

A combined pathway of sulphur compound disproportionation by a sulphate-reducing bacterium (*Desulfovibrio desulfuricans*): Evidence from stable sulphur isotopes

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Elemental sulphur and thiosulphate are important intermediates in the sulphur cycle of marine and limnic sediments. They are mainly formed during reoxidation of sulphide, the product of dissimilatory sulphate reduction, and can undergo various transformations, i.e. oxidation, reduction or disproportionation (Jørgensen, 1990; Canfield and Thamdrup, 1994). It has been shown that in sediments a large part of sulphide is recycled via thiosulphate or sulphur disproportionation to sulphide and sulphate (Jørgensen, 1990; Canfield and Thamdrup, 1994). Large ^{34}S depletions are found in sedimentary sulphides, which are much higher than fractionations observed in pure culture studies on dissimilatory sulphate reduction. It has been considered that sulphur isotope fractionation during disproportionation processes contributes to the additional isotope fractionation observed in nature (Jørgensen, 1990), and it was shown experimentally for disproportionation of elemental sulphur (Canfield and Thamdrup, 1994) and sulphite (Habicht, 1997). In our present study we have followed the fate of the inner (sulphonate) and outer (sulphane) sulphur atoms during thiosulphate disproportionation by *Desulfovibrio desulfuricans*.

Experimental methods

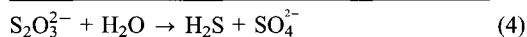
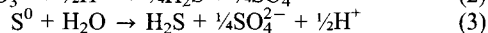
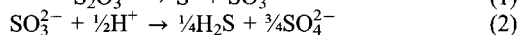
Sulphur isotope fractionation during disproportionation was investigated with growing batch cultures of *Desulfovibrio desulfuricans* CSN (DSM9104) at 30 °C. Sulphide concentration was determined potentiometrically using an Ag/Ag₂S electrode. Sulphate and thiosulphate were determined by ion chromatography. Thiosulphate was either oxidized for analysis of the total thiosulphate sulphur or selectively decomposed for separation of sulphonate and sulphane sulphur (Smock *et al.*, 1998). The sulphur isotopic composition was measured by combustion isotope-ratio-monitoring mass spectrometry

(Böttcher *et al.*, 1998). The isotopic composition is expressed as $\delta^{34}\text{S}$ relative to the V-CDT.

Results and discussion

In our present study we have followed the fate of the sulphonate and sulphane sulphur atoms during thiosulphate disproportionation by washed cells of *Desulfovibrio desulfuricans*. This bacterium has a constitutive thiosulphate reductase and a constitutive capacity of thiosulphate disproportionation. We expected that disproportionation is catalyzed by thiosulphate reductase and some of the enzymes involved in sulphate reduction. Thiosulphate should be reduced to sulphide and sulphite in a first step, followed by oxidation of sulphite to sulphate, which is necessary to regain the electrons consumed for thiosulphate reduction. For the complete disproportionation we therefore expected to find the isotope signature of the inner sulphur in the produced sulphate and the signature of the outer sulphur in the produced sulphide. During disproportionation, ^{32}S -thiosulphate was preferentially metabolized, and the residual thiosulphate became enriched in ^{34}S (Fig. 1). This result was mainly due to discrimination against ^{34}S of the inner sulphur atom. The sulphate formed was isotopically heavier than the inner sulphur of the consumed thiosulphate. *Vice versa*, the sulphide formed was isotopically lighter than the outer sulphur of the thiosulphate consumed.

These observations are not in agreement with a direct transformation of the inner and outer sulphur atom to sulphate and sulphide, respectively. Instead, it must be assumed that thiosulphate is first transformed to intermediates that undergo further reactions coupled to sulphur isotope fractionation. We suggest that thiosulphate is not reduced in the first step, but cleaved to sulphur and sulphite. Both of these intermediates can undergo further disproportionation, coupled to sulphur isotope discrimination.



Thus, disproportionation of thiosulphate, sulphite and elemental sulphur would be parts of a combined pathway. Thamdrup *et al.* (1993) suggested that thiosulphate could possibly be an intermediate of sulphur disproportionation. By contrast, our results indicate that elemental sulphur is an intermediate of thiosulphate disproportionation.

If one assumes that the oxidative part during elemental sulphur disproportionation includes sulphite as an intermediate, and that sulphite disproportionation results in a ^{34}S depletion of -30% in the produced sulphide (Habicht, 1997), the remaining three fractionation factors can be calculated according to the mass balances. This yields a depletion of -13% in ^{34}S for the reduction of elemental sulphur to sulphide. Sulphur isotope fractionation during oxidation to sulphate must be $+10\%$, that of sulphur oxidation to sulphite $+26\%$.

References

- Böttcher, M.E., Brumsack, H.-J. and de Lange, G.J. (1998) *Proc. ODP, Sci. Res.*, **160**.
 Canfield, D.E. and Thamdrup, B. (1994) *Science*.
 Habicht, K. (1997) *PhD thesis, Bremen*.
 Jørgensen, B.B. (1990) *Science*, **249**, 152–4.
 Thamdrup, B. *et al.* (1993) *Appl. Environm. Microbiol.*, **59**, 101.
 Smock, A.M., Böttcher, M.E. and Cypionka, H. (1998) *Arch. Mikrobiol.*, in press.

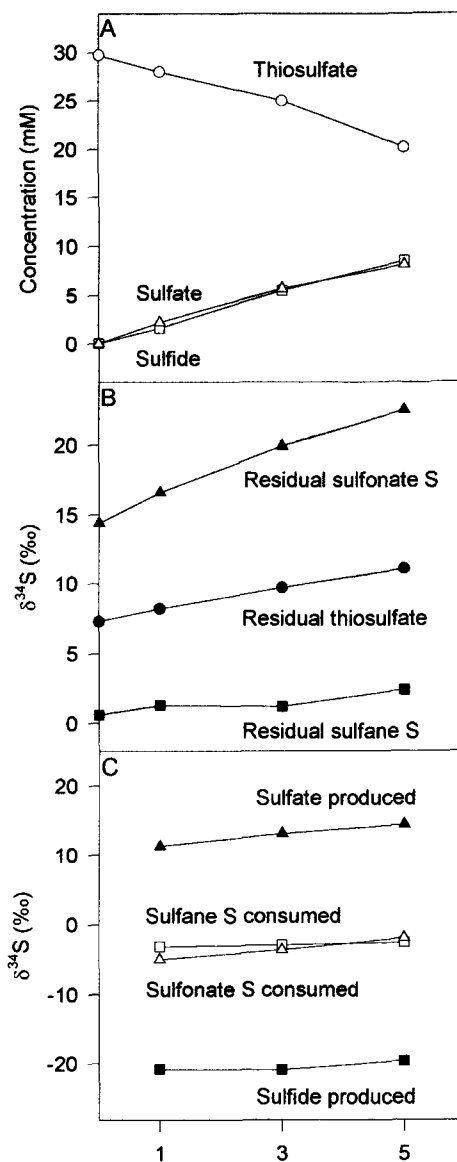


FIG. 1. Sulphur isotope fractionation during disproportionation by *Desulfovibrio desulfuricans*.