

# The stable isotopic composition of sulphur species in the Black Sea water column

L. N. Neretin  
M. E. Böttcher

I. I. Volkov

Max-Planck-Institute for Marine Microbiology, D-28359 Bremen,  
Germany

P.P. Shirshov Institute of Oceanology, 117851, Moscow, Russia

The Black Sea is the unique anoxic quasi-stationary basin characterised by a total hydrogen sulphide inventory of about  $519 \text{ M m}^{-2}$ . In the Black Sea water column large isotopic fractionation factor between sulphate and hydrogen sulphide of about  $60\text{\textperthousand}$  is observed which is mainly due to microbial sulphate reduction. Until now such high fractionation factors have not been reported in culture experiments including sulphate reducing bacteria cultures isolated from the Black Sea water (Fry *et al.*, 1991). Factors that determine isotopic fractionation in sulphur cycle of anoxic environments are poorly understood. Recent works give evidence for participation of reactions in the oxidative part of the sulphur cycle on the formation of very isotopically light sedimentary sulphides. It is still unclear, to what extent oxidation processes in the Black Sea could influence the isotopic composition of sulphur species in the deeper anoxic zone taking into account significant spatial separation of chemocline layer from entire sulphide water. In this paper we present new data on sulphur isotopic composition of sulphate and hydrogen sulphide with emphasis on chemocline layer and first data on isotopic composition of intermediate species (elemental sulphur and thiosulphate).

## Methods

Analysis and separation for isotopic composition of reduced sulphur species were done using technique described by Volkov and Zhabina (1990). Separation of sulphide and elemental (polysulphide) sulphur from thiosulphate (sulphite), possible polythionates is made by precipitation of the former using  $\text{Zn}_2(\text{OH}_2)\text{CO}_3$  in slightly base conditions. All S forms are reduced into hydrogen sulphide by  $\text{CrCl}_2$  solution. Reproducibility of the method is 3–5%, lower detection limit is  $0.03 \mu\text{M}$ .

$^{34}\text{S}/^{32}\text{S}$  ratios relative to CDT standard were measured by means of dual-inlet mass-spectrometer MS-2M and of combustion isotope-ratio-monitoring mass spectrometry (C-irmMS) using a Carlo Erba EA

1108 elemental analyser connected to a Finnigan MAT 252 mass spectrometer via a Finnigan MAT Conflo II split interface, as described by Böttcher *et al.* (1998). The latter equipment was applied for measurements of sulphate isotopic composition in the chemocline layer and for  $\delta^{34}\text{S}$  of S intermediates.

## Results

Sulphate: Present study was addressed primarily on sulphate isotopic composition in chemocline layer. The average  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  in this layer is  $+20.69 \pm 0.15\text{\textperthousand}$  ( $n = 25$ ). Enrichment of  $^{32}\text{S}$  in sulphate (maximum of sulphate chlorinity ratio) is observed 20–30 m above  $\text{H}_2\text{S}$  appearance and seems to be explained by successive hydrogen sulphide oxidation in the Black Sea chemocline through sulphur intermediates and supported by vertical distribution of  $\text{S}^0 (+\text{S}_n^{2-})$  and  $\text{S}_2\text{O}_3^{2-} (+\text{SO}_3^{2-})$  in the Black Sea chemocline (Volkov, 1995) (Fig. 1).

Hydrogen sulphide: According to  $\delta^{34}\text{S}$  of dissolved  $\text{H}_2\text{S}$  the Black Sea anoxic column is divided into three zones: (1) from the upper  $\text{H}_2\text{S}$  boundary below to 200–300 m  $\delta^{34}\text{S} = -38.5 \pm 1.9$  ( $-40.8$ – $-32.6\text{\textperthousand}$ ): 17 samples; (2) from 300 to 1500 m:  $\delta^{34}\text{S} = -39.9 \pm 1.1\text{\textperthousand}$  ( $n = 63$ ); (3) below 1500 m:  $\delta^{34}\text{S} = -38.8 \pm 0.9\text{\textperthousand}$  ( $n = 12$ ) (Fig. 2). Based on the model of linear mixing hydrogen sulphide just below the upper boundary should have  $\delta^{34}\text{S}$  values as much as  $-35$ – $-32\text{\textperthousand}$ . Tendency of  $^{34}\text{S}$  enrichment of about 5–8% in the upper anoxic zone might be explained by two mechanisms: decreasing of isotopic fractionation factor (relative to underlying waters) due to higher rates of sulphate reduction and/or an additional small isotope fractionation upon  $\text{H}_2\text{S}$  oxidation. These two hypotheses have been modelled for differential distributions of  $^{34}\text{S}$  and  $^{32}\text{S}$  isotopes by means of the model of Yakushev and Neretin (1997) and with equations developed by Jørgensen (1979). Application of two scenarios (fractionation factor 5% during oxidation or decreasing of the fractionation factor of 5% during sulphate reduction just below the anoxic

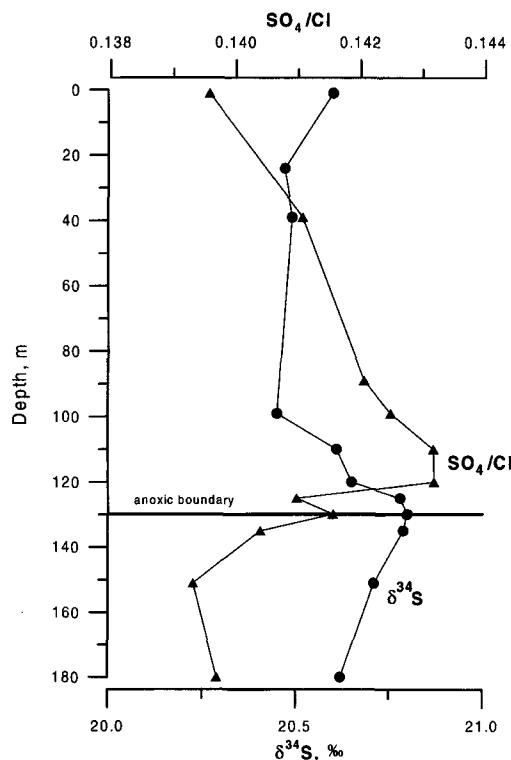


FIG. 1. Distribution of  $\text{SO}_4^{2-}/\text{Cl}$  ratio and  $\delta^{34}\text{S}$ - $\text{SO}_4^{2-}$  at St. 40 ( $43^{\circ}10'\text{N}$ ,  $38^{\circ}45'\text{E}$ , 2106 m, 07.1996, R/V 'Yantar').

boundary) in conditions of the open system give  $^{34}\text{S}$  enrichment of about 1.3–2.4‰, combination of two modelled situations led to the 'heavening' of sulphide sulphur of about 5.7‰. Thus, model calculations showed that in conditions of the open system within chemocline layer, enrichment of  $^{34}\text{S}$  in  $\text{H}_2\text{S}$  up to –35 to –32‰ might be associated with isotopic fractionation factor of about 10–12‰ during oxidation or decreasing of fractionation factor at the same value upon sulphate reduction just below the anoxic boundary. Our new data on free  $\text{H}_2\text{S}$  isotopic composition in the uppermost Black Sea sediments give average value of –37.4‰. Based on isotope mass balance calculation the enrichment by  $^{34}\text{S}$  in  $\text{H}_2\text{S}$  in the deeper part of the anoxic zone seems to be result of hydrogen sulphide flux from bottom sediments.

**Intermediate sulphur species:** In this study we present the first data on stable isotope composition of sulphur intermediate species in natural environment (deep Black Sea water).  $\delta^{34}\text{S}-\text{S}^0$  has a tendency to increase with depth from –39‰ (952 m) up to –29‰ (1896 m) ( $n = 5$ ), isotopic composition of one  $\text{S}_2\text{O}_3^{2-}$  sample is –39‰. Most values are only

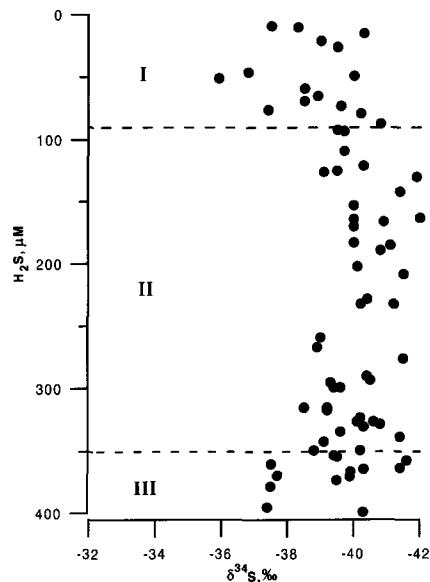


FIG. 2.  $\delta^{34}\text{S}-\text{H}_2\text{S}$  vs  $\text{H}_2\text{S}$  in the Black Sea water column (6 stations, NE and W parts of the Black Sea).

slightly enriched in  $^{34}\text{S}$  when compared with co-existing  $\text{H}_2\text{S}$ .  $\delta^{34}\text{S}$  of  $\text{S}^0$  in our samples seems to represent isotopic signature of polysulphide then elemental sulphur in suspended phase. Isotopic composition of S intermediates can be the result of  $\text{H}_2\text{S}$  oxidation, probably superimposed by isotope exchange reactions. Enrichment of  $^{34}\text{S}$  in  $\text{S}^0$  and decrease of its concentration with depth in the lowest part of anoxic zone could be explained by four processes: 1) supply of isotopically heavy  $\text{S}_n^{2-}$  from bottom sediments 2) elemental sulphur hydrolysis; 3)  $\text{S}^0$  reduction; 4) isotope exchange reactions between  $\text{S}^0(\text{S}_n^{2-})$  and co-existing  $\text{H}_2\text{S}$ .

## References

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