

## Energetics of Sulphate Reduction in Deep Bedrock Groundwater

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Sulphide, mainly present in groundwater as the result of microbial sulphate reduction, is considered to corrode copper which will be used as a canister material in the multi-barrier based geological repositories for spent nuclear fuel in Finland and Sweden. Thus, energetics of sulphate reduction play an important role in the safety assessment. Major factors controlling microbial sulphate reduction in the geosphere are known to include concentration of sulphate, availability of electron donors, temperature and absence of oxygen, however, few studies have examined geochemical constraints of sulphate reduction in deep bedrock groundwater.

We investigated two sites in Finland to determine energetics of sulphate reduction down to 2.5 km in the Early Proterozoic (1.9 Ga) bedrock in more detail: The Outokumpu Deep Drill Hole representative of a metasedimentary environment with minor occurrence of ophiolitic and granitic rocks, and the Pyhäsalmi Cu-Zn-sulphide mine representative of a more sulphur rich metavolcanic setting. In previous studies, anoxic conditions and temperature below 40°C, suitable for sulphate reducing microbes, has been confirmed at the sites [1, 2].

We determined the availability of sulphate and important electron donors (CH<sub>4</sub>, H<sub>2</sub>) and used thermodynamics to predict the most favourable reaction pathways for sulphate reduction. Energy densities and potential power supply for a timespan of 100 ka relevant for nuclear waste disposal were calculated.

Sulphate concentrations were 0.3 mM and 2.6 mM at most and sulphide concentrations up to 28 μM and 18 μM at Outokumpu and Pyhäsalmi, respectively. Typical energy densities were below 0.4 J L<sup>-1</sup> for the reaction SO<sub>4</sub><sup>2-</sup>+4H<sub>2</sub>+H<sup>+</sup> = HS<sup>-</sup>+4H<sub>2</sub>O and below 0.1 J L<sup>-1</sup> for the reaction SO<sub>4</sub><sup>2-</sup>+CH<sub>4</sub> = HCO<sub>3</sub><sup>-</sup>+HS<sup>-</sup>+H<sub>2</sub>O. At Outokumpu, sulphide production seems to be mostly limited by the availability of sulphate, while availability of electron donors is more important control at Pyhäsalmi. Power available from the reactions described was 10<sup>-15</sup> - 10<sup>-13</sup> W L<sup>-1</sup>. Considering the minimum maintenance power for one microbial cell to be 10<sup>-21</sup> W [3] we estimate that, in these environments, sulphate reduction can sustain 10<sup>8</sup> cells L<sup>-1</sup> at most.

[1] Kietäväinen *et al.* (2017), *GCA* 202, 124-145. [2] Miettinen *et al.* (2015), *Front Microbiol* 6, 1203. [3] LaRowe & Amend (2015), *Front Microbiol* 6, 1-11.