# Carbon Cycling and Nuclear Waste Disposal: Evidence for Methanogenesis at Low Temperature Bedrock Setting

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Long-term safety of geological disposal of nuclear waste rely on the integrity and functionality of the engineered and natural barriers. Safety and performance analysis of the repository system must rely on sound scientific reasoning, and analysis of features, events and processes possibly taking place in the geological environment. For example, mobility and fate of radioactive $^{14}C$ is directly connected to the natural carbon cycle, linking the geosphere and the biosphere.

For this study samples were obtained from the Outokumpu Deep Drill Hole (2516 m) in eastern Finland. Carbon cycling was studied by determining isotopic composition of carbon in dissolved phases and minerals [1] and by calculating Gibbs free energies for carbon related reactions at *in situ* temperatures (5 - 40 ºC). To make these calculations as realistic as possible, and to assess their biological importance, energy densities were also calculated.

The results of the isotope and geochemical analyses indicate that $CH_4$ formation outcompetes $CH_4$ oxidation reactions at Outokumpu. Furthermore, abiotic processes are indicated to prevail especially below 1.5 km depth where isotopic composition of $CH_4$ is clearly enriched in $^{13}C$ and relative isotopic composition among alkanes shows v-shaped pattern possibly related to abiotic polymerisation reactions. Isotopic compositions of graphite and $CH_4$ are closely related, which could be due to formation of methane from graphite at closed system conditions [1].

The results of the thermodynamic calculations support the findings of the isotope analyses. They show that the formation of $CH_4$ both from dissolved carbonate ($HCO_3^-$ and $CaCO_3$) and aqueous $CO_2$ in the presence of $H_2$ is clearly exergonic. However, energy densities of these reactions remain below 13 J $L^{-1}$, and, for instance, methanogenesis from $CO_2$ and $H_2$ seems favourable only at 900 - 1500 m depth. Formation of $CH_4$ from graphite and $H_2$ was also found to be exergonic. Energy densities of this reaction are the highest among the reactions studied, up to 42 J $L^{-1}$, which may suggest important role of graphite in carbon cycling also at low temperatures.

[1] Kietäväinen *et al.* (2017) *GCA* 202, 124-145.