

## **Multiple sulfur isotope fractionation in the chemocline of warm monomictic lake with sub-millimolar sulfate concentrations**

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The multiple isotope composition of sulfate and hydrogen sulfide at the chemocline of monomictic Lake Kinneret during a 24-hour period was studied. This freshwater lake contains sub-millimolar concentrations of sulfate (0.5-0.6 mM) in the epilimnion of the water column, which are similar to those suggested for the water column of the Proterozoic Ocean. Sampling was performed at a water depth of 17.1 m. At this depth, sulfide was detected during the day and oxygen during night, due to internal wave activity that caused variations in the chemocline depth at an amplitude of 5.3 m and a 24 h period.

The lowest values of both  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  of sulfate (11.3 - 12.1 ‰ and -0.026 - (-0.004) ‰, respectively) were measured in the chemocline and epilimnion, during night. Below the chemocline  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values of sulfate were 12.2 - 14.8 ‰ and -0.017 - 0.049 ‰, respectively. In the case of hydrogen sulfide,  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  were in the range of -9.2 - 4.8 ‰ and 0.021 - 0.125 ‰, respectively.

The  $\delta^{34}\text{S}$  values of hydrogen sulfide and sulfate are consistent with the formation of hydrogen sulfide by microbial sulfate reduction with a fractionation of -19‰ at the chemocline, which increases to -23‰ 4 m below the chemocline.

The multiple sulfur isotope fractionations between sulfate and sulfide all fall in the area of experimental data for microbial sulfate reducing microorganisms, with the exception of one point. Although some increase in  $^{34}\epsilon_{\text{net}}$  and  $^{33}\lambda$  values with depth is observed, even at depths characterized by the highest concentrations of zero-valent sulfur, the sulfur isotope fractionation may be explained by sulfate reduction alone.