

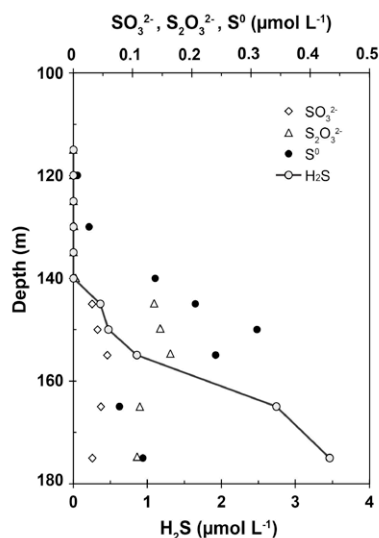
## Sulphur driven denitrification dominates N-removal in the water column of Lake Lugano

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Besides organotrophic denitrification, alternative pathways, such as anaerobic ammonium oxidation (anammox) or sulphide-dependent denitrification are potentially important for the removal of fixed nitrogen from lakes. We identified the dominant N<sub>2</sub> forming processes in the permanently stratified northern basin of Lake Lugano (Switzerland) using <sup>15</sup>N labelling experiments, molecular and cultivation based microbiological approaches.

Potential rate measurements suggest that anammox can contribute up to 30% to total N<sub>2</sub> formation but denitrification remained the dominant process at all depths. Additional incubation experiments with potential substrates for denitrifying bacteria identified sulphide and thiosulphate as important substrates [1]. Enrichment cultures of sulphide dependent nitrate-reducing bacteria were established to determine the products of sulphur and nitrogen transformations, respectively, and for molecular characterisation.



**Figure 1:** Concentrations of sulphide and sulphur intermediates at the RTZ in the stratified deep northern basin of Lake Lugano

Our study highlights that despite of the mesotrophic nature of the lake and the very low concentrations of sulphur species (Figure 1), water column denitrifications is mainly driven by sulphur compounds rather than organic matter.

[1] Wenk *et al.* (2013) *Limnol. Oceanogr.* **58**, 1–12.

## Cs and Sr mass transfer constrained via ion beam analysis

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Micro-Reactor Simulated-Channel (MRSC) methods have been developed to rapidly determine mass transfer coefficients of intact low-permeability rock samples [1,2]. The design uses a thin fluid channel in the centre of the solid system which increases reaction rates due to a high surface area to liquid volume ratio. This enables fast measurements using only small reactor volumes. The MRSC consists of two injection syringe pumps, a reaction unit, an auto sampler, and a drainage tank. Unlike the conventional column method, an intact hard rock sample also produces flat surfaces for direct chemical analysis. <sup>90</sup>Sr and <sup>137</sup>Cs isotopes are both of great concern in disposal scenarios, with half-lives of approximately 30 years. In the MRSC experiments presented here, aqueous fluids with dissolved Sr and Cs have been pumped through simulated fractures at constant rates. Breakthrough curves were constructed by time resolved analysis of the effluent solution until steady state was observed. Differences between inlet and outlet concentrations are caused by two dominant processes; 1) diffusion into grain boundaries, micropores, and microfractures, and 2) sorption from the simulated fracture onto mineral surfaces. Mass difference is much higher than would be predicted from surface adsorption, and hence it is concluded that appreciable Sr and Cs has diffused into grain boundaries. In order to further constrain the tracer inventory, an analytical regimen was developed using ion beam techniques. This allowed us to fully characterise the reacted surfaces and to carry out depth-profiling. In particular, we designed these measurements to take advantage of the extremely low background radiation levels at the Sr and Cs K $\alpha$  energies in particle induced X-ray emission (PIXE) analysis in order to accurately quantify Sr and Cs [3]. In addition, the depth profiling capability of Rutherford backscattering spectrometry (RBS) is able to non-destructively constrain diffusion profiles at concentrations down to a few parts per million from areas 1  $\mu$ m in diameter. Results of these provide critical constraints on mass transfer parameters produced from MRSC experiments.

[1] Ohe *et al.*, (2012) *Min. Mag.* **76**, 3203-3215. [2] Okuyama *et al.*, (2008). *App. Geochem.* **23**, 2130-2136. [3] Wogelius *et al.* (1992) *Geochim. Cosmochim. Acta*, **56**, 319-334.