

# Multiple sulfur isotopes reveal a shift of the chemocline in an Upper Carboniferous ocean basin

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We present  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values for disulfides of the Chokier Formation, Belgium (Upper Carboniferous) investigating changing environmental conditions during its deposition. The Chokier Formation consists of laminated silty mudstones in the lower section and carbonate-rich mudstones and laminated mudstones in the upper one. Total sulfur (TS) contents vary from 0.1 and 6.3 wt%, total organic carbon (TOC) from 0.4 to 6.4 wt%, and total inorganic carbon (TIC) from 0.0 to 8.0 wt%. There is a stratigraphical change in the core section at 26.6 m depth. TS and TOC contents are higher in the upper than in the lower part of the formation. TIC is generally low (mean TIC = 0.42 wt%) with locally higher values > 1 wt% in the upper section. Iron speciation indicates euxinic conditions throughout the entire profile. The mean  $\delta^{34}\text{S}$  is -24.6‰ in the upper and -9.7‰ in the lower section.  $\Delta^{33}\text{S}$  values are positive in the upper (mean  $\Delta^{33}\text{S}$  = 0.040‰) and negative in the lower part (mean  $\Delta^{33}\text{S}$  = -0.029‰).

In a  $\delta^{34}\text{S}$  vs  $\Delta^{33}\text{S}$  plot, samples from the upper part plot in the field with negative  $\delta^{34}\text{S}$  and positive  $\Delta^{33}\text{S}$ , which is assigned to microbial sulfate reduction (MSR) and microbial sulfur disproportionation (MSD). Samples from the lower part have both negative  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values. We assume that their isotopic compositions is located on a mixing curve indicating the mixing of two sulfur sources: (1) a mixture of MSR and/or MSD, and (2) (nearly) quantitatively reduced sulfate. Sulfate is quantitatively reduced when the sulfate reduction rate exceeds the sulfate supply.

We infer that the two different sulfur signatures indicate different depositional regimes, specifically a shift in the position of the chemocline. The sediments of the lower section were deposited under a stagnant water column that restricted the exchange at the sediment/water boundary, hence limiting the sulfate supply. The chemocline was displaced downward by well-mixed water masses during the deposition of the upper section enabling an unrestricted exchange of sulfate between seawater and sediment.