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How anoxic is the anoxic deep continental biosphere?

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The view has been almost unanimous: the deep biosphere is anoxic. Although molecular oxygen is often detected in deep groundwaters, it has been related to air contamination. For example, underground nuclear waste repositories are estimated to be anoxic within 200 years [1]. However, recent discovery of non-atmospheric oxygen in Canadian groundwaters [2] has challenged this view. Inspired by these findings, our study explores the presence of oxygen and related microbial metabolisms in crystalline bedrock groundwaters in Finland.

As a start, one fracture zone at 128 m depth in Kopparnäs, Inkoo, southern Finland, was isolated with packers and pumped over several days to collect samples for dissolved and free gas analysis and microbiological studies. The groundwater contained 3.41–3.69 mg L^{-1} of dissolved oxygen. Small amounts of oxygen (~1 vol-%) were found also in the free gas phase and continuously detected with on-line monitoring during the pumping. The dissolved gases and their isotopic ratios showed no signs of atmospheric origin, and their composition clearly differed from a sample that was intentionally contaminated with air. Instead, the $\delta^{18}O(O_2)$ values from 19.05 to 21.86 ‰ VSMOW suggest in-situ oxygen production through biotic or abiotic reactions, such as dismutation reactions or radiolysis of water. Substantial amounts of presumably nucleogenic helium (up to 2.65 vol-%) suggest long groundwater residence time and high radiolytic oxygen forming potential within the studied fracture zone.

The presence of free oxygen in deep groundwater environments can have a profound effect on elemental cycles of redox sensitive nutrients, such as sulfur. Indeed, our extensive set of metagenomic and isotope geochemical data from across Finland reveals aerobic sulfur cycling metabolisms even at depths down to 1.5 km. For example, oxygen demanding sulfur dioxygenase and sulfhydrogenase enzymes were found from Kopparnäs and Outokumpu (eastern Finland), and potential for sulfide oxidation was commonly detected throughout the samples, further emphasising that the deep biosphere might not be as anoxic as previously considered.

References:

[1] King et al. (2010), SKB-TR-10-67, Swedish Nuclear Fuel and Waste Management Co.

[2] Ruff et al. (2023), *Nature Communications* 14, 3194.