41 to -37</td>
<td>-40.5</td>
<td>(3)</td>
<td></td>
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<td></td>
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<tr>
<td>BS2–3 2220</td>
<td>0–300 m</td>
<td></td>
<td>-41 to -35</td>
<td>-40.5</td>
<td>(3)</td>
<td></td>
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</tr>
<tr>
<td>1136 2000</td>
<td>&gt;200 m</td>
<td></td>
<td>+19.4 (σ=0.7)</td>
<td>-39.6 (σ=0.7)</td>
<td>-31.3 to -39.3</td>
<td>-38.5</td>
<td>(1)</td>
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<td>BS2–1 2128</td>
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<td>(3)</td>
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<tr>
<td>BS2–2 2130</td>
<td>&gt;300 m</td>
<td></td>
<td>-41 to -37</td>
<td>-40.5</td>
<td>(3)</td>
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<tr>
<td>BS2–3 2220</td>
<td>&gt;300 m</td>
<td></td>
<td>-41 to -35</td>
<td>-40.5</td>
<td>(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Sediment traps** | | | | | | | | |
| BS2C ~2100 | 1065 m | | -37.6 (σ=1.6) | -32.7 | (4) |
| BSK2S ~2100 | 477 m | | (2) |

| **Sediments** | | | | | | | | |
| Station 26 | 0–21 cm | | -13.7 (σ=4.6) | (5) |
| Station 57 | 2–31 cm | | -42.5 (σ=1.8) | (5) |
| Station 72 | 7–26 cm | | -45.3 (σ=0.7) | (5) |
| Station 24 | 5–26 cm | | -28.6 (σ=17.8) | (5) |
| 198 Slope | >200 m | | -27.6 (σ=1.1) | (6) |
| Shelf **<200 m** | Surface **<200 m** | | +19.6 (σ=1.0) | -30.7 (σ=14.5) | (7) |
| Deep-Sea **>200 m** | Surface **>200 m** | | +20.4 (σ=0.5) | -33.4 (σ=3.3) | (7) |
| St.6 396 | 2–4 cm | | -38.2 (σ=0.6) | (5) |
| St.7 1176 | 2–10 cm | | -38.2 (σ=0.6) | (5) |
| Station 22 | 0–9 cm | | -38.2 (σ=0.6) | (5) |
| 2000 Surface || | -27.0 | (2) |
| 2045 10–18 cm | 10–18 cm | | -40.4 | (1) |
| 2050 Surface || | -27.4 | (2) |
| 9 Unit 1 | Unit 1 | | -33.5 (σ=1.2) | -29.4 (σ=0.1) | (8) |
| 2117 Unit 1 | Unit 1 | | -37.0 (σ=1.1) | -27.3 (σ=0.6) | (8) |
| 2218 Unit 1 | Unit 1 | | (6) |

Data are derived from: (1) (Neretin et al., 2000), (2) (Sweeney and Kaplan, 1980), (3) (Fry et al., 1991), (4) (Muramoto et al., 1991), (5) This study, (6) (Lyons, 1997), (7) (Vaynshteyn et al., 1986) and (8) (Calvert et al., 1996)

* Average value for deep-water (> 300 m) at all 3 stations
† Water sample taken at 500 m depth
§ TIRS: Total reduced inorganic sulfur
# Chromium reducible sulfur fraction (including AVS)
** Surface sediments (0–10 cm). Data averaged for all stations
†† Surface sediments, depth not specified

Wijsman et al. (1999) show that the macrofauna community in the offshore shelf stations are dominated by suspension feeders. Their irrigation activity could result in more oxidized conditions of the sediments.

The organic loading to the sediments at the stations located near the shelf-edge is low compared to the other shelf stations. This is reflected in low concentrations of AVS. The sulfur and iron cycling in these sediments is to a large extent influenced by changes in the oxygen concentration in the near-bottom water, which is highly variable in this region. The shallowest station 19 is dominated by iron reduction. The extremely high concentrations of FeD in the upper part of the sediment column suggest intensive recycling of iron by oxidation reactions. This is clearly not the case at station 24 where FeD concentrations in the upper sediments are two orders of magnitude lower.
magnitude lower. Although the concentration of AVS is low at station 24 (<2.5 µmole S g\(^{-1}\)), it increases with depth in the sediment. This might be related to a recent shift from anoxic to oxic conditions of the near-bottom water. During anoxia, AVS could also exist near the sediment water interface. During the oxic conditions this AVS becomes readily oxidized.

The processes in the water column largely determine the cycling of iron and sulfur in the sediments of the deep-sea station 22. The flux of labile organic matter to these sediments is very low and consequently the rate of sulfate reduction in these sediments is also very low. According to the depth profile of AVS, some of the FeS that is deposited on the sediment is converted to pyrite in the upper centimeters. In normal, non-euxinic sediments, pyrite is formed near the redox boundary through the reaction of FeS with intermediate sulfur species such as elemental sulfur and polysulfides (Berner, 1970; Rickard, 1975). In the euxinic sediments of station 22, it is not likely that intermediate sulfur species are present and pyrite could only be formed through the reaction of FeS with H\(_2\)S (Rickard, 1997a).

**Sulfur isotopic composition of sedimentary pyrite**

In the surface sediments at station 2 in front of the river Danube relatively heavy \(\delta^{34}S\) values (-13.7 ‰; \(\sigma = 4.6 \%e\)) were observed which differ significantly from the compositions at the stations 9, 10, 22, and 24 (Figure 5.7). However, the apparent isotope fractionation is well within the range observed in experiments with pure sulfate-reducing bacteria (Chambers and Trudinger, 1979). Experimental studies have shown that sulfur isotope fractionation decreases with increasing cellular sulfate reduction rate (e.g. Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979). Therefore, the data at station 2 suggest that the cellular rates of microbial sulfate reduction were probably high when compared to the other stations. Additionally, the sediment at station 2 was (partially) closed for bottom water sulfate, as indicated by a decrease in pore water sulfate with depth (Figure 5.3). The pore water profile of the other station in front of a river delta (station 13) shows also a distinct decrease with sediment depth, suggesting that sulfate reduction out competes sulfide oxidation and sulfate resupply by diffusion. In a (partially) closed system, the diffusive transport processes are not sufficient to prevent a depletion of the sulfate pool with depth, resulting in an increase of the \(\delta^{34}S\) value for the remaining sedimentary sulfate pool and consequently of the produced sulfide (Hartmann and Nielsen, 1969). As a result, the apparent isotope fractionation with respect to seawater will decrease. Also the openness of the sediments with respect to sulfide could affect the isotopic composition of the sediment (Jørgensen, 1979). If all sulfide produced by sulfate reduction is trapped as pyrite immediately and buried permanently in the sediments, the system is closed with respect to sulfide. Conversely, if most of the produced sulfide is reoxidized via intermediates to sulfate in the upper sediment layers, the sediment experiences open system diagenesis (Jørgensen, 1979). In general, large apparent isotopic fractionations are often associated with open systems, while small differences in isotopic composition between seawater sulfate and pyrite are an indication for a (partially) closed diagenesis system of sulfur. The isotopic composition of dissolved species may additionally be influenced by preferential diffusion of \(^{32}SO_4^{2-}\) into the sediment (Goldhaber and Kaplan, 1974; Jørgensen, 1979; Chanton and Martens, 1987). Although the diffusion coefficients for \(^{32}SO_4^{2-}\) and \(^{34}SO_4^{2-}\) are almost the same (Trudinger, pers. communication in Jørgensen, 1979; Piel and Böttcher, unpublished experimental data), the concentration gradient of \(^{32}SO_4^{2-}\)
could be higher due to the preferential microbial consumption of $^{32}\text{SO}_4^{2-}$ in the sediments. The same could apply for the diffusion of dissolved sulfide into the water column when dissolved sulfide accumulates at the sediment water interface (Chanton and Martens, 1987; Chanton et al., 1987).

Several factors could cause the (partial) closed diagenesis system for sulfur at the coastal stations. Since the rivers discharge large amounts of suspended solids, the sedimentation rates are supposed to be high in this area. These high deposition rates could restrict the exchange of sulfate with the water column. Also high sulfate reduction rates in the sediments of these coastal stations could reduce the openness of the system for sulfate. The relatively high SCOC rates recorded at stations 2 and 13 (37.9 and 26.3 mmole O$_2$ m$^{-2}$ d$^{-1}$, respectively) suggest a high sulfate reduction activity in these sediments. Finally, the availability of large amounts of reactive iron in these sediments (Chapter 6 of this thesis, Figure 6.2) could partially be responsible for the relatively low apparent isotopic fractionation. The reactive iron will trap most of the produced sulfide in the form of iron sulfides preventing re-oxidation of sulfide after diffusion to the oxidized upper sediment layers. Bioturbating organisms may additionally have influenced the depth variation in the isotopic composition of pyrite.

In the central part of the continental shelf (Stations 9 and 10) the $\delta^{34}\text{S}$ values are very light (-38.5 ‰ to -46.3 ‰). These results are comparable to data from Vaynshteyn et al. (1986), who report a value of -45 ‰ in the upper 10 cm of a station located in the southern part of the northwestern continental shelf. Assuming that the $\delta^{34}\text{S}$ value of the sulfate in the near bottom water of the continental shelf is equal to sulfate in the upper 200 meter of the deep-sea (i.e. +19 ‰, Sweeney and Kaplan, 1980), this corresponds to an apparent maximum isotope fractionation of -65 ‰ at the central shelf stations. In an open system, (bio-enhanced) transport processes are faster than the microbial rate of sulfate reduction (Jørgensen, 1979; Chanton et al., 1987). As a result, the sulfate concentration in the sediment will not decrease and its isotopic composition will not change due to sulfate reduction. In such an open system, the apparent and instantaneous isotope fractionations coincide. The light isotopic values at stations 9 and 10 and the more or less constant concentrations of sulfate with depth, therefore, indicate that the sediments were open with respect to sulfate. The abundance of bio-irrigating benthic fauna in this area (Wijsman et al., 1999) might have enhanced the openness of these sediments for sulfate due to enhanced sulfate supply and enhanced re-oxidation. The magnitude of isotopic fractionation at stations 9 and 10, however, is extremely high when compared to the results of experimental studies. Laboratory experiments with pure-cultures of sulfate-reducing bacteria yielded isotope enrichment factors up to a maximum of -46 ‰ (Kaplan and Rittenberg, 1964). This indicates that isotope discrimination was not only controlled by microbial sulfate reduction alone and additional processes may have contributed to the observed overall isotopic effect. Reoxidation of H$_2$S leads to the formation of sulfur species with intermediate oxidation states, as elemental sulfur and thiosulfate (Zhang and Millero, 1993). Whereas only minor isotope fractionation seems to occur during oxidation of H$_2$S (Fry et al., 1986), the microbial disproportionation of the sulfur intermediate has experimentally been shown to produce isotopically light H$_2$S (Canfield and Thamdrup, 1994; Cypionka et al., 1998), therefore, increasing the overall isotope discrimination between sulfate and H$_2$S. In sediments that are open to the supply of oxidants, repetitive cycles of sulfate reduction, oxidation and disproportionation have been suggested to result in progressively lighter isotopic sulfur values (Canfield and Thamdrup, 1994).
A significant variability with a steep down core increase in the $\delta^{34}S$ values was observed in the depth profile of station 24 (Figure 5.7). This trend is in agreement with data of Vaynshteyn et al. (1986) for shelf sediments near the oxic/anoxic interface. At present, there is no indication for a limited supply of dissolved sulfate and a related “reservoir effect” (Jørgensen, 1979) on the isotopic composition of pyrite because the sulfate concentrations remained nearly constant with depth (Figure 5.5). We, therefore, suggest that the observed increase in $\delta^{34}S$ values has to be attributed to a non-steady state process where the system was essentially closed in a previous period. Possibly a high carbon input or a high sedimentation rate in the past had restricted the diffusion of sulfate into the sediments. However, there is no indication for an abrupt decrease in sedimentation rate and/or carbon flux to the sediment in this area in a previous period. Also a switch between oxic and anoxic conditions of the near bottom water could affect the openness of the system for sulfate. At low oxygen and anoxic conditions re-oxidation of reduced sulfide, hence sulfate resupply in the sediment is low, enhancing the closed behavior of the system and limiting the substrate for the activity of disproportionating bacteria. Moreover, anoxic conditions could reduce the bio-irrigation activity of the benthic fauna, decreasing the openness of the system for sulfate (Jørgensen, 1979; Chanton and Martens, 1987). It is possible that as a result of the long-term fluctuations of the oxic/anoxic interface (Lyons et al., 1993) the bottom water at this station has recently changed from anoxic to oxic, which caused more depleted $\delta^{34}S$ values in the upper part of the sediment column. As discussed in the previous section, the AVS profile at station 24 also indicates a recent change from anoxic to oxic conditions of the near bottom water at this station.

Isotope results for pyrite in sediments from the deep-sea station 22 are light (-37.0 to -38.9 ‰) and compare well with the results of previous studies on deep-sea surface sediments of the Black Sea (Table 5.2). They are similar to the isotopic composition of $H_2S$ near the chemocline or close to the sediment-water interface (Table 5.2; Sweeney and Kaplan, 1980; Fry et al., 1991; Neretin et al., 1998; Neretin et al., 2000) and pore waters of deep-sea surface sediments (Neretin et al., 2000). It has previously been argued that the isotopic composition of deep-sea sediments is indicative for pyrite formation in the water column. From the compiled data for deepwater column and pore water $H_2S$ in Table 5.2, however, it is obvious that part of the pyrite may also form in the surface sediments of the deep-sea, in agreement with balance calculations by Neretin et al. (2000). Data on suspended particle composition in the anoxic water column (Cutter and Kluckhohn, 1999) indicate that significant concentrations of FeS and greigite are present in the near bottom water of the deepsea. These components could act as an iron source for pyrite formation at these depths. The extremely light $\delta^{34}S$ values of $H_2S$ in the anoxic water column have been attributed to internal recycling of sulfur (Canfield and Thamdrup, 1994). Elemental sulfur that is extensively formed by oxidation of hydrogen sulfide near the chemocline (Jørgensen et al., 1991; Luther et al., 1991), settles through the water column where it might be subjected to bacterial disproportionation, resulting in more negative values of the reduced sulfur pool (Canfield and Thamdrup, 1994). Unfortunately, there are only very limited isotope data available for sulfur intermediates from the anoxic water column (Neretin et al., 1998; Neretin et al., 2000) and no measurements have been done on samples from the chemocline, yet. Sulfur intermediates as elemental sulfur and thiosulfate seem to follow closely the isotopic composition of $H_2S$ (Table 5.2), indicating isotope exchange reactions to occur. The trend in $S^0$ may additionally be explained by microbial reduction with depth (Kaplan and Rittenberg, 1964; Böttcher
and Surkov, unpublished experimental data). A comparison of the concentrations of \( H_2S \) and coexisting \( S^0 \) (Neretin et al., 2000), indicating that in the deeper part of the anoxic water column hydrogen sulfide should control the isotopic composition of elemental sulfur by isotope exchange reactions via polysulfides and not vice versa. The present study demonstrates that pyrite which is extremely enriched in \(^{32}S\) can be found in the Black Sea surface sediments which are positioned both above and below the chemocline, in spite of different biogeochemical and microbial controlling factors.

The upper slope sediments are a major source for the turbidite mud layers that are observed in the abyssal plane of the Black Sea (Lyons, 1997). During earth quake-related events, \( FeS \)-rich upper slope sediments can be transported to the deep-sea where the \( FeS \) may react with the \( H_2S \) present in the near bottom water to pyrite. According to the model of Lyons (1997) \( \delta^{34}S \) values of turbidite sediments are therefore determined by both the concentration and isotopic composition of the \( FeS \) and pyrite in the upper slope sediments and the \( \delta^{34}S \)-value of \( H_2S \) in the deep anoxic water (Fry et al., 1991; Neretin et al., 1998). In the model of Lyons (1997), the upper slope muds were assumed to be relatively constant in contents and \( \delta^{34}S \) values of AVS (152 \( \mu mol \ S \ g^{-1}; -25.0 \% \)) and pyrite (90 \( \mu mol \ S \ g^{-1}; -27.6 \% \)).

In contrast, the present study demonstrates that shelf and upper slope sediments in the Black Sea are highly variable in AVS and pyrite contents and sulfur isotopic compositions. Differences in carbon load and oxygen conditions in the overlying bottom water on the shelf are the major causes for these variations. Even the upper slope sediments vary not only in AVS and pyrite concentrations but also in \( \delta^{34}S \)-composition. This is mainly caused by variations in redox conditions of the bottom water overlying these upper slope sediments. Since it is most likely that the turbidite mud layers originate from those upper slope sediments, their isotopic composition is expected to be variable and largely determined by the oxygen conditions in the area where the turbidite originate from and cannot be assumed to be constant.