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Elucidating the fate of hydrogen gas in a clay-rich rock by means of deuterium injections and Raman spectroscopy

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In deep geological repositories for high-level and/or long-life nuclear waste, hydrogen gas is expected to be generated by corrosion and radiolysis. The "Hydrogen Transfer" experiment was implemented in 2009 in the Mont Terri Rock Laboratory (Switzerland) to determine *in situ* the fate of hydrogen in Opalinus Clay and to evaluate whether hydrogen consumption can be detected *in situ* and whether microorganisms play a role in this potential consumption.

The experimental concept is based on continuous gas circulation and water sampling in a 15-m long borehole [1]. In the drift, a gas circulation module allows to inject pure hydrogen or deuterium at a controlled flow rate and to monitor H_2, HD and D_2 with a Raman spectrometer.

After both initial punctual injections of H_2 (p(H_2) ~60 mbar, total pressure ~1.5 bar), H_2 completely disappeared within 65 days, 20 times faster than calculated when considering only dissolution and diffusion. The proposed hypothesis, consolidated with observed evolution of the water composition and geochemical modelling [2], is that H_2 consumption is mainly controlled by hydrogen-fuelled, microbially mediated sulphate reduction (equation 1).

To confirm this hypothesis, we injected pure D_2 twice (p(D_2) ~50 mbar) and monitored the evolution of the isotope label in water and gas. In the gas phase, we observed a fast decay and rise of the Raman peak intensities of D_2 and H_2, respectively (fig.1), followed by a decrease of the generated H_2 over a similar duration as compared to previous H_2 injections.

Hydrogenase enzymes catalyse the reversible oxidation of H_2. In the presence of D_2 gas (in a D_2/H_2O system), hydrogenases rapidly catalyse the proton/hydrogen-deuterium exchange reaction, which results in the formation of HD and H_2 [3, 4]. And, more slowly, they are responsible for the net oxidation of hydrogen to water, resulting in the long-term decrease of H_2.

Consequently, our measurements provide additional evidence that hydrogenase-containing and net H_2-oxidising microorganisms are active in this clay-rich rock.

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[1] Vinsot *et al* (2017)
[2] Hax-Damiani *et al* (2021)
[3] Vignais (2005)
[4] Kawahara-Nakagawa *et al* (2019)

$$SO_4^{2-} + Fe^{2+} + 4(D/H)_2 = FeS + 4(D/H)_2O \qquad \text{(equation 1)}$$

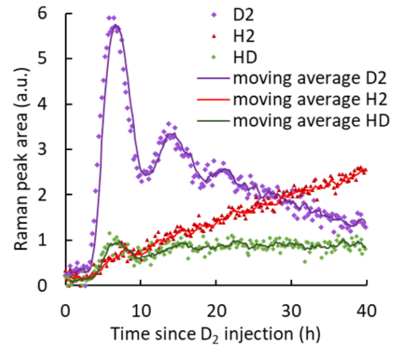

Figure 1 *Evolution of D_2, HD and H_2 in the circulating gas measured by Raman spectroscopy, the initial sinusoidal shape is due to the mixing in the gas circuit.*