



DELIVERABLE D2.1
<Inventory of reducing gases>

Editors: Riikka Kietäväinen (GTK), Karsten Pedersen (Micans)

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Publishable Summary

In order to provide data needed to address the question on geochemical constraints of biological activity at spent nuclear fuel waste repository sites, geochemical data of dissolved gases from deep drill holes and mines in Finland and Sweden were collected based on a literature and database survey. Gas data were found from 20 separate localities in Finland with the deepest drill holes extending down to 2500 m below surface. The gas phase is dominated by nitrogen and methane, although significant variation exists between different sites and with depth. At least partly this variation can be related to differences in lithology (rock types) and residence time of water within the bedrock. Corresponding data from Sweden were from 2 localities extending to at most 1000 m below surface.

In the context of microbiological risks related to SNF waste disposal, the geochemistry of gases in deep groundwater is an integral part of the determination of geochemical constraints of biological activity at disposal depths. Data on gas compositions and concentrations do exist from several separate locations in Finland and two locations in Sweden. Site to site as well as depth dependent variation should be taken into account in Finland and could possibly be used to predict changes related to for example different rock types. For Sweden, there is a need to increase the number of gas samples from the selected site in Forsmark and also the number of sites and geological types for comparisons and increased understanding of generation and transport of reducing gases in deep geological formations.

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1 Introduction

High-level radioactive waste, mostly spent nuclear fuel (SNF) and waste from re-processed fuel, will be encapsulated in steel or copper canisters (Fig. 1). In some concepts, so-called super containers will have a concrete barrier encapsulating steel shells that contain the waste. The canisters will either be surrounded by an engineered barrier consisting of swelling clay, or, they will be placed directly in the host rock. The metal and the clay barriers are commonly denoted engineered barrier systems (EBS) and are susceptible to deterioration processes. Possible microbial deterioration processes for the safety case are (a) metal corrosion, (b) destabilisation of smectite clay minerals to be used as buffers, and (c) degradation of concrete. Corrosion will eventually cause the canister to breach, leading to radionuclide release; destabilisation may compromise the clay buffer's swelling and sorption properties, reducing its barrier function; concrete degradation may prematurely destabilize plugs and seal system. Microbial activity could impact the rate of each of these barrier systems and thus impact the safety case by compromising a repository's isolation and containment functions. The MIND work package 2 aims at addressing these issues individually and providing actionable information to the implementers in order to improve their safety case.

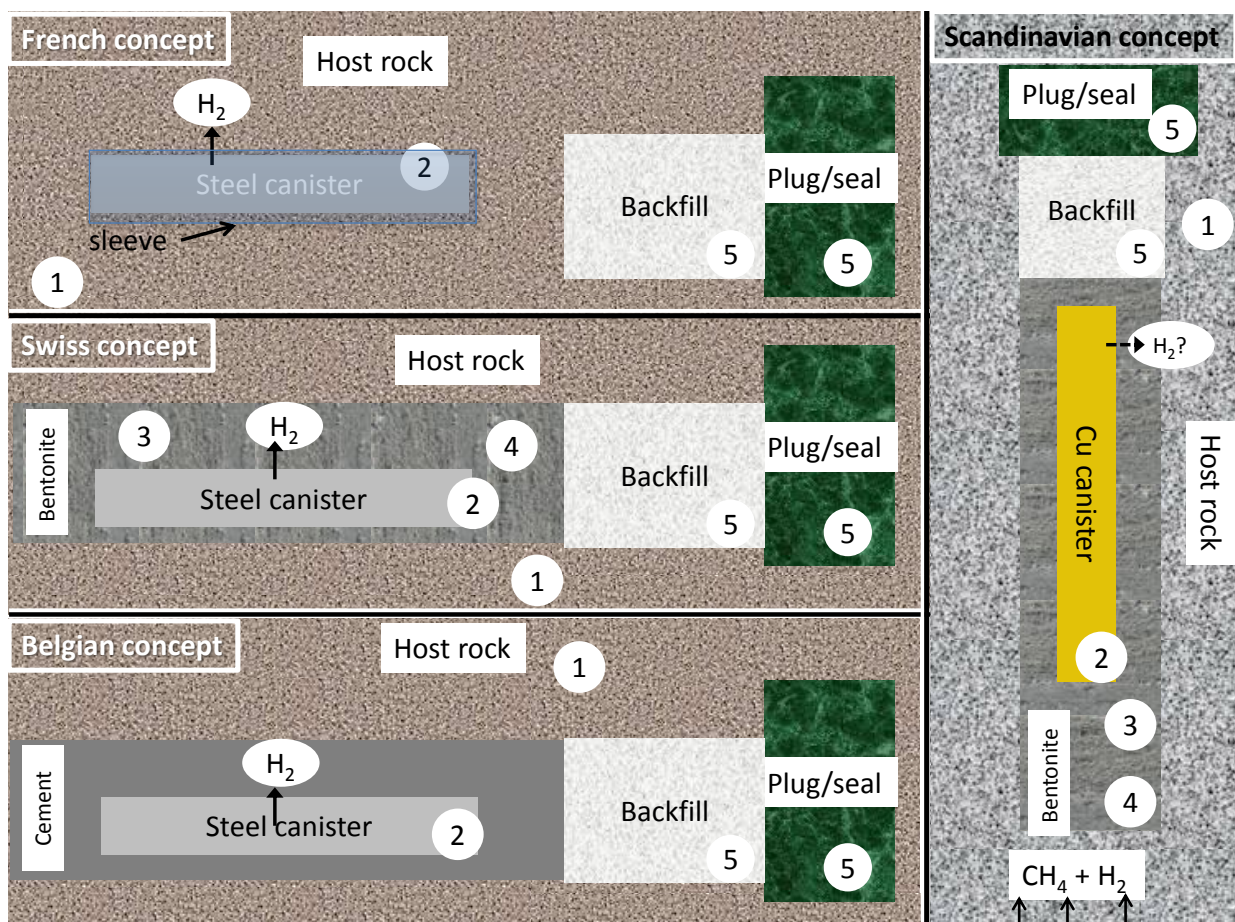


Figure 1. Representation of European high level waste disposal concepts (not to scale). Microbial processes are possible at the numbered points, which correspond to task numbers. 1. Microbial generation of sulphide in the geosphere. 2. Microbially induced corrosion of canisters. 3. Microbial activity in bentonite buffer. 4. Microbial degradation of bentonite buffer. 5. microbial activity in backfill and plug/seals.

2 Microbial production of sulphide in the geosphere

The presence and activity of sulphide producing bacteria in host rock groundwater and clays/shale is well documented. The sulphide they produce is not expected to reach the canisters because of slow diffusion through compacted bentonite buffers and the very low diffusion rate of sulphide in concrete. However, in the case of a failing clay buffer, e.g. due to erosion, or cracks in a concrete shell, sulphide will have a larger probability to contact with canisters and generate pitting corrosion. It is, therefore, important to understand what conditions foster sulphide production in the geosphere (often called the far-field) and its migration towards canisters. The action of competing iron reducing bacteria may mitigate sulphide production due to precipitation of iron sulphide phases.

While the presence, numbers and diversity of sulphide producing bacteria have been well documented, their activity is less well studied. There are cases when sulphide concentrations exceed the safety case limits more than 100 times and the underlying reasons for this accumulation are not fully understood. Hence, a remaining key issue for the safety case is to identify the factors controlling sulphide production in the geosphere, including man-made artifacts. Availability of electron donors, such as hydrogen (H₂) and methane (CH₄) from deep geological sources, is hypothesized to be one of several controlling factors.

Within fractured bedrock, the fluid phase can both mobilize and disperse potentially hazardous or corrosive compounds such as ¹⁴C and sulphide, respectively and to provide energy and nutrients to microorganisms. Some of the most important electron donors in anoxic deep biosphere, namely H₂ and CH₄ are gases. Furthermore, dissolved gases in groundwater can be used to determine diffusive transportation rates and groundwater residence times which can give valuable information on the gradients, production rates and isolation of groundwater from the surface water cycle. Therefore, biogeochemistry of gases plays an important role in the safety assessment of geological disposal of SNF waste.

3 Inventory of reducing gases in deep groundwater of Finland

Based on a literature review and hydrogeochemical databases owned by the Geological Survey of Finland, 20 different deep groundwater study sites where the determination of gases has been done, were identified across Finland (Fig. 2). Of these, the absolute concentrations of gases are available from 11 locations. The sites include both drill holes and deep mines in central and southern Finland with the deepest samples from 2480 m depth.

The earliest studies were carried out already in the 1960's [1,2]. Most of the studies date back to 1980's and 1990's [3,4,5,6,7] with many of them already related to nuclear waste disposal research. The more recent investigations include the studies at the Olkiluoto nuclear waste repository site (e.g. [8]), Outokumpu Deep Drill Hole geolaboratory [9,10,11,12] and the Pyhäsalmi Cu-Zn mine [13]. These sites comprise a wide spectrum of geochemical data including gas compositions with depth.



Figure 1: Sites of geochemical investigations of deep groundwater (>200 m) in Finland including determination of gas composition.

3.1 General features

Based on dissolved gas composition, two types of deep groundwater can be distinguished: 1) methane dominated and 2) nitrogen dominated. Other commonly detected gases include H_2 , He, Ar and occasionally CO_2 . Longer chained hydrocarbons have rarely been investigated in the earlier works but even though hydrocarbons up to pentane have been found in the more recent studies [13] their concentrations are often minor compared to methane. Oxygen is also often detected, although mainly result from contamination with air [10].

Significant variation in the gas composition and concentrations exists from site to site and also with depth. Saline groundwaters tend to contain the highest amounts of gas. For example, concentration of H_2 as high as 2.2 mM at Outokumpu with total dissolved solids (TDS) up to 70 g L^{-1} [9] and the concentration of CH_4 more than 40 mM at saline groundwater (TDS up to 84 g L^{-1}) at Olkiluoto [8] have been detected. Methane dominated groundwater also have higher gas/water ratios clearly indicative of accumulation of gas after groundwater recharge in the crust (Fig. 2).

At least in some cases variation in geochemical compositions (including gases) could be related to changes in lithology and this variation has been found to correlate also with microbial community structure [9]. Residence time of water within the bedrock also affects the gas composition and concentrations.

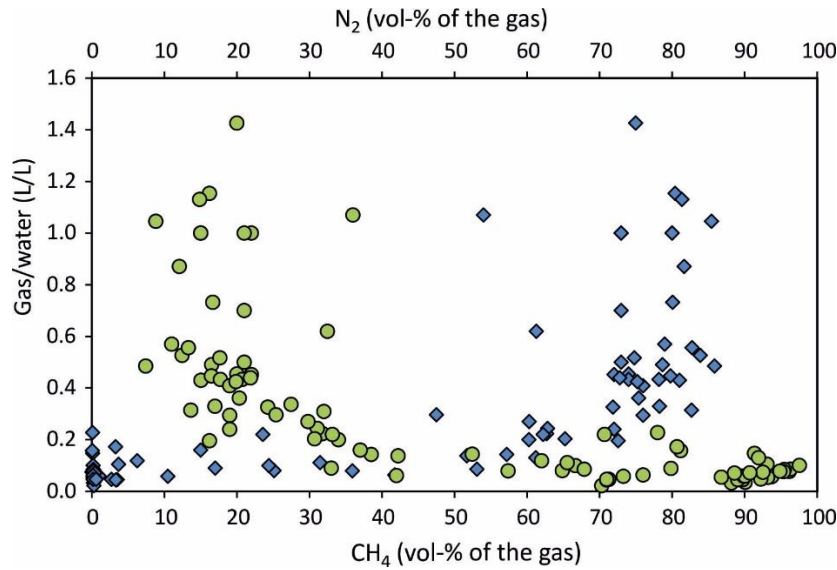


Figure 2: Diagram showing the gas/water ratio vs. the proportion of nitrogen (green circles) and methane (blue diamonds) in the gas phase of deep groundwater in Finland. The increase in total amount of gas is clearly correlated with change from nitrogen dominated to methane dominated groundwater.

3.1.1 Methane

Within crystalline bedrock groundwater in Finland the concentration of methane typically increases with depth although where data from greater depths are available (Outokumpu Deep Drill Hole) the concentration begins to decrease below 1000 m depth (Fig. 3). However, more data would be needed to verify if this feature is more widespread. Most likely due to the lack of *in situ* carbon source, groundwater within granitic rocks (represented by the Loviisa (Hästhölmén) site in Fig. 3) generally contain less methane than groundwater occupying metasedimentary rocks [12].

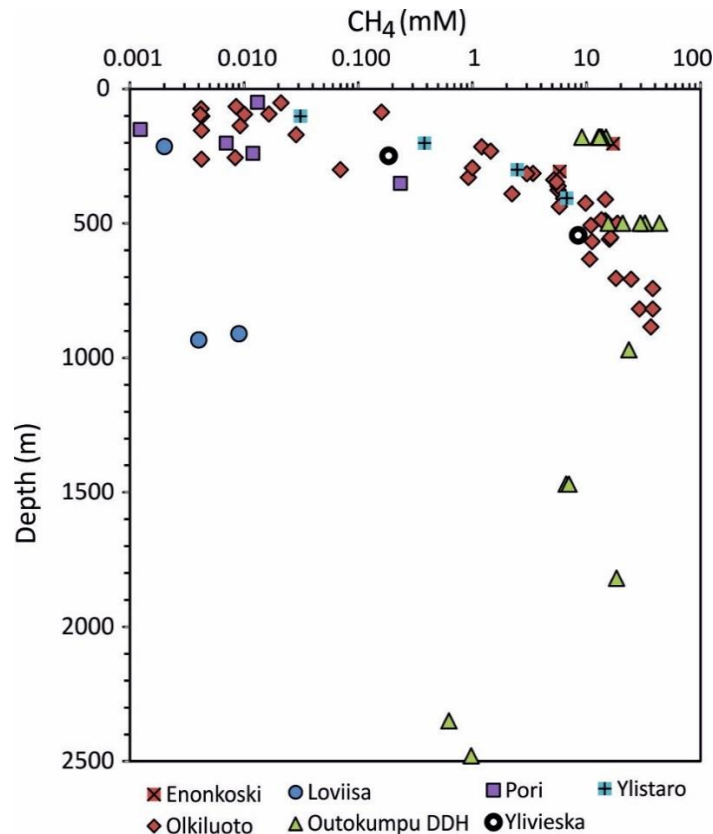


Figure 3: The concentration of methane with depth at seven different study sites within the Fennoscandian Shield in Finland.

Three different sources of methane can be recognised with the upper crust: 1) Thermogenic from the decay of organic matter at increased temperature and pressure, 2) microbial produced by methanogenic archaea, and 3) abiotic (or abiogenic) from chemical reactions between inorganic carbon (such as CO₂, CO or graphite) and H₂ [e.g. 14]. Two most widely utilised geochemical criteria for distinguishing microbial methane are the isotopic composition enriched in ¹²C, which originates from the weaker bond strength in carbon compounds compared to ¹³C and thus preferential use of the more easily available isotope, and low amount of other hydrocarbons, which generally are not produced by microorganisms [15]. These simple principles can, however, be challenged in deep groundwater environments due to the initially ¹²C-poor carbon pool, closed system conditions, mixing of methane from different sources, and effective carbon recycling by microbial communities consisting of species capable of producing and oxidising methane by using various pathways. For example, deep bedrock groundwater in Finland, many of which are known to host methanogenic microbes [13,14], commonly reveal carbon isotopic signatures more enriched in ¹³C than would be expected for typical microbial methane (Fig. 4).

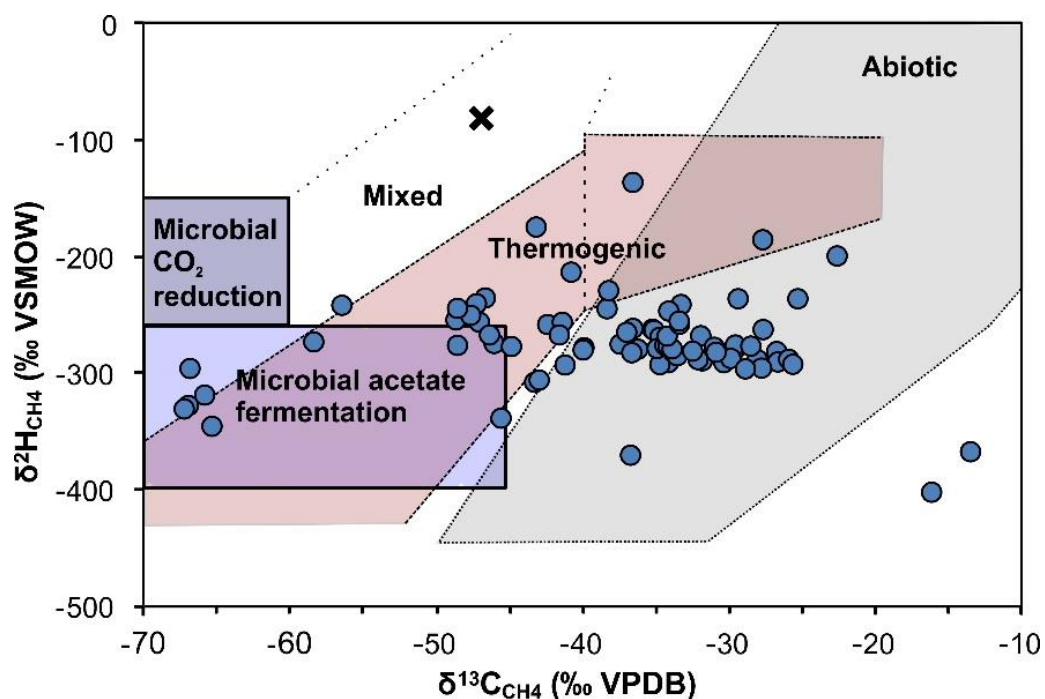


Figure 4: Suggested genetic classification of hydrocarbons based on hydrogen and carbon isotopic composition of methane [16]. Data from deep groundwater in Finland are shown as blue circles. Isotopic composition of methane in the Earth's atmosphere [17], marked with X, is shown for comparison. Enrichment in ¹³C is common and only few samples represent traditional microbial methane. A trend where $\delta^{13}C_{CH_4}$ increases while $\delta^2H_{CH_4}$ remains the same has been related to substrate depletion while the increase in both values is indicative of methane oxidation [15].

Within the sites showed in Figure 1, the CH₄/C₂₊ ratio varies from 3 (at Palmottu) to 7350 (at Liminka) with a median value of 113. Majority of the samples thus seem to represent gas with major thermogenic or abiotic component or have been affected by oxidation of methane.

3.1.2 Hydrogen

As a general feature, the concentration of hydrogen increases with depth in bedrock groundwater in Finland (Fig. 5). Major sources for hydrogen in the upper crust include radiolysis of water [18,19], water-rock reactions such as serpentinization [20,21,22] and microbial activity [23]. Important hydrogen consuming processes include methane production, either microbial or abiotic, and sulphate reduction.

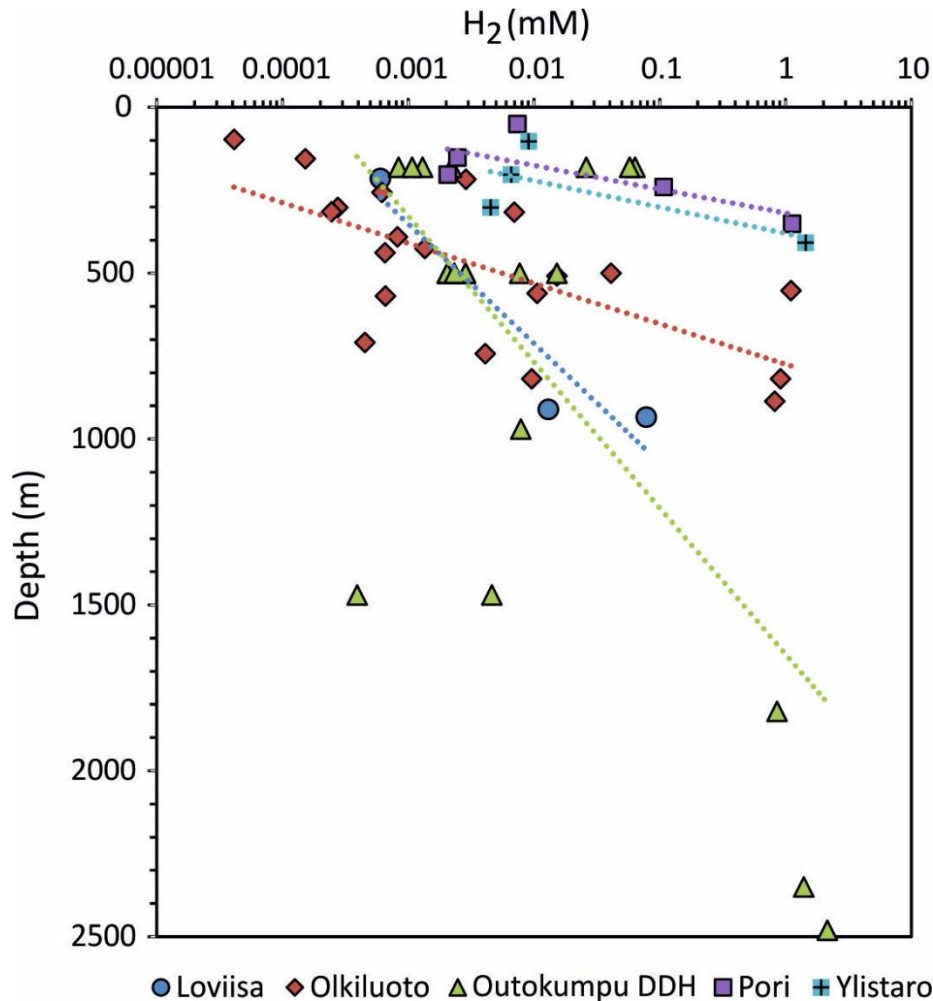


Figure 5: The concentration of hydrogen with depth at five different study sites within the Fennoscandian Shield in Finland.

4 Inventory of reducing gases in deep groundwater of Sweden

The information on reducing gases in deep groundwater is limited to a relatively small data set compared to what is known for Finland. During the site investigations for a Swedish SNF repository, 29 samples distributed over 2 locations were analysed, the Ävrö-Laxemar and the Forsmark areas [24, 25].

4.1 General features

Based on dissolved gas composition, just one of the two types of deep groundwater found in Finland can be distinguished, the nitrogen dominated groundwater type. Other commonly detected gases include H_2 , He, Ar and occasionally CO_2 . Hydrocarbons up to propane have been found in the more recent studies but their concentrations are often minor compared to methane. Oxygen is also often detected, although mainly result from contamination with air during extraction and analysis. Both Swedish sites are dominated by granitic rocks which is in line with observations in Finland that methane dominated groundwaters are associated with metasedimentary rocks

4.1.1 Methane

Methane shows no clear increase or decrease over the investigated depth range (Fig 6). The values found are generally much lower than what has been found in Finland at large depths in Olkiluoto and Outokumpu (Fig 3). The Swedish data are similar to what was found in Loviisa and Pori.

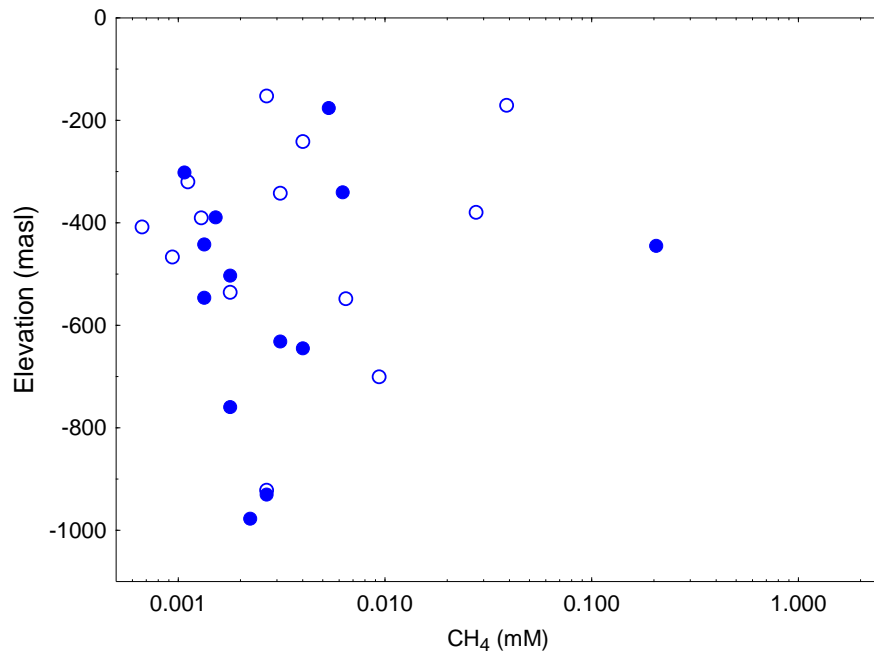


Figure 6. The concentration of methane with depth at two different study sites within the Fennoscandian Shield in Sweden. Filled symbols represent Forsmark and open symbols represent Ävrö-Laxemar. (masl = meter above sea level).

4.1.2 Hydrogen

Hydrogen, just like methane, shows no clear increase or decrease over the investigated depth range (Fig 7). The values found are generally much lower and the range is narrower than what has been found in Finland (Fig 5).

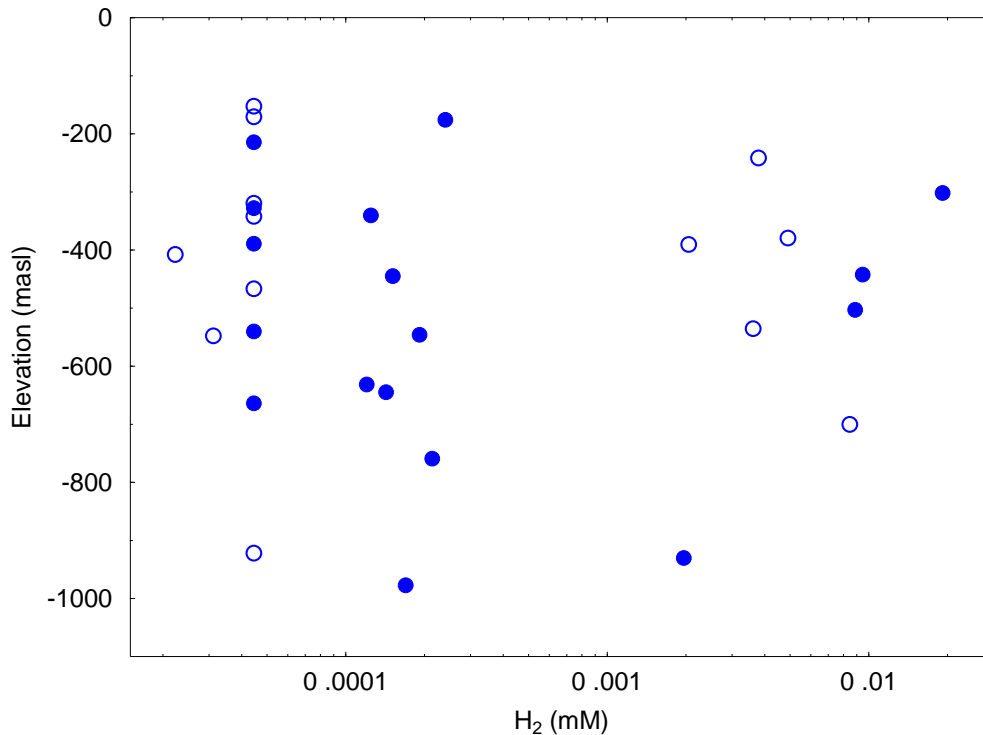


Figure 7. The concentration of hydrogen with depth at two different study sites within the Fennoscandian Shield in Sweden. Filled symbols represent Forsmark and open symbols represent Ävrö-Laxemar. (masl = meter above sea level).

5 Conclusions

In the context of microbiological risks related to SNF waste disposal, the geochemistry of gases in deep groundwater is an integral part of the determination of geochemical constraints of biological activity at disposal depths. Data on gas compositions and concentrations do exist from several separate locations in Finland and two locations in Sweden. Site to site as well as depth dependent variation should be taken into account in Finland and could possibly be used to predict changes related to for example different rock types. For Sweden, there is a need to increase the number of gas samples from the selected site in Forsmark and also the number of sites and geological types for comparisons and increased understanding of generation and transport of reducing gases in deep geological formations.

6 Acknowledgements

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