

Assessing the origin of molecular hydrogen in bedrock groundwaters

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Molecular hydrogen (H₂) is commonly encountered in deep (> 200 m) bedrock groundwaters. Within the Precambrian Fennoscandian Shield in Finland, H₂ concentrations exceeding 2 mM have been reported [1]. The presence of H₂ in bedrock groundwater plays an important role in the safety assessment of radioactive waste disposal as well as underground mining. In addition, naturally occurring H₂ potentially forms energy reserves that might become economically important.

Known H₂ producing mechanisms in the subsurface span from serpentinisation and other iron related redox reactions to microbial hydrogenesis, radiolysis and mechanochemical grinding. While geological constraints and experimental approaches can provide clues on potential and preferential pathways, their relative importance and diagnostic features still remain elusive.

In this study, we investigated isotope systematics of hydrogen in bedrock groundwaters within various rock types in Finland, in order to identify potential H₂ formation pathways and their geochemical fingerprints. Our analysis is based on both previously published [2, 3] and new data from scientific and exploration drill holes. Lithologies assessed include classical serpentinite systems, but also sandstone, metavolcanic rocks and mica schist. Temperature remains below 40 °C at all sampling depths.

Isotopic composition of molecular hydrogen from bedrock groundwaters in Finland, 11 samples in total, ranges from -619 to -848 ‰ VSMOW. Except the most negative values below -770 ‰, comparison of δ²H values of H₂ and associated water indicates equilibrium fractionation at or slightly above ambient temperatures.

Diagnostics are complicated by groundwater residence times of tens of millions of years, microbial reprocessing and subsequent re-equilibration of the isotopic composition of H₂. Estimation of H₂ production potential, and related risk and economic assessments, heavily rely on the understanding of these processes.

[1] Kietäväinen *et al.* (2013) *Appl. Geochem.* **32**, 37-51. [2] Sherwood Lollar *et al.* (1993) *GCA* **57**, 5087-5097. [3] Kietäväinen *et al.* (2017) *GCA* **202**, 124-145.