

Sulfur isotope geochemistry of the Black Sea water column

Lev N. Neretin^{a,*}, Michael E. Böttcher^a, Vladimir A. Grinenko^b

^aDepartment of Biogeochemistry, Max Planck Institute for Marine Microbiology, Celsiusstrasse, 1, D-28359 Bremen, Germany

^bV.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Kosygina st., 19, 117975 Moscow, Russia

Received 17 December 2001; accepted 28 March 2003

Abstract

We studied the isotopic composition of dissolved sulfide in the Black Sea water column during different seasons at a total of 15 stations spanning the entire basin. The isotopic composition of dissolved sulfide averaged over all depths varies between -42.0‰ and -32.6‰ , ave. $-39.6 \pm 1.3\text{‰}$ (1σ) (118 data points). Seasonal and spatial (open sea vs. coastal stations) differences in the $\delta^{34}\text{S}\text{-H}_2\text{S}$ values are not observed. Slight ^{34}S enrichments in the sulfide isotope composition are revealed in the uppermost and the lowest parts of the anoxic water column. The upper trend is explained as (i) the effect of mixing with ^{34}S -enriched sulfide produced near the interface by chemical oxidation with MnO_2 or O_2 , (ii) small fractionation during biological sulfide oxidation, (iii) a result of a decreased isotope fractionation factor due to higher sulfate reduction rates. The lower trend is likely the result of the mixing with ^{34}S -enriched pore water sulfide. We generated the first isotope data for sulfur intermediates in the lower part of the anoxic zone, which show values close to the isotope composition of dissolved sulfide. We hypothesize that the high isotope depletions of sulfide observed in the entire Black Sea water column are a result of low sulfate reduction rates and superimposed disproportionation reactions within the oxidative part of the sulfur cycle. Different physical and chemical mechanisms facilitating the formation and transport of sulfur intermediates in the anoxic interior are discussed.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen sulfide; Sulfur isotopes; Black Sea; Water column

1. Introduction

The Black Sea is the largest euxinic water mass on the earth. The average hydrogen sulfide concentration in bottom waters is $368\ \mu\text{M}$ (Neretin et al., 2001). Most of the H_2S in the Black Sea water column originates from bacterially mediated dissimilatory sulfate reduction. Vinogradov et al. (1962), and

recently Neretin et al. (2001), argued that the Black Sea hydrogen sulfide is essentially formed within the water column ($30\text{--}50\ \text{Tg}\ \text{year}^{-1}$), and the upward flux from sediments provides a minor contribution in the total H_2S pool ($3\text{--}5\ \text{Tg}\ \text{year}^{-1}$).

Sulfate-reducing bacteria produce sulfide depleted in ^{34}S compared to the initial sulfate (Kaplan and Rittenberg, 1964). For pure cultures of sulfate-reducing bacteria grown with an excess of sulfate, a broad range of fractionation factors (ϵ) between 2‰ and 47‰ has been measured (Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979; Bolliger et al.,

* Corresponding author. Tel.: +49-421-2028-653; fax: +49-421-2028-690.

E-mail address: lneretin@mpi-bremen.de (L.N. Neretin).

2001; Canfield, 2001; Detmers et al., 2001). Habicht and Canfield (1997) concluded that the specific rate of sulfate reduction per cell determines the ϵ value. Cell-specific sulfate reduction rates are function of temperature, cell size, substrate concentration, type of the electron acceptor and growth phase (Knoblauch et al., 1999; Detmers et al., 2001). However, the availability of organic substrates and the type of carbon metabolism of sulfate-reducing bacteria also have important effects on fractionation factors (Canfield, 2001; Detmers et al., 2001), and ϵ may not always correlate with cell-specific sulfate reduction rates (Detmers et al., 2001). Yet, there is no experimental evidence that pure cultures of sulfate-reducing bacteria can produce fractionation factors higher than 47‰.

The observed isotope difference between dissolved sulfate and sedimentary pyrite in modern and ancient sediments of 51 ± 10 ‰ on average (Canfield and Teske, 1996) commonly extends far beyond the ϵ values reported for pure cultures. Discrepancies between the isotope fractionations observed in culture experiments with sulfate reducers and those observed in nature have been attributed to oxidation processes within the sulfur cycle (Jørgensen, 1990; Canfield and Thamdrup, 1994; Cypionka et al., 1998; Habicht et al., 1998; Böttcher and Thamdrup, 2001; Böttcher et al., 2001). The disproportionation reactions of sulfur intermediates (S^0 , SO_3^- and $S_2O_3^{2-}$) lead to ^{32}S and ^{34}S enrichment in the resulting sulfide and sulfate, respectively. There is an indication that in deep hypersaline subsurface environments the observed extreme isotope differences between sulfates and sulfide (up to 72‰) can be generated during microbial fractionation in a “single-step” without sulfide reoxidation and disproportionation of sulfur intermediates (Wortmann et al., 2001). However, the microorganisms adapted to such extreme environments have so far not been isolated and cultured in isotope discrimination studies. Therefore, at present there is a common view among geochemists that the high isotope differences observed between sulfate and sulfide in natural systems can only be attributed with the reactions associated with the oxidative part of the sulfur cycle—i.e., disproportionation reactions of intermediate sulfur species.

Previous studies show a sulfur isotope difference between sulfate and coexisting sulfide in the Black Sea water of about 60‰ (Vinogradov et al., 1962; Sweeney and Kaplan, 1980; Fry et al., 1991; Neretin

et al., 1996), which is close to the sulfur isotope differences of pore water H_2S and SO_4^{2-} observed in Black Sea Unit I permanently anoxic sediments (Vinogradov et al., 1962; Neretin et al., 2001). Sulfide produced by enrichment cultures of sulfate-reducing bacteria obtained from the Black Sea anoxic water and mud was not more than 34‰ depleted relative to co-existing sulfate (Fry et al., 1991).

The earlier data for the isotope composition of sulfide and sulfate in the Black Sea water column have been obtained mainly in the central part of the basin at selected stations. The isotope data for the Black Sea coastal zone were not previously available. We have undertaken a systematic study to test whether the intensified vertical and horizontal mixing processes between the oxic and anoxic layers in the continental slope area have influenced the isotope composition of sulfide in the water column. We also present here isotope data for the western part of the Black Sea where deep oxygen intrusions via the Lower Bosphorus Current (LBC) occur. Using the previously developed analytical scheme (Volkov and Zhabina, 1990a,b), we report the first results for the isotope composition of sulfur intermediates in the lower part of the anoxic zone below 1400 m and discuss the mechanisms that may have caused high sulfur isotope depletion of the Black Sea water column sulfide.

2. Methods

Samples were collected in the northeastern, eastern and western parts of the Black Sea. The location stations sampled for the isotopic measurements of sulfur species are given in Fig. 1. Most samples for sulfur isotope measurements were prepared as described by Ustinov and Grinenko (1965) and Neretin et al. (1996). As outlined below, we used the method of Volkov and Zhabina (1990a,b), to isolate sulfur species for analytical determinations and the isotope analysis.

Water samples for all measurements were collected using 5 or 10 l Teflon-coated Go Flo bottles (General Oceanics) attached to a PVC-coated stainless steel CTD-rosette. Subsamples for analysis of both H_2S and sulfur intermediates were collected in Erlenmeyer flasks with a suspension of $Zn_2(OH)_2CO_3$ buffered at

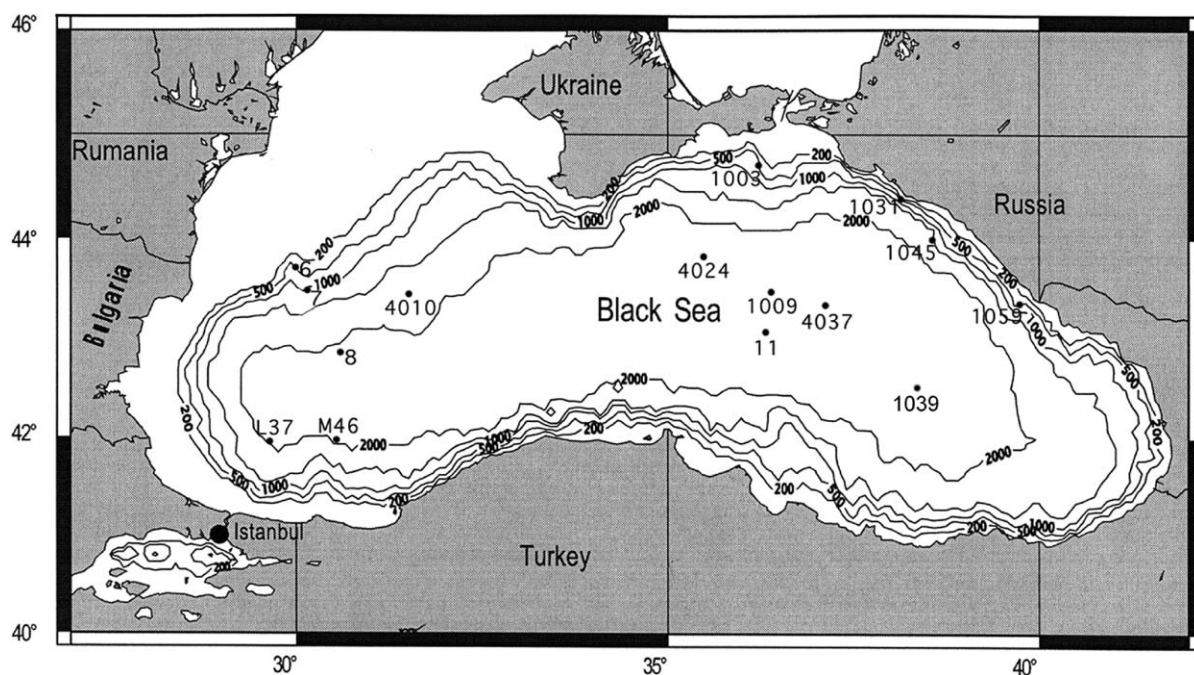
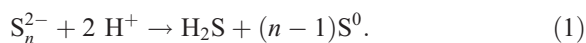


Fig. 1. Stations sampled for the isotope composition of sulfur species (St. 4010 (143), 4024 (141), 4037 (118)—27th cruise R/V “Vityaz”, November 1993; St. 1003 (150), 1009 (120), 1031 (156), 1039 (109), 1045 (170), 1059 (146)—R/V “Akvanavt”, September 1994; St. 11 (110)—R/V “Yantar” June–July 1996; St. M46 (n.d.), L37 (n.d.)—R/V “Bilim”, July 1997; St. 6 (155), 7 (~ 100), 8 (~ 90)—R/V “Petr Kotzov”, September 1997). The depths of the upper anoxic boundary are given after the station number in parentheses.

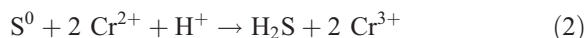
a pH above neutral or with Zn acetate for only H_2S analysis. Before sampling started, each flask was flushed with an argon gas. During sampling, the pump flow from the rosette bottle was adjusted to prevent oxidation due to bubbles. A summary of the analytical protocol is presented in Fig. 2. Using these procedures, polysulfides, S_n^{2-} ($n=2-7$) precipitate together with S^0 and H_2S by the Zn carbonate suspension. Sulfate, thiosulfate, sulfite and polythionates in the supernatant were separated by filtration through 0.45 μm HA Millipore filter. Sulfur distillations were performed under N_2 flow. The method was calibrated with standard solutions of elemental sulfur in acetone and sodium sulfite and thiosulfate solutions in distilled water. The precision of the original method is $\pm 3-5\%$ and the detection limit is $0.03 \mu\text{mol l}^{-1}$ (Volkov and Zhabina, 1990a,b).

After the initial treatment of the sedimented ZnS with HCl, S_n^{2-} will decompose to H_2S and S^0 . Therefore, the sulfane-S atom of polysulfides cannot be

analyzed separately and will be measured together with $\Sigma\text{H}_2\text{S}$:



In contrast, the zero-valent elemental sulfur and the elemental sulfur deriving from polysulfides are not reduced during the acidification but will be reduced using a $\text{CrCl}_2\text{-HCl}$ treatment (Volkov and Zhabina, 1990b):



Therefore, “elemental sulfur” (S^0) data presented here are defined operationally and refer to the sum of original elemental sulfur allotropes (zero-valent sulfur) and the zero-valent sulfur deriving from some fraction ($n-1$) of the original polysulfide S_n^{2-} (reaction 1).

Dissolved S species defined operationally in the text as “ $\text{S}_2\text{O}_3^{2-}$ ” represent the total amount of thio-

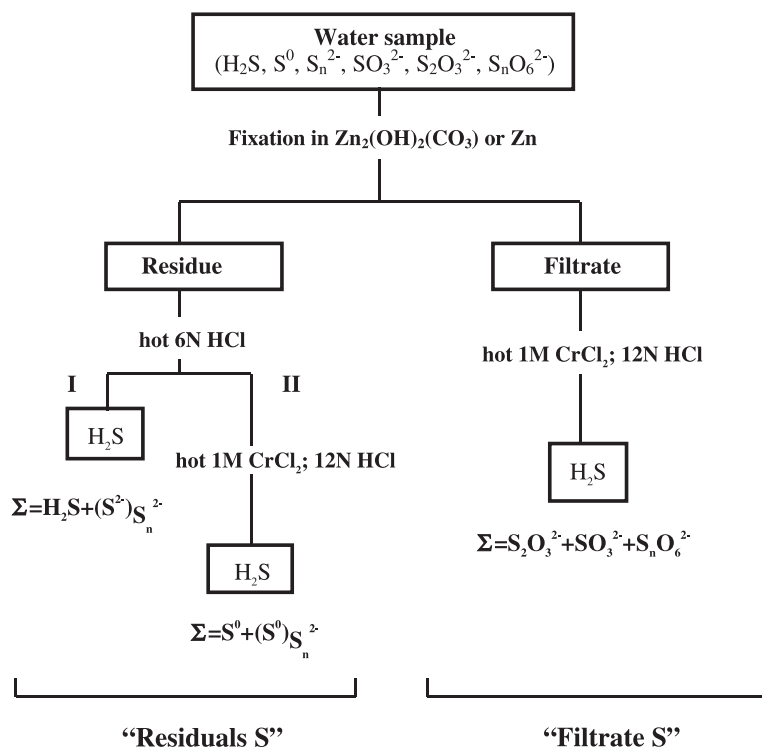
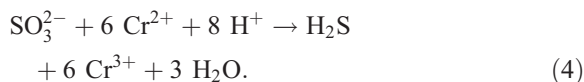
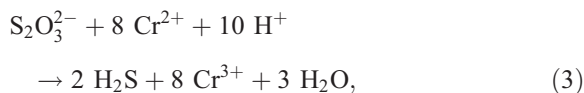


Fig. 2. Flow chart of sulfur species analysis.

sulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}) and polythionates ($\text{S}_n\text{O}_6^{2-}$, $n=2-5$). During the CrCl_2 treatment under acidic conditions, SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ (Volkov and Zhabina, 1990a) and probably $\text{S}_n\text{O}_6^{2-}$ (I. Volkov, personal communication) will be completely reduced to H_2S (Volkov and Zhabina, 1990a):



Sulfide is the product of reactions (1)–(4), which is trapped with Zn acetate and determined for each step by the methylene blue method of Cline (1969).

For the H_2S isotope measurements, evolved sulfide was trapped in 6% (w/v) AgNO_3 as Ag_2S . Apart from Stations 6 to 8, Ag_2S was converted to SO_2 on a vacuum line by reaction with CuO (Ustinov and Grinenko, 1965), and the isotope ratios of SO_2 were

measured by means of a double-collector mass-spectrometer MS-2M. The reproducibility is $\pm 0.5\%$. $^{34}\text{S}/^{32}\text{S}$ values of sulfur species at Stations 6–8 were measured by combustion-isotope-ratio-monitoring mass spectrometry (C-irmMS) using a Carlo Erba EA 1108 elemental analyzer connected to a Finnigan MAT 252 mass spectrometer via a Finnigan MAT Conflo II split interface as described by Böttcher et al. (1998). Reproducibility of the method is $\pm 0.2\%$.

$^{34}\text{S}/^{32}\text{S}$ ratios are reported using the δ notation with respect to the CDT (or Vienna CDT) standard, according to:

$$\delta^{34}\text{S} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{CTD(VCTD)}}} - 1 \right] \cdot 1000\% \quad (5)$$

Besides the data for Stations 6–8, most of our measurements are reported for the earlier used CDT standard. However, the difference between CDT and VCDT standardization scales should not exceed 0.4% (Coplen and Krouse, 1998).

3. Results and discussion

3.1. The isotopic composition of hydrogen sulfide

The sulfur isotope composition of H_2S in the Black Sea water column has been investigated in several studies (Vinogradov et al., 1962; Sweeney and Kaplan, 1980; Fry et al., 1991; Lein and Ivanov, 1991; Neretin et al., 1996). Apart from the study of Vinogradov et al. (1962), results of other authors are generally consistent. In the study of Vinogradov et al. (1962), samples for sulfide isotope composition were not washed thoroughly to remove residual seawater sulfate (V. Grinenko, personal communication). As a result, the dissolved sulfide $\delta^{34}\text{S}$ values of Vinogradov et al. (1962) are about 10‰ higher than the data of other authors.

Samples for $\Sigma\text{H}_2\text{S}$ isotope compositions were collected from a diverse array of settings and spanning different seasons (Fig. 1). The upper boundary of the anoxic zone varied between 90 m (Station 8) and 170 m (Station 1045). In total, 118 measurements of $\delta^{34}\text{S}(\text{H}_2\text{S})$ were performed. The isotope composition of dissolved sulfide in the Black Sea water column varies over a range between -42.0‰ and -32.6‰ , averaging $-39.6 \pm 1.3\text{‰}$ (1σ). These data are in the same range as those reported by Sweeney and Kaplan (1980) and Fry et al. (1991) for five stations in the central Black Sea. The average sulfide isotope compositions determined separately for the coastal and slope stations with water depths above 1800 m and for stations in the central basin are essentially identical (data not shown). We also do not see seasonal trends in our data. Therefore, to correct for differences in the thickness of the sulfidic zone we plotted all our $\delta^{34}\text{S}(\text{H}_2\text{S})$ data vs. H_2S concentration on one graph (Fig. 3). The trends observed in Fig. 3 would be difficult to see in a single plot of $\delta^{34}\text{S}(\text{H}_2\text{S})$ vs. depth, because the isotopic variations in the uppermost part of the sulfide zone occur at different depths. Two trends in the vertical distribution of $\delta^{34}\text{S}(\text{H}_2\text{S})$ are distinguished in Fig. 3 (separated by a dashed line), reflecting slight ^{34}S enrichments in the uppermost and lowest parts of the anoxic water column.

The uppermost trend, also seen in the measurements of Vinogradov et al. (1962) and Sweeney and Kaplan (1980), was investigated by Fry et al. (1991) in detail. Our $\delta^{34}\text{S}(\text{H}_2\text{S})$ vertical profiles for the upper

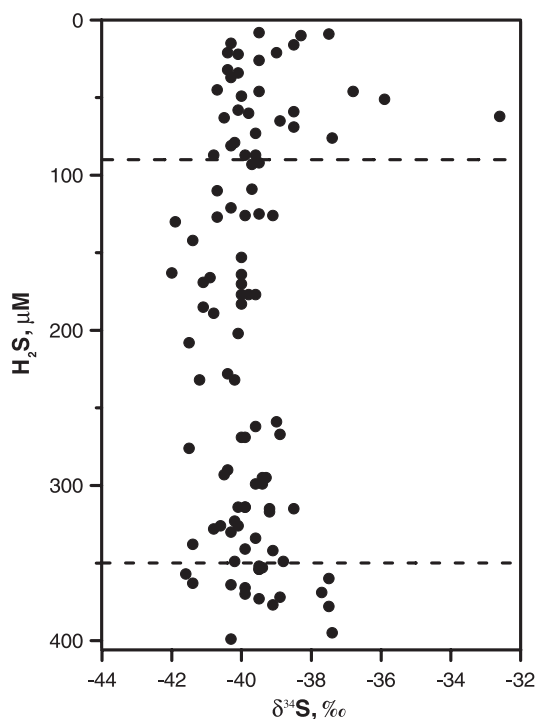


Fig. 3. $\delta^{34}\text{S}(\text{H}_2\text{S}; \text{CDT})$ vs. H_2S concentration in the Black Sea water column ($n=105$). Two dotted lines represent and arbitrarily defined the upper and lower parts of the anoxic zone where tendencies toward isotopically heavier sulfide are observed.

part of the anoxic zone at selected stations are presented in Fig. 4. These stations were located in the continental slope (St. 4010 and 1045) and central regions (St. 4024, 4037, 1039) of the eastern Black Sea. A ^{34}S enrichment in sulfide was generally observed immediately below the chemocline at every station. The isotope compositions vary over a range from -32.6‰ to -40.8‰ in these five profiles. The observed trend was interpreted by Fry et al. (1991) as the effect of mixing with ^{34}S -enriched sulfide produced near the interface by chemical oxidation with metals or O_2 ($\epsilon = -5.2\text{‰}$, Fry et al., 1988) or as a small fractionation during biological sulfide consumption ($\epsilon = -18\text{‰}$ to -1‰ , Kaplan and Rittenberg, 1964), but not during anoxygenic photosynthesis (Fry et al., 1991). Mn oxide reduction by sulfide was proposed to mediate partially sulfide oxidation in the Black Sea (e.g., Millero, 1991; Murray et al., 1995). Experimental results of Böttcher and Thamdrup (2001) indicate that sulfur isotope effects during sulfur dis-

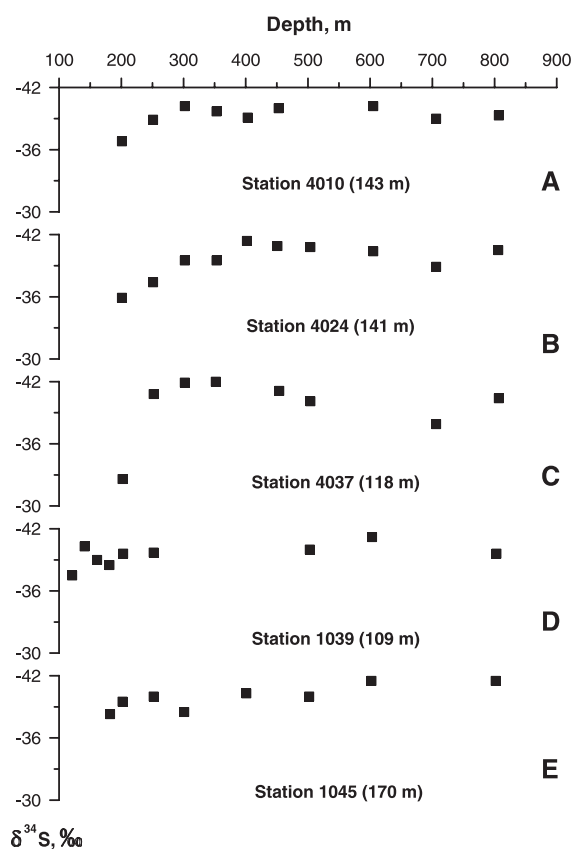


Fig. 4. The vertical distribution of $\delta^{34}\text{S}(\text{H}_2\text{S}; \text{CDT})$ in the upper 800 m of the anoxic zone at the selected stations. The upper sulfide interface is given in parentheses after the station number.

proportionation are much smaller when MnO_2 is present due to the superimposed chemical reoxidation of the resulting H_2S by MnO_2 to sulfate. Sulfide immediately below the interface enriched in ^{34}S may also result from decreased isotope fractionation in these layers due to higher sulfate reduction rates relative to the deeper waters (Albert et al., 1995). Decreased isotope fractionations can also originate from substrate quantity and carbon metabolism of sulfate reducers (Canfield, 2001; Detmers et al., 2001) in the chemocline different from underlying waters.

The lower part of the anoxic zone (below about 1500 m) is also characterized by a relative enrichment of ^{34}S in sulfide. This relationship is not observed at all the sampled stations (three of five stations sampled)

but can be recognized in the data compiled in the scatter plot of H_2S concentration vs. isotopic composition (Fig. 3). The trend can be explained by mixing with ^{34}S -enriched hydrogen sulfide diffused from pore waters or linked to high sulfate reduction rates in the uppermost “fluffy” layer (Albert et al., 1995). The reported isotope composition of dissolved sulfide in sediments is between -16.2‰ and -38.7‰ (ave. $28.4 \pm 10.6\text{‰}$ [1σ]), although only four measurements in surface sediments were reported (Neretin et al., 2001). The sulfur fractionation factor during SR in sediments is probably lower than in the water column because sulfate reduction rates in Black Sea surface sediments are one to three orders of magnitude higher than the rates in the water column (e.g., Albert et al., 1995; Weber et al., 2001).

3.2. The isotopic composition of intermediate sulfur species

In this study, we present for the first time results for the isotopic compositions of intermediate sulfur species from the deeper part of the Black Sea water column (Table 1). The sulfur intermediates have isotopic compositions close to coexisting H_2S , with only slight enrichments in ^{34}S . The average values for $\delta^{34}\text{S}(\text{S}^0)$ and $\delta^{34}\text{S}(\text{S}_2\text{O}_3^{2-})$ are $-36.8 \pm 3.8\text{‰}$ (1σ) ($n=4$) and -38.5‰ ($n=1$), respectively. S^0 and $\text{S}_2\text{O}_3^{2-}$ concentrations do not exceed 1.7 and 6.4 μM , respectively.

S^0 , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} and $\text{S}_n\text{O}_6^{2-}$ are intermediates formed during hydrogen sulfide oxidation (e.g., Cline and Richards, 1969; Jørgensen, 1990; Yao and Millero, 1995). Thiosulfate can also originate from chemically mediated reactions of elemental sulfur (polysulfide) hydrolysis (reaction 6) (Bouleque and Michard, 1979), polythionate disproportionation (reaction 7) and from reactions between elemental sulfur and sulfite (reaction 8) (Goldhaber and Kaplan, 1974; Zhang and Millero, 1994):

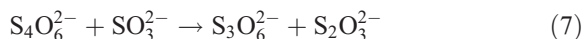


Table 1

Concentration and the isotopic composition of S species (vs. VCDT) in the deep and bottom water of the Black Sea (September 1997; R/V “Petr Kotzov”)

Station	Sampling depth (m)	H ₂ S (+ S ²⁻ (S _n ²⁻))		S ⁰ (+ S ⁰ (S _n ²⁻))		S ₂ O ₃ ²⁻ (+ SO ₃ ²⁻ and S _n O ₆ ²⁻)	
		μmol l ⁻¹	δ ³⁴ S (‰)	μmol l ⁻¹	δ ³⁴ S (‰)	μmol l ⁻¹	δ ³⁴ S (‰)
6 (401)	324	60.3	-39.8	-	-	-	-
	60 cm above bottom	-	-40.3	-	-39.7	-	-
	10 cm above bottom	-	-39.5	-	-	-	-
7 (1204)	472	126	-39.9	-	-	-	-
	945	262	-39.6	-	-	-	-
	1040	295	-39.4	-	-	-	-
	60 cm above bottom	-	-38.7	-	-	-	-
8 (2045)	475	170	-40.0	-	-	-	-
	952	299	-39.4	1.72	-	3.39	-
	1189	326	-40.1	1.53	-	2.43	-
	1422	342	-39.1	1.56	-	6.38	-38.5
	1660	353	-39.4	1.11	-39.3	2.08	-
	1801	357	-	-	-36.8	-	-
	1896	366	-39.9	0.75	-31.3	3.99	-

“-”: not measured.

Station depths are given in parentheses together with their numbers.

Elemental sulfur and thiosulfate can also form below the chemocline by the chemical reaction of sulfide with Mn oxyhydroxides (Yao and Millero, 1995):



There is a lack of information about formation of sulfur intermediates extracellularly during sulfate reduction. Vainshtein et al. (1980) were the first to report formation of sulfite, thiosulfate and polythionate in the growth media of sulfate reducing bacteria. Sass et al. (1992) also observed that cultures of *Desulfovibrio desulfuricans* formed up to 400 μM thiosulfate and 40 μM trithionate during growth in a chemostat under limited electron-donor (H₂) conditions. The study of Brüchert et al. (2001) of sulfur isotope fractionation by psychrophilic sulfate reducers indicates that at low temperatures, about one third of the sulfate pool is not entirely converted into sulfide and can reside in intermediate sulfur species. Therefore, the experimental evidence does not exclude the possibility that sulfur intermediates can originate during sulfate reduction in strictly anoxic conditions.

Considering the predominant H₂S influence on the sulfur cycle in the anoxic water column and the significant excess of hydrogen sulfide compared to the intermediate sulfur species (Table 1), the isotopic

composition of these intermediates in the deeper part of the anoxic water column may also be influenced by isotope exchange reactions with hydrogen sulfide. Experiments with ³⁵S-labeled sulfur compounds demonstrated the isotope exchange between H₂S and S⁰, S_n²⁻, and FeS at pH 7.6 and 20 °C (Fossing and Jørgensen, 1990; Fossing et al., 1992). Theoretical calculations by Thudge and Thode (1950) yielded equilibrium enrichment in ³⁴S of S⁰ relative to H₂S by 3‰ at 25 °C. Experimental data on isotope exchange reactions at low temperatures, however, are unavailable.

An experimental bias in our isotope measurements of sulfur intermediates may be associated with the distillation using Cr(II) chloride. However, the isotope effect during chromium reduction is rather small and has been estimated to a 0.55‰ enrichment in ³⁴S in evolved H₂S compared with the initial pyrite (Newton et al., 1995). Although care was taken during sampling and analysis, we cannot exclude the possibility that measured concentrations of sulfur intermediates are partly caused by oxygen introduced with reagents. Additional data generated stringently under more anaerobic conditions are needed to confirm the results of the present study. However, the sampling scheme for collecting sulfur intermediates for the isotope measurements used in this study can be recommended.

3.3. The sulfur isotope difference in the Black Sea water column

Here we present the largest data set currently available for the isotopic composition of hydrogen sulfide in the Black Sea water column. Our data for $\delta^{34}\text{S}(\text{H}_2\text{S})$, which represent the entire basin unequivocally show uniform values of $-39.6 \pm 0.3\text{‰}$ (99% CI) for the entire Black Sea water column independent of sample location and season. These data corroborate the earlier results of Sweeney and Kaplan (1980) and Fry et al. (1991) for the central Black Sea and confirm the reported isotope difference between sulfide and sulfate of about 60‰. A model involving repeated oxidation–reduction reactions in the sulfur cycle is commonly used to explain the origin of such high isotope differences (Canfield and Teske, 1996). The prerequisite for the model is the existence of continuous supply of inorganic sulfur intermediates (e.g., elemental sulfur, thiosulfate) formed by sulfide oxidation at the oxic/anoxic interfaces.

Sulfur intermediates in the Black Sea water column can originate from the sulfide oxidation in the chemocline but also in the basin interior by sulfide oxidation from dissolved oxygen introduced with the LBC. Sulfide oxidation rates and mechanisms in the Black Sea chemocline have been studied extensively (Sorokin, 1972; Repeta et al., 1989; Jørgensen et al., 1991; Luther et al., 1991) but there is no general agreement on the predominant mechanism(s). The presence of the suboxic ($\text{O}_2 < 5 \mu\text{M}$) nonsulfidic zone 10–40 m above the sulfide interface demands that sulfide oxidation in the Black Sea chemocline is not or at least not entirely mediated by oxygen (Murray et al., 1995). Three main mechanisms independent of O_2 availability were hypothesized: (i) anoxygenic photosynthesis, (ii) sulfide oxidation by metal oxides and (iii) horizontal ventilation of the suboxic zone. Experimental studies have shown that elemental sulfur, sulfite, thiosulfate and sulfate are the main products of chemical sulfide oxidation (Zhang and Millero, 1994). Elemental sulfur can be formed by phototrophic or chemolithotrophic sulfide oxidation (Madigan, 1988; Kelly 1989), whereas elemental sulfur, polysulfides and thiosulfate can originate from reduction of Mn (oxyhydro)oxides by sulfide (Yao and Millero, 1995). Through vertical mixing, these reactions may provide sulfur intermediates into the

anoxic part where they can be further disproportionated.

Recent advances in our understanding of the Black Sea coastal zone, and in particular, of the Rim Current, Cold Intermediate Water (CIW) formation and horizontal transport point to the crucial role of mesoscale eddies in the ventilation of the suboxic zone and the upper part of the anoxic zone (Ovchinnikov et al., 1994; Oguz and Besiktepe, 1999). Oguz et al. (1993) analyzed all the available published hydrographic data up to 1990 and concluded that about nine mesoscale anticyclonic eddies propagate cyclonically around the basin at a given time. In some of the very deep anticyclonic gyres in the western Black Sea, downwelling of the CIW waters can be traced to depths of up to 1000–1200 m (Andrianova and Ovchinnikov, 1991). Overall, the cascade of these mesoscale gyres forming the so-called “near-shore zone of convergence” (Ovchinnikov et al., 1994) provide an efficient mechanism of the ventilation of subpycnocline anoxic waters.

Efficient ventilation of the chemocline and underlying anoxic waters may also occur during severe winter conditions observed with a periodicity of ca. 20 years (Titov, 2000). Under these severe conditions, the location of the upper pycnocline boundary and the sulfide interface in the central Black Sea have been recorded at depths of 2530 and 75–80 m, respectively (Krivosheya et al., 2000). Intensified winter density convection overprinted by internal wave forcing has been proposed as the main factor facilitating the erosion of the upper pycnocline and ventilation of the upper anoxic waters (Krivosheya et al., 2000).

The Lower Bosphorus Current provides another important mechanism for ventilation of anoxic waters and for sulfide oxidation below the interface. Based on their physical and chemical properties, intrusions of oxygen-containing Bosphorus waters can be distinguished down to a 500–600 m water depth (Özsoy et al., 1993). Their role in the total sulfur cycling of the Black Sea is significant. More specifically, up to 10–20% of the total sulfide produced in the anoxic part of the water column can be oxidized by O_2 -containing waters intruding below the interface (Neretin et al., 2001).

Experimental data generated using radiolabeled sulfide demonstrate maximum gross rates of sulfide oxidation within the Black Sea chemocline (e.g.,

Jørgensen et al., 1991). However, a simulation of the average annual vertical distribution of hydrogen sulfide using a one-dimensional model indicates net consumption over the upper 500 m of the anoxic water, which is balanced by sulfide production below 500 m. Most of this amount (78%) is produced between 500 and 950 m (Neretin et al., 2001).

Summarizing, analysis of existing information on the vertical and horizontal dynamics of the Black Sea water column shows that there is a range of known physical processes that can facilitate formation and/or transport of sulfur intermediates down into the anoxic zone (winter mixing, coastal dynamics). In addition, there is an internal source for these species within the interior of the anoxic water column driven by sulfide oxidation from oxygen intrusions with the LBC. We hypothesize that a combination of very low sulfate reduction rates throughout most of the water column ($<< 1 \text{ nM day}^{-1}$, Albert et al., 1995) and efficient mixing mechanisms below the chemocline are the factors that cause high isotope depletion in sulfide observed in the Black Sea water column. Due to strong seasonal and temporal variability of vertical mixing processes, testing the proposed mechanisms experimentally will be difficult to impossible. However, sulfide isotope anomalies should be measurable in the western part of the Black Sea near the Bosphorus, where direct contact between sulfidic and oxygenated waters occurs. Combined hydrophysical and geochemical studies tracing the propagation of LBC water lenses may help to reveal whether the oxidation events in the anoxic interior are crucial for the establishment of the sulfide isotope composition in the water column.

Acknowledgements

A special thanks to T.P. Demidova and N.N. Zhabina (P.P. Shirshov Institute of Oceanology, Moscow) for the extensive analytical help during cruises. Collaboration with the captains and the crews of R/Vs “Akvanavt”, “Yantar” and “Petr Kotzov” is gratefully acknowledged. M.E.B. wishes to thank J. Rullkötter from the Institute of Chemistry and Biology of the Marine Environment (University of Oldenburg, Germany) for the allowance to use the mass spectrometer. We thank Timothy W. Lyons and Hilde F. Passier for constructive and very helpful

reviews of the manuscript and editorial assistance. This work was financially supported by the Max-Planck-Society and the NATO Scientific and Environmental Affairs Division (Collaborative Linkage Grant EST.CLG.977129 for L.N.N.) and the Russian Science Support Foundation (for L.N.N.). [LW]

References

- Albert, D.B., Taylor, G., Martens, C., 1995. Sulfate reduction rates and low molecular weight fatty acid concentrations in the water column and surficial sediments of the Black Sea. *Deep-Sea Res.* 42, 1239–1260.
- Andrianova, O.P., Ovchinnikov, I.M., 1991. Transformation of fresh waters in the western Black Sea. *Meteorol. Gidrol.* 7, 74–79 (in Russian).
- Bolliger, C., Schroth, M.H., Bernasconi, S.M., Kleikemper, J., Zeyer, J., 2001. Sulfur isotope fractionation during microbial sulfate reduction by toluene-degrading bacteria. *Geochim. Cosmochim. Acta* 65, 3289–3298.
- Böttcher, M.E., Thamdrup, B., 2001. Anaerobic sulfide oxidation and stable isotope fractionation associated with bacterial sulfur disproportionation in the presence of MnO_2 . *Geochim. Cosmochim. Acta* 65, 1573–1581.
- Böttcher, M.E., Brumsack, H.-J., de Lange, G.J., 1998. Sulfate reduction and related stable isotope (^{34}S , ^{18}O) variations in interstitial waters of the Eastern Mediterranean. *Proc. Ocean Drill Prog., Sci. Results* 160, 365–373.
- Böttcher, M.E., Thamdrup, B.B., Vennemann, T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochim. Cosmochim. Acta* 65, 1601–1609.
- Bouleque, J., Michard, G., 1979. Sulfur speciations and redox processes in reducing environments. In: Jenne, E.A. (Ed.), *Chemical Modeling in Aqueous Systems*. ACS Symposium Series, vol. 93, pp. 25–50. American Chemical Society, Washington, WA.
- Brüchert, V., Knoblauch, C., Jørgensen, B.B., 2001. Controls on stable sulfur isotope fractionation during bacterial sulfate reduction in Arctic sediments. *Geochim. Cosmochim. Acta* 65, 763–776.
- Canfield, D.E., 2001. Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochim. Cosmochim. Acta* 65, 1117–1124.
- Canfield, D.E., Teske, A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulfur-isotope studies. *Nature* 382, 127–132.
- Canfield, D.E., Thamdrup, B., 1994. The production of ^{34}S -depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* 266, 1973–1975.
- Chambers, L.A., Trudinger, P.A., 1979. Microbiological fractionation of stable sulfur isotopes: a review and critique. *Geomicrobiol. J.* 1, 249–293.
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454–458.

- Cline, J.D., Richards, F.A., 1969. Oxygenation of hydrogen sulphide in sea water at constant salinity, temperature and pH. *Environ. Sci. Technol.* 3, 838–843.
- Coplen, T.B., Krouse, H.R., 1998. Sulphur isotope data inconsistency improved. *Nature* 392, 32.
- Cypionka, H., Smock, A.M., Böttcher, M.E., 1998. A combined pathway of sulfur compound disproportionation in *Desulfovibrio desulfuricans*. *FEMS Microbiol. Lett.* 166, 181–186.
- Detmers, J., Brüchert, V., Habicht, K., Küver, J., 2001. Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes. *Appl. Environ. Microbiol.* 67, 888–894.
- Fossing, H., Jørgensen, B.B., 1990. Isotope exchange reactions with radiolabeled sulfur compounds in anoxic seawater. *Biogeochemistry* 9, 223–245.
- Fossing, H., Thode-Anderson, S., Jørgensen, B.B., 1992. Sulfur isotope exchange between ^{35}S -labeled inorganic sulfur compounds in anoxic marine sediments. *Mar. Chem.* 38, 117–132.
- Fry, B., Ruf, W., Gest, H., Hayes, J.M., 1988. Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chem. Geol.* 73, 205–210.
- Fry, B., Jannasch, H.W., Molyneux, S.J., Wirsén, C., Muramoto, J., King, S., 1991. Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench. *Deep-Sea Res.*, II 38, S1003–S1019.
- Habicht, K.S., Canfield, D.E., 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochim. Cosmochim. Acta* 61, 5351–5361.
- Habicht, K.S., Canfield, D.E., Rethemeier, J., 1998. Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochim. Cosmochim. Acta* 62, 2585–2595.
- Goldhaber, M.B., Kaplan, I.R., 1974. The sulfur cycle. In: Goldberg, E.D. (Ed.), *The Sea*, vol. 5. Wiley, New York, pp. 569–655.
- Jørgensen, B.B., 1990. A thiosulfate shunt in the sulfur cycle of marine sediments. *Science* 249, 152–154.
- Jørgensen, B.B., Fossing, H., Wirsén, C.O., Jannasch, H.W., 1991. Sulfide oxidation in the anoxic Black Sea chemocline. *Deep-Sea Res.*, II 38, S1083–S1103.
- Kaplan, I.R., Rittenberg, S.C., 1964. Microbiological fractionation of sulfur isotopes. *J. Gen. Microbiol.* 34, 195–212.
- Kelly, D.P., 1989. Physiology and biochemistry of unicellular sulfur bacteria. In: Schlegel, H.G., Bowen, B. (Eds.), *Biology of Autotrophic Bacteria*. Springer, Berlin, pp. 193–217.
- Knoblauch, C., Jørgensen, B.B., Harder, J., 1999. Community size and metabolic rates of psychrophilic sulfate-reducing bacteria in arctic marine sediments. *Appl. Environ. Microbiol.* 65, 4230–4233.
- Krivosheya, V.G., Titov, V.B., Ovchinnikov, I.M., Kosyan, R.D., Skirta, A.Yu., 2000. Influence of circulation and mesoscale eddies on the location of the upper sulfide boundary and on the ventilation of the anoxic zone. *Oceanologiya* 40, 816–825 (in Russian with English summary).
- Lein, A.Yu., Ivanov, M.V., 1991. On the sulfur and carbon balances in the Black Sea. In: Izdar, E., Murray, J.W. (Eds.), *The Black Sea Oceanography*. Kluwer Academic Publishers, Amsterdam, pp. 307–318.
- Luther III, G.W., Church, T.M., Powell, D., 1991. Sulfur speciation and sulfide oxidation in the water column of the Black Sea. *Deep-Sea Res.*, II 38, S1121–S1138.
- Madigan, M.T., 1988. Microbiology, physiology, and ecology of phototrophic bacteria. In: Zehnder, A.J.B. (Ed.), *Biology of Anaerobic Microorganisms*. Wiley, New York, pp. 39–111.
- Millero, F.J., 1991. The oxidation of H_2S in Black Sea waters. *Deep-Sea Res.*, II 38, S1139–S1150.
- Murray, J.W., Codispoti, L.A., Friederich, G.E., 1995. Oxidation–reduction environments: the suboxic zone in the Black Sea. In: Huang, C., et al. (Eds.), *Aquatic Chemistry*. Kluwer Academic Publishers, Amsterdam, pp. 157–176.
- Neretin, L.N., Grinenko, V.A., Volkov, I.I., 1996. Isotopic composition of hydrogen sulfide in deep water of the Black Sea. *Trans. (Dokl.) Russ. Acad. Sci.* 349A, 1015–1019.
- Neretin, L.N., Volkov, I.I., Böttcher, M.E., Grinenko, V.A., 2001. A sulfur budget for the Black Sea anoxic zone. *Deep-Sea Res.*, I 48, 2569–2593.
- Newton, R.J., Bottrell, S.H., Dean, S.P., Hatfield, D., Raiswell, R., 1995. An evaluation of the use of the chromous chloride reduction method for isotopic analyses of pyrite in rocks and sediment. *Chem. Geol.* 125, 317–320.
- Oguz, T., Besiktepe, S., 1999. Observations on the Rim Current structure, CIW formation and transport in the western Black Sea. *Deep-Sea Res.*, I 46, 1733–1753.
- Oguz, T., Latun, V.S., Latif, M.A., Vladimirov, V.V., Sur, H.I., Markov, A.A., Özsoy, E., Kotovschikov, B.B., Eremeev, V.V., Unluata, U., 1993. Circulation in the surface and intermediate layers of the Black Sea. *Deep-Sea Res.*, I 40, 1597–1612.
- Ovchinnikov, I.M., Titov, V.B., Krivosheya, V.G., Popov, Yu.I., 1994. Major fluid dynamical processes and their role in the ecology of the Black Sea waters. *Oceanologiya* 33, 707–712 (in Russian with English summary).
- Özsoy, E., Unluata, U., Top, Z., 1993. The evolution of Mediterranean water in the Black Sea: interior mixing and material transport by double diffusive intrusions. *Prog. Oceanogr.* 31, 275–320.
- Repeta, D.J., Simpson, D.J., Jørgensen, B.B., Jannasch, H.W., 1989. Evidence for anoxygenic photosynthesis from the distribution of bacterio-chlorophylls in the Black Sea. *Nature* 342, 69–72.
- Sass, H., Steuber, J., Kroder, M., Kroneck, P.M.H., Cypionka, H., 1992. Formation of thionates by freshwater and marine strains of sulfate-reducing bacteria. *Arch. Microbiol.* 158, 418–421.
- Sorokin, Yu.I., 1972. The bacterial population and the processes of hydrogen sulfide oxidation in the Black Sea. *J. Cons. Int. Explor. Mer.* 34, 423–454.
- Sweeney, R.E., Kaplan, I.R., 1980. Stable isotope composition of dissolved sulfate and hydrogen sulfide in the Black Sea. *Mar. Chem.* 9, 145–152.
- Thudge, A.P., Thode, H.G., 1950. Thermodynamic properties of isotopic compounds of sulfur. *Can. J. Res.* 28B, 567–578.
- Titov, V.B., 2000. The formation of winter hydrological structure of the Black Sea depending on the severity of winter conditions. *Oceanologiya* 40, 826–832 (in Russian with English summary).
- Ustinov, V.I., Grinenko, V.A., 1965. Pretsezionniy Mass-Spektrometricheskii Metod Opredeleniya Izotopnogo Sostava Sery

- (Precise Mass-Spectrometry For Sulfur Isotopic Measurements). Nauka, Moscow. In Russian.
- Vainshtein, M.B., Matrosov, A.G., Baskunov, B.P., Zyakun, A.M., Ivanov, M.V., 1980. Thiosulfate as an intermediate product of bacterial sulfate reduction. *Mikrobiologiya* 49, 855–858 (in Russian with English summary).
- Vinogradov, A.P., Grinenko, V.A., Ustinov, V.I., 1962. Isotopic compositions of sulfur compounds in the Black Sea. *Geochem. Int.* 10, 973–997.
- Volkov, I.I., Zhabina, N.N., 1990a. Determination of thiosulfate and sulfite in seawater. *Oceanologiya* 30, 582–587 (in Russian with English summary).
- Volkov, I.I., Zhabina, N.N., 1990b. The method of reduced sulfur species determination in sea water. *Oceanologiya* 30, 778–782 (in Russian with English summary).
- Weber, A., Riess, W., Wentzhöfer, F., Jørgensen, B.B., 2001. Sulfate reduction in Black Sea sediments: in situ and laboratory radiotracer measurements from the shelf to 2000 m depth. *Deep-Sea Res.*, I 48, 2073–2096.
- Wortmann, U.G., Bernasconi, S.M., Böttcher, M.E., 2001. Hyper-sulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology* 29, 647–650.
- Yao, W., Millero, F.H., 1995. Oxidation of hydrogen sulfide by Mn(IV) and Fe(III) (hydro)oxides in seawater. In: Vairavamurthy, M.A., Schoonen, M.A.A. (Eds.), *Geochemical transformation of sedimentary sulfur*, ACS Symposium Series, vol. 612, pp. 260–279. American Chemical Society, Washington, WA.
- Zhang, J.-Z., Millero, F.J., 1994. Kinetics of oxidation of hydrogen sulfide in natural waters. In: Alpers, C.N., Blowes, D.W. (Eds.), *Environmental Geochemistry of Sulfide Oxidation*. Am. Chem. Soc., ACS Symposium Series, vol. 550, pp. 393–409. American Chemical Society, Washington, WA.