



DELIVERABLE D2.3

Interim report on deep gases and sulphur compounds as biogeochemical energy sources in crystalline rock

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Publishable Summary

Geochemical data on sulphur compounds and dissolved gases from deep drill holes and deep mines in Finland were compiled to a database. Data is used as a background of MIND work package 2, in which microbial production of sulphide in the geosphere will be assessed from the point of view of canister corrosion. This report summarizes the present knowledge on the mode of occurrence of sulphur compounds and dissolved gases in groundwaters of crystalline bedrock. Prerequisites of microbial sulphate reduction are discussed based on the data available.

The most abundant sulphur compound in deep groundwaters is sulphate (SO_4). A distinct sulphate reduction zone is often observed, situating at different depths at different sites but most often above 400 m. Below the reduction zone sulphate concentration drop abruptly, and a transient sulphide-rich zone may exist. Sulphide concentrations observed are typically below 10^{-5} M, indicating that solubility of iron sulphide controls the concentration.

Methane is the most abundant dissolved gas, possibly acting as an electron donor for microbial sulphate reduction. Small amount of hydrogen is often observed in deep water samples and much larger amounts can be found in porewater of rocks. In some conditions sulphate shows distinct stability in deep anoxic systems, existing together with high amounts of methane. This was observed to be more common in groundwaters hosted by basic rocks (e.g. gabbro), which are generally considered to be less permeable than common granites and gneisses. Anomalous, high sulphate/high methane groundwater type was found in Jotnian metamorphosed clay rock of Muhos formation.

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1 Introduction

One of the objectives of WP2 of MIND is to quantify the contribution of microbially produced sulphide in the geosphere, buffer and backfill. Geosphere around the repository forms the outer boundary of the near-field, in which the buffer-backfill system has the target to protect the waste containers. Iron or copper metals are considered as canister materials. Both of these elements have strong affinities to form sulphide compounds in geological environment. Sulphur is also one of the key elements of microbes living deep in the bedrock.

For the safe geological disposal of nuclear waste, sulphidic corrosion of copper is an important process to be evaluated in detail for copper canister. Neither can sulphide formation in corrosion of metallic iron be ruled out, but competitive reaction paths and reaction products are possible. Quantification of the canister corrosion requires that the constraints of microbially induced sulphide corrosion are well understood and are based on firm knowledge on the geochemical conditions at the disposal depth.

Thermodynamic limitations do not rule out reaction between metallic copper and sulphide, but the controlling processes are availability, solubility and mass transfer of sulphide in geosphere. Sulphide concentration and availability in the bedrock is not a sufficient limiting factor alone, because microbial studies of deep bedrock environments have demonstrated the importance of microbial reduction of sulphate to sulphide as a viable process in anoxic conditions. Additionally, in oxic conditions microbes catalyse oxidation of sulphide minerals to soluble and mobile aqueous sulphates. In other words, sulphur system constitutes an important reduction-oxidation system in natural conditions: sulphur in sulphate molecule provides all six outer electrons to oxygen, whereas sulphide is the stable form with a full eight-electron cloud. Sulphur system constitutes a complex redox system, in which the possible roles of various electron acceptors and donors must be accounted for. Energy released in these electron transfer processes is an important driving force of microbial life in the deep dark bio-geosphere.

The aim of this interim report is describe and quantify the key geochemical properties of the crystalline bedrock with respect to the longevity of waste canisters. The report summarizes the present knowledge on the mode of occurrence of sulphur compounds in groundwaters of the Finnish crystalline bedrock. This report has the main emphasis on sulphur geochemistry, thus complementing the report "Inventory of reducing gases" by Kietäväinen & Pedersen 2016 (D2.1). Potential role of rock matrix fluids for sulphide production was also identified as an important issue, and results of pore gas extraction experiments using rock samples from Olkiluoto are presented in this report.

2 Sampling sites and database

Interest in deep bedrock hydrogeochemistry arose parallel to the site selection program for nuclear waste disposal in Finland. A nationwide survey of deep hydrogeochemistry started in mid-80's at the Geological Survey of Finland (GTK). Deep drill holes ($\approx 300 - 1200$ m) originally targeting for ore exploration were sampled mainly using the so called "tube sampler". The advantage of the sampling technique was that the continuous water column retrieved from the drill hole could be divided to sub-samples as a function of depth. After the first nation-wide survey, Outokumpu area in eastern Finland was chosen for targeted studies, because deep drill holes were available in abundance in the old mining district.

The Palmottu U-Th mineralization in Nummi-Pusula, SW Finland was originally a target of uranium exploration, and after 1987 gradually became one of the main natural analogue sites providing data on uranium geochemistry and migration in the crystalline bedrock of the Fennoscandian Shield (Blomqvist et al. 2000). Hydrogeochemical data of Palmottu were summarized in Kaija et al. (1998). Data from Palmottu are mainly limited to the depth range of about 0 – 300 m, but is very detailed in terms of hydrogeochemical variation within the bedrock block studied ($\approx 200 \times 300 \times 300$ m³).

Outokumpu become once again a main target of hydrogeochemical research after that a 2500 m deep research drill hole was completed in 2005. The new drillhole proved to be an excellent research target for bio-hydrogeochemical studies of the deep crystalline rock. Results of these studies are summarized by Kietäväinen (2017). Pyhäsalmi mine in central Finland has provided another possibility to study hydrogeochemistry, gases and microbes deep in crystalline rock (Miettinen et al. 2016).

Site selection program conducted by the nuclear power industry in Finland led to the selection of four sites for site characterisation (Kivetty, Romuvaara, Olkiluoto and Hästholmen), of which Olkiluoto was chosen as the site for detailed characterisation, and further considered as the candidate site for disposal. Deep groundwater data (≈ 1000 m) is available from all those sites and from some additional sites (Lavia, Veitsivaara, Sievi) included in the earlier phases of study.

Posiva Oy has studied thoroughly the hydrogeochemical conditions in Olkiluoto during the last 20 years. Representative data obtained in those studies have been published in Posiva's working reports and publications. We have included published data from Olkiluoto and earlier site characterization data (Kivetty, Romuvaara etc.) to our database, but data of GTK and that of Posiva are considered complementary to each other.

All hydrogeochemical data are compiled to an Excel database, which is continuously updated and available for MIND project partners.

3 Dissolved gases in groundwaters

3.1 Gas composition and lithology

Total number of chemical analyses of dissolved gas phase in groundwaters of crystalline rock are much less than those of dissolved ionic components. Location of the deep gas sampling sites in Finland are shown in Figure 1 together with a simplified lithological map. Nurmi et al. (1988) reported compositions of deep gas samples from four places in Finland. Two of the sites were of special interest, Outokumpu (DH 741, Sukkulansalo) and Liminka (R-60). The former is drilled in mica schist – gneiss dominated Svecokarelian crystalline complex to dissect the ore-critical Outokumpu formation composing of serpentinites, carbonate rocks and black schist, whereas the other is situated in an unmetamorphosed middle Proterozoic Jotnian siltstone/clayrock. The siltstone is a unique rock formation in Finland and it is actually more a clay-type rock than typical crystalline rock of the Fennoscandian Shield. Surficial emanations of methane from the siltstone have been known for long time, they have been even utilized in small scale for household purposes.

Sherwood-Lollar (1993a,b) made a systematic study of deep gases in Shield areas including several Finnish sites. Sampling sites comprised several drillholes within the “Outokumpu type” of lithologies (Outokumpu-Juuka area), Enonkoski Ni-Cu mine hosted by an ultramafic complex in graphite-rich metasedimentary environment, Ylivieska mafic-ultramafic intrusion. With the exception of the deep drillhole in Pori sandstone, all drillholes were situated in mafic rock environments or graphite-rich metapelites.

The two most extensively studied “deep gas” sites in Finland are Olkiluoto planned repository site and Outokumpu Cu-district in eastern Finland. They show similar characteristics in chemical and isotopic composition as well as gas concentrations. Pyhäsalmi Cu-Zn-sulphide deposit is hosted by metavolcanic rock complex. Kivetty and Hästholmen represents Proterozoic granitic rocks, and Romuvaara is situated within Archean granitoids.

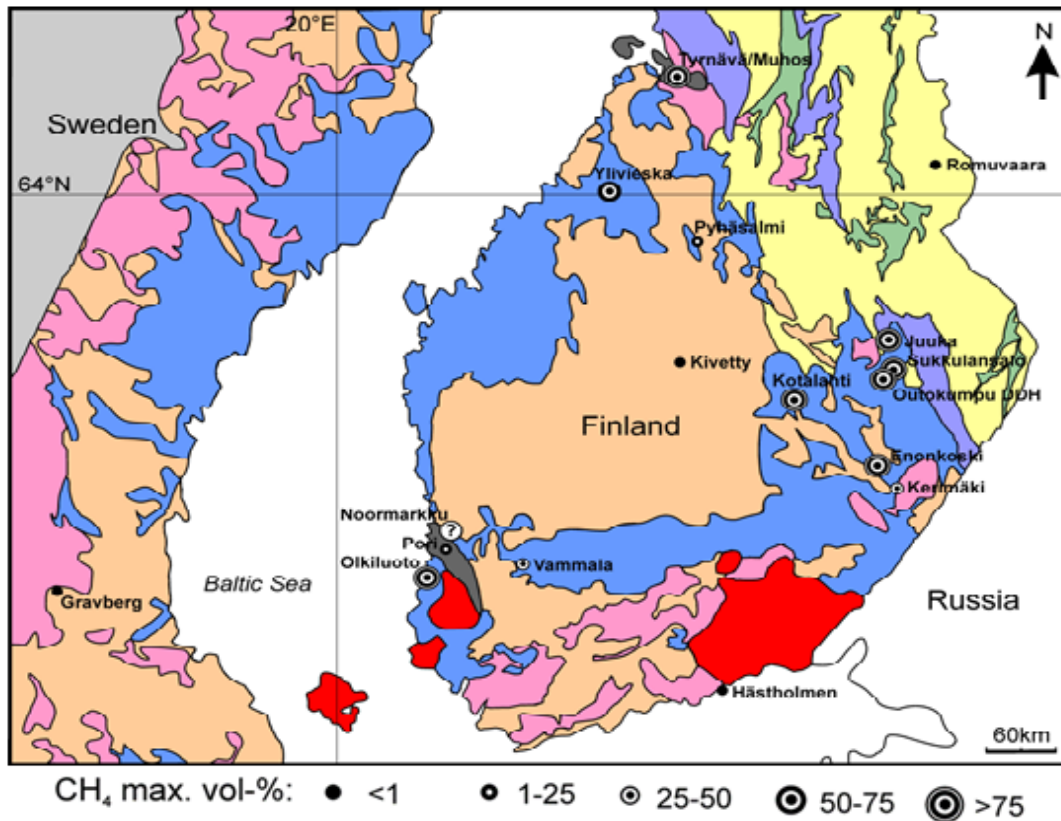


Figure 1. Deep gas sampling sites, methane percentages and associated lithology: blue = Svecofennian arc complex and Karelian domain rocks with abundant argillaceous (pelitic) source rock; beige, pink = Svecofennian granitoids and migmatites; red = post-orogenic granitic intrusions; dark grey = Jotnian sandstone and clayrock; yellow = Archean granitoids; Green = greenstones (Modified from Kietäväinen et al. 2017).

3.2 Gas concentrations and solubility

Main dissolved gas components of groundwaters in crystalline rocks are nitrogen and methane. Gas volumes and gas-phase compositions determined in Outokumpu and Pyhäsalmi are given in Figure 2. Nitrogen forms a chemically stable covalent molecule N_2 , having insignificant tendency to act as electron acceptor or donor without microbial catalysis. Dissolved nitrogen can be a major component both in near-surface oxic waters as in deep anoxic waters together with methane. Methane is often a major component of dissolved gases in crystalline rocks, concentration of methane increases typically with depth and with increasing salinity of waters (Figure 3). Evidently, hydrogen is the most reactive reducing gas component of groundwaters, but the analyzed concentrations remain at < 2 mM in groundwaters of crystalline rock. Helium formed in uranium and thorium series decay may be a major component of dissolved gas phase in Precambrian crystalline rocks.

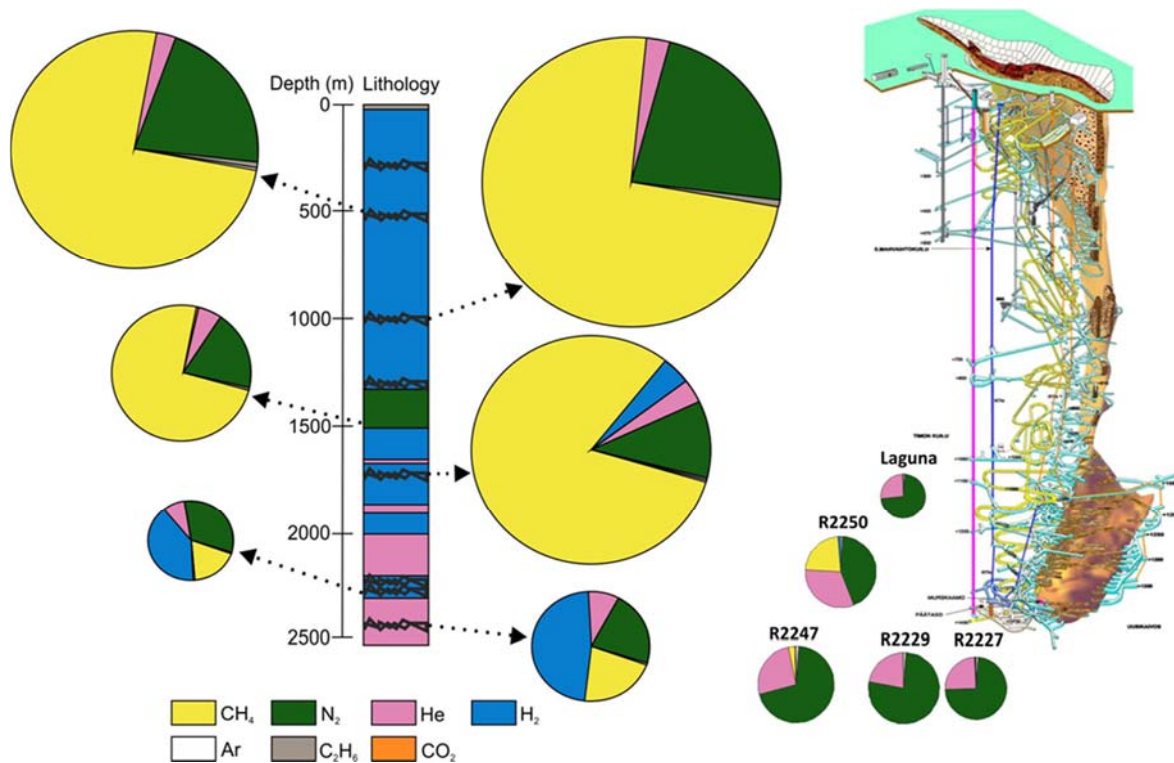


Figure 2. Gas concentrations and compositions in Outokumpu deep drillhole and Pyhäsalmi mine. Areas of pies represent total gas volumes (largest ≈ 1 L/L at NTP)

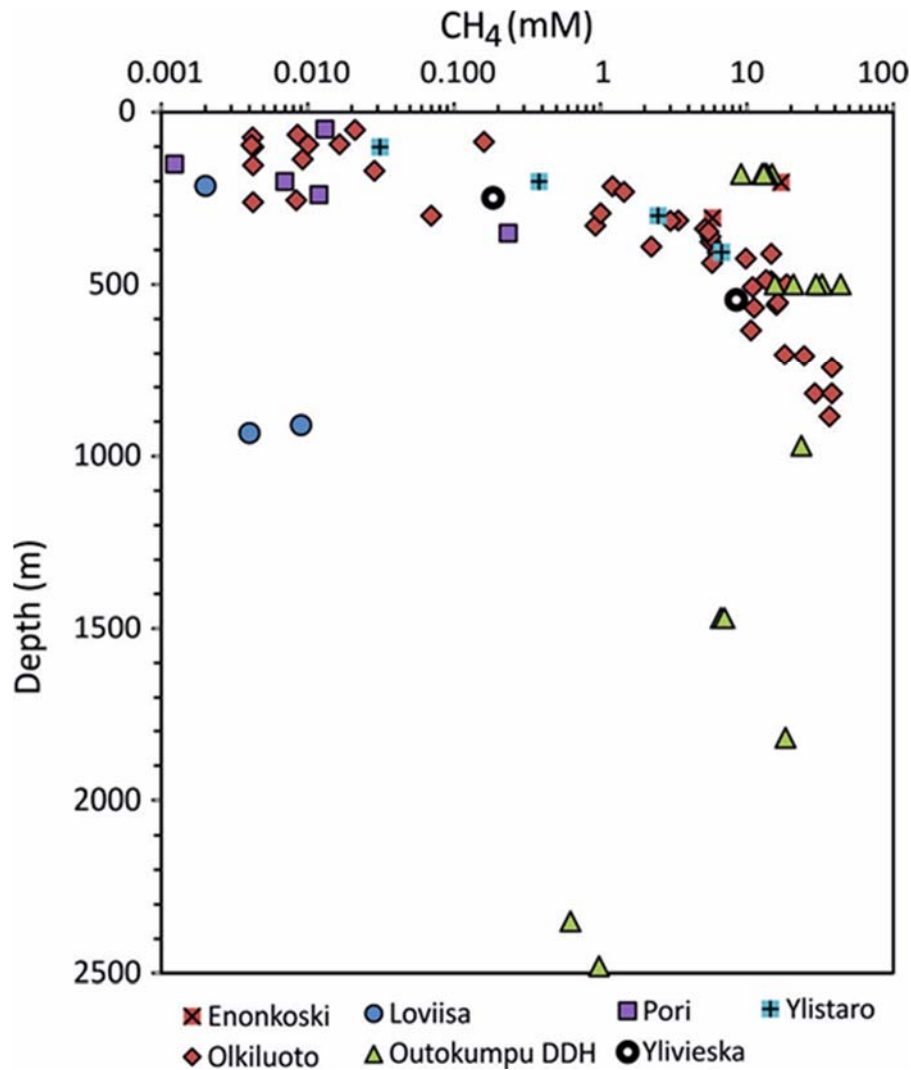


Figure 3: The concentration of methane with depth at seven different study sites within the Fennoscandian Shield in Finland.

Solubility of gases in groundwater is mainly a function of (hydrostatic) pressure, but temperature and salinity become more important in deep conditions. This is demonstrated in Figure 4, based on data from Outokumpu deep drillhole. Methane solubility increases approximately in a linear way down to more than 1000 metres, below which effects of temperature and salinity become gradually more important. It was estimated that methane solubility limit is exceeded at about 180 m in the Outokumpu deep drillhole. Continuous bubbling of gases on the water table is a characteristic feature of that drillhole.

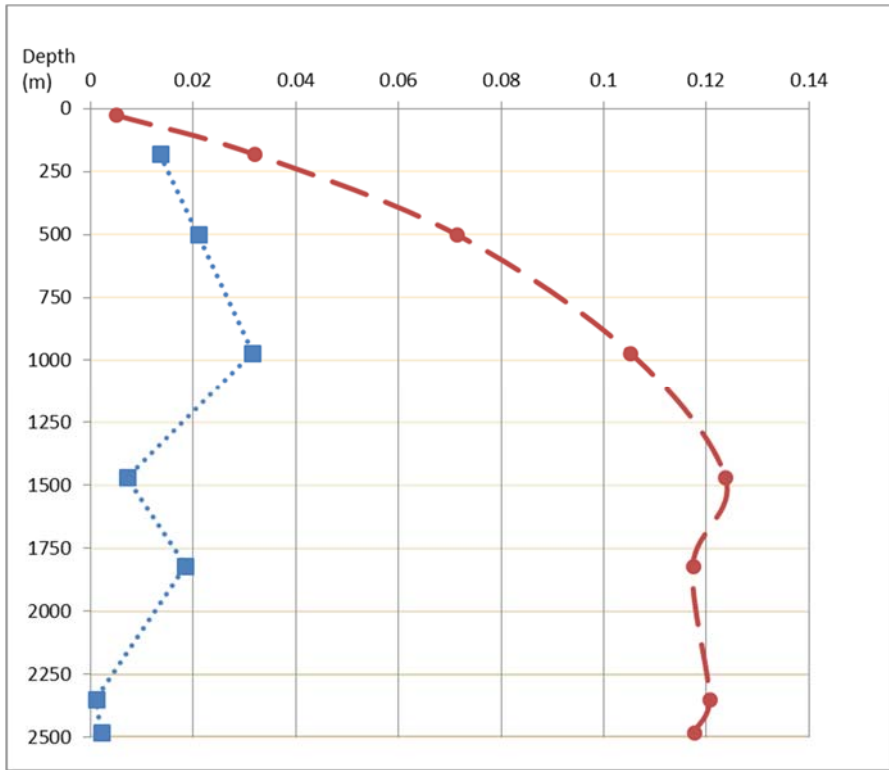


Figure 4: Observed concentrations (M) of methane (blue squares) and calculated solubility of methane in Outokumpu deep drillhole (Heikkinen 2016).

4 Dissolved gases in pore water

Gases can migrate in pores of rocks. It was, therefore deemed important to study the composition of gases in porewater. Drill cores from two different drillholes were supplied in kind from Posiva Oy. The budgets of H₂ and CH₄ in these cores were analysed. This budget is needed to resolve the key issue on long-term sulphide production rates in the geosphere. While the concentrations of these gases are reasonably well documented in groundwater, the amount in the host rock matrix was, previously, unknown.

4.1 Method

Drillcores were immediately after drilling put in gas-tight brass tubes as shown in Figure 5. The emitted gas was withdrawn in intervals and analysed for H₂ and CH₄ content. The sum of each gas amount was calculated when no more gas was emitted from the cores. Gases were analysed on gas chromatographs.

Five drill cores from the ONK-KR17 drillhole at approximately 400 m depth in the ONKALO tunnel were incubated during 160 days. Five drill cores from different depths of drillhole OL-KR58 where incubated for 217 days. The cores were distributed over the following drillhole lengths: 227 m, 501 m, 564 m, 691 m and 1092 m.



Figure 5. Brass tubes used for inoculation and analysis of gases emitted from porewater in drillcores.

4.2 Results

The amount of gases emitted from the cores were calculated as mL gas per L of pore water assuming a porewater volume of 0.5%. There were on average 18 mL/L H₂ and 31 mL/L CH₄ in the porewater of the ONK-KR17 cores (Table 1). The amount of hydrogen and methane increased with increasing depth in OL-KR58 (Table 2).

Table 1. Total amount of gases per L of pore water from ONK-KR17 drillcores.

Drill core number	H ₂ mM	CH ₄ mM
1	1.33	1.54
2	0.12	1.42
3	1.29	2.04
4	0.50	0.75
5	0.54	0.63
Average	0.75	1.29

Table 2. Total amount of gases per L of pore water from OL-KR58 drillcores.

Drill hole length (m)	H ₂ mM	CH ₄ mM
227	0.00	0.46
501	0.17	1.25
564	0.08	2.83
691	0.04	3.88
1092	0.43	3.54

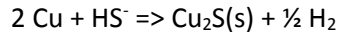
4.3 Implications

While the concentration of CH₄ was within the range of what is found in deep groundwater (Figure 3), H₂ was much higher. H₂ is rapidly used by sulphate reducing bacteria (Pedersen 2012a, b), acetogens and methanogens in deep groundwater. Therefore, any H₂ that leaves porewater to groundwater by diffusion has a great chance to be grazed down to concentrations below Km for H₂ (approximately 1 μM).

5 Sulphur compounds in crystalline rock

5.1 Significance for safe disposal

Sulphide (H_2S , HS^- , S^{2-}) is the most important factor possibly affecting the integrity of metallic copper in anoxic conditions, because the reaction between copper metal and sulphide causes formation of cuprous sulphide. Hydrogen ion from sulphide or water may be the electron acceptor:



Both copper and iron have high affinities to form sulphides, iron sulphides are the most important hosts of sulphide sulphur in earth's crust.

5.2 Sulphide sources, sinks and solubility

Sulphide concentrations in groundwaters are typically low because of the low solubility, i.e. precipitation of sulphide minerals or amorphous precipitates. The two most important iron sulphide minerals pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S) have clearly dissimilar dissolution characteristics: pyrite is practically insoluble in anoxic conditions. It existed as a detrital residue together with uraninite in Archean – early Proterozoic anoxically weathered environments (e.g. Witwaterstrand), but is rapidly oxidized in oxic conditions in the presence of iron and sulphur oxidizing microbes.

Contrary to the disulphides (pyrite, marcasite), iron monosulphide polymorphs dissolve in ionic forms. Pyrrhotite (Fe_{1-x}S) is an important rock forming iron monosulphide having several polytypes (monoclinic-rhombic). Tetragonal mackinawite exist both as Ni-bearing primary mineral and as a secondary metastable sulphidisation product. Rapid precipitation in sulphide-iron solution may also lead to the formation of an amorphous precipitate. Iron monosulphides are usually non-stoichiometric (iron-deficient), but the solubility equation may be simplified as:



From which solubility constraint for dissolved sulphide can be expressed as a function of pH and iron concentration, e.g.

$$\log(\text{HS}^-) = \log K_{\text{sp}} - \log(\text{Fe}^{2+}) - \text{pH}$$

Making a further simplification ($\log(\text{HS}^-) = \log(\text{Fe}^{2+})$), solubility constraint for sulphide can be presented as a line on a graph (sulphide vs. pH).

Analysis of dissolved sulphide from field samples is complicated because of the poor preservation of dissolved sulphide. Consequently, GTK has sulphide data available only from the main study sites Outokumpu and Pyhäsalmi. These sulphide concentrations are plotted together with published data from Olkiluoto as a function of pH in Figure 6. Concentrations were also over-estimated by plotting the detection limit value, if the actual concentration was below that value.

Figure 6 indicates that sulphide concentrations are typically at the level determined by iron sulphide solubility, decreasing with increasing pH. However, very deep samples (> 1500 m) from Outokumpu and Pyhäsalmi indicate "supersaturation". The apparent discrepancy can be due to lack of dissolved ferrous iron in these waters (pH > 8.5), i.e. the assumption made for the graph is not valid.

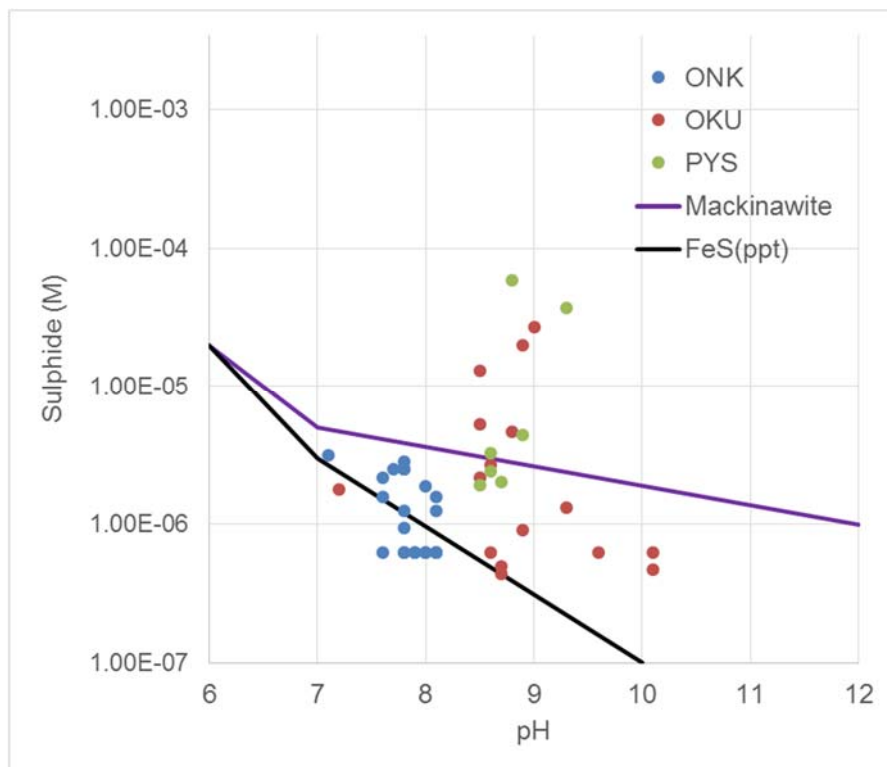


Figure 6. Sulphide concentrations as a function of pH in ONKALO (Olkiluoto), Outokumpu and Pyhäsalmi mine waters. Solid lines indicate the solubility limits for mackinawite and fresh iron monosulphide as the solubility-controlling phases, respectively. Assumptions: sulphide concentration \approx ferrous iron concentration; predominant sulphide species is H_2S at $pH < 7$; HS^- at $pH > 7$. Lines are constructed according to Ahonen (1995).

5.3 Sulphur: redox system

Sulphate is the most soluble stable species of sulphur in groundwaters, whereas sulphide is the stable and most common rock-forming species typically associated with iron, copper and other base metals. Reduced sulphur is an essential component of living organisms as a building block of proteins and other macromolecules. Redox transitions of sulphur compounds also provide energetic premises for sulphide oxidizing and sulphate reducing microbes depending on the general redox conditions of the environment.

Definition of the environmental parameter redox (reduction-oxidation potential) is not a straightforward task in most geological environments, and particularly difficult in fractured crystalline rock. The electrochemical approach using inert electrode potential (expressed as Eh or pE) as determinant of the system redox state often fails to produce unambiguous results in the nernstian sense. Berner (1981) proposed a geochemical classification of redox environments defined by characteristic redox processes in sedimentary systems (Figure 7). Figure shows schematically the redox sequence commonly observed cored seabed sediments within a depth range of metres to tens of metres: near-surface oxic system \Rightarrow sub-oxic, possibly with slightly elevated Fe^{2+} \Rightarrow sulphate reduction leading to sulphidic zone \Rightarrow deepest methanic zone, possibly with H_2 .

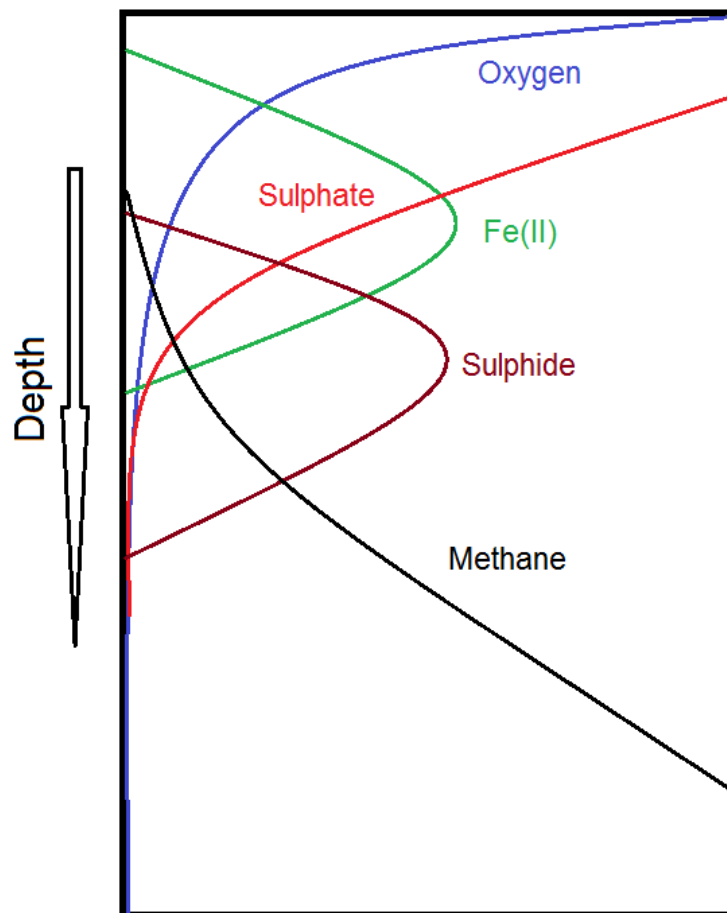


Figure 7. Schematic redox sequence in sedimentary environments after Berner (1981).

The same redox zones can be observed in crystalline rock, but the depth scale is different. Figures 8 and 9 show the general trend of sulphate concentrations as a function of depth observed at Finnish crystalline sites. Sulphate reduction front is typically at the depth of about 300 – 400 m, which is in accordance with the result from Olkiluoto (presented in details by Wersin et al. 2014).

However, as indicated by Figure 9, the depth of sulphate reduction front may also vary considerably or sulphate reduction may be inhibited. The reasons may be due to lithology and/or rock properties affecting hydrodynamics. Inverse correlation between methane and sulphate concentrations is not necessarily true, as in Juuka116 having highest sulphate at the depth of 1000 m in very saline methane-rich water. Contribution of sulphide oxidation may be speculated in case of samples from Pyhäsalmi mine, but waters collected at the depth level 1430 m in Pyhäsalmi mine are actually coming from much deeper bedrock levels in drillholes reaching the depth of about 2500 m. Samples “Kolari” and “Leppävirta” are also mine waters.

A conspicuous set of samples in Figure 9 is that denoted “Liminka”, the drillhole where high methane was observed by Nurmi et al (1988) in the lithologically very special clayrock environment. Petrophysical and hydrogeological properties of this rock remain to be studied later in more details, but evidently the rock properties differ clearly from those of the typical crystalline rocks.

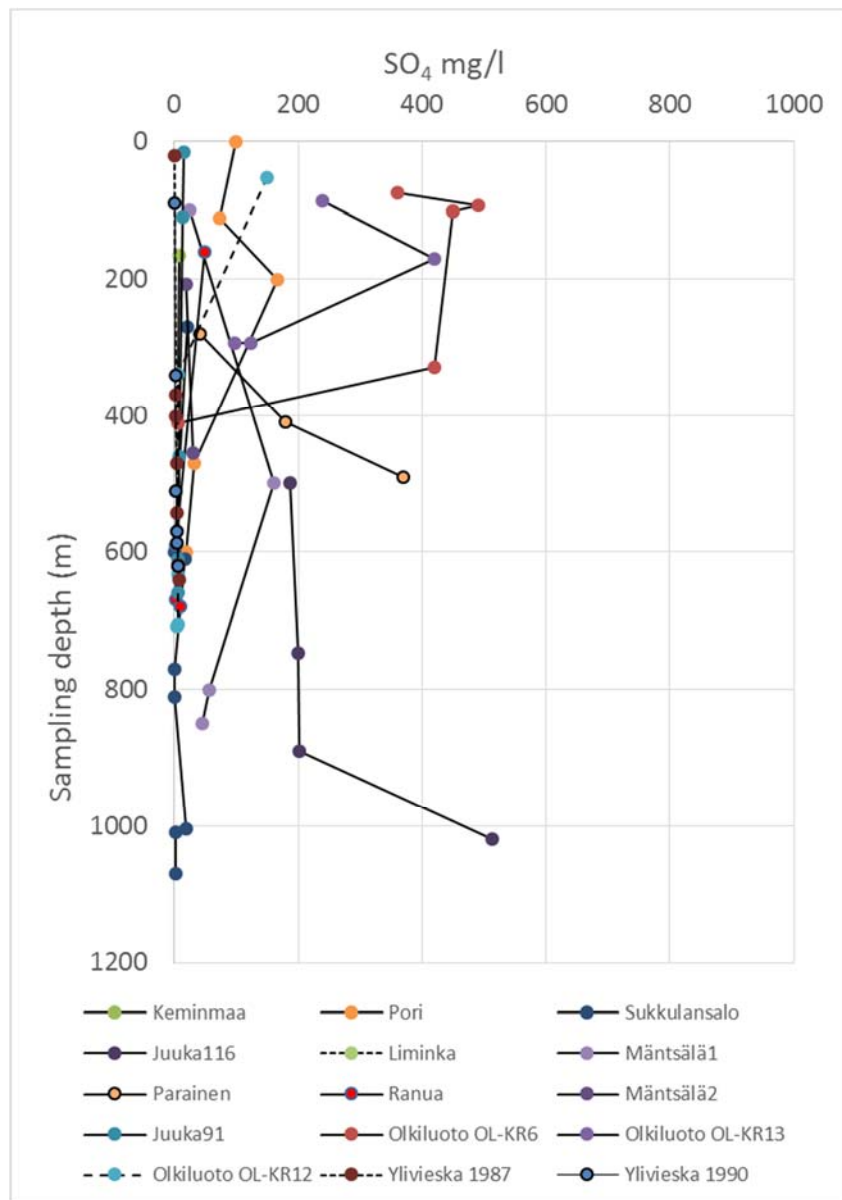


Figure 8. Sulphate concentrations as a function of depth observed in different localities in Finland.

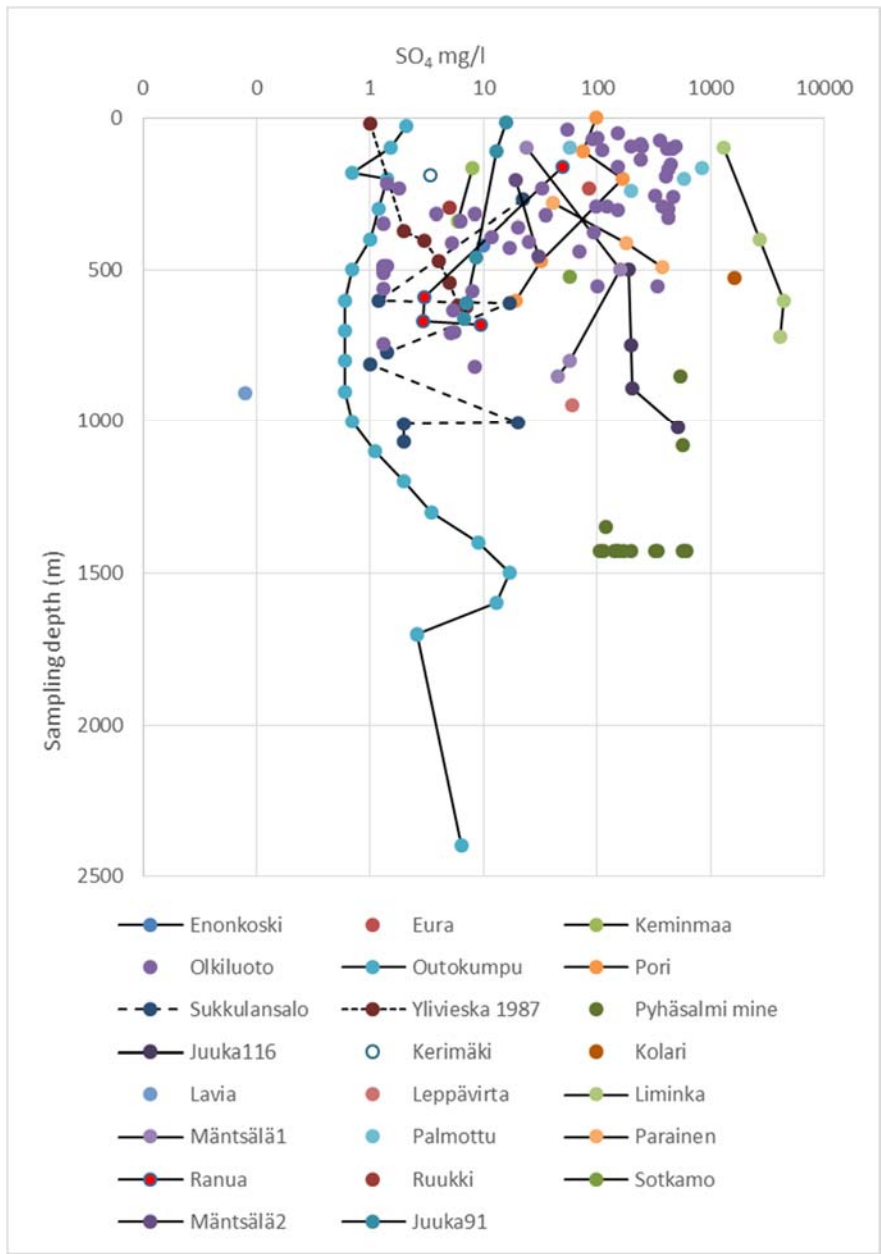


Figure 9. Sulphate concentrations as a function of depth observed in different localities in Finland.

Sulphate and sulphide concentrations in Outokumpu deep drillhole are very low through the uppermost one kilometre, but sulphate increases slightly at the depth range of 1300 – 1500 m (Figure 10). Increased sulphate correlates with increased Mg concentration, and they may have a common lithological control. The rock unit at that depth is the Outokumpu ophiolite, a rock sequence representing ancient oceanic crust. Sulphate reduction takes place at the depth of about 1700 m, and sulphate reduction zone is associated with a sulphidic front.

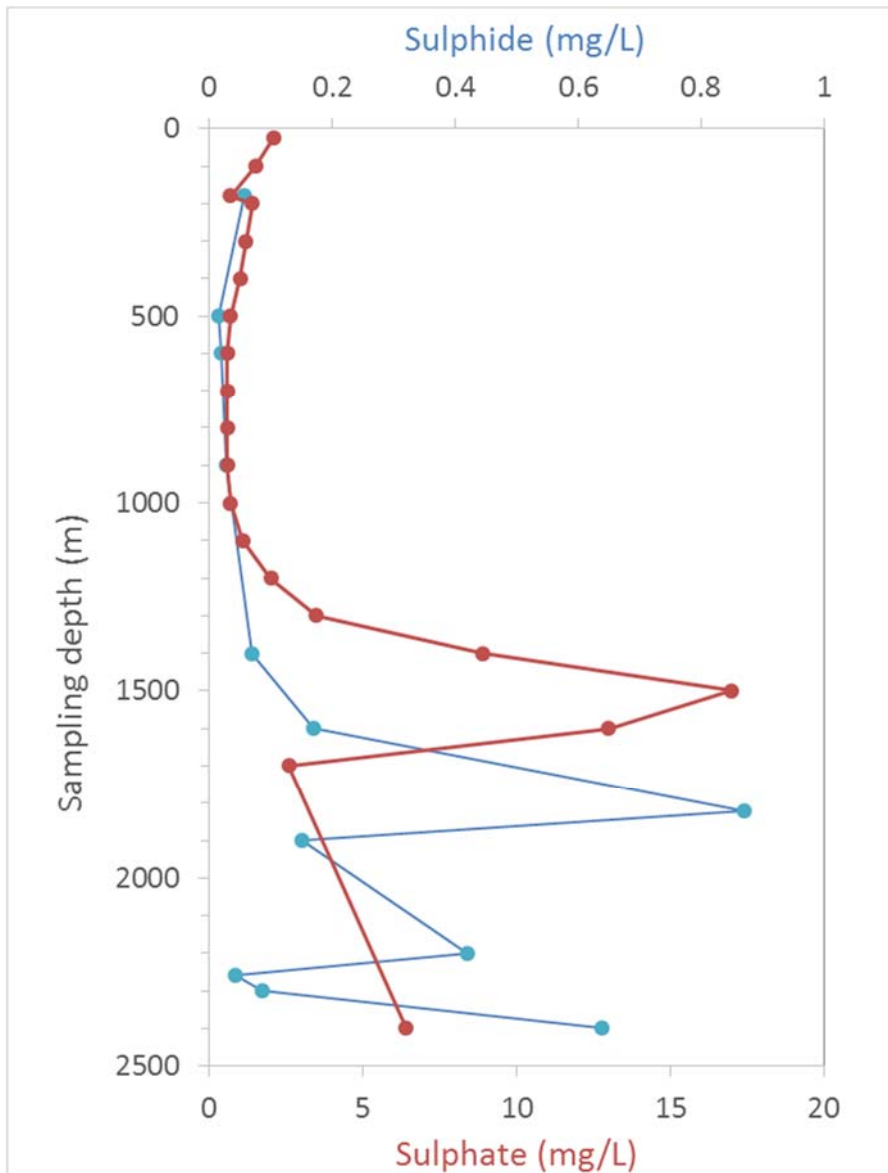


Figure 10. Sulphate-sulphide concentration profiles in Outokumpu deep drillhole

Detailed site characterization has shown that fracture waters in crystalline rock may have large spatial variability, indicating that waters are not completely mixed forming large homogeneous bodies. Detailed hydrogeochemical studies of Palmottu revealed the presence of brackish Na-SO₄ water type between upper fresh bicarbonate water and lower Na-Cl dominated water (Figure 11). A striking feature of the sulphate-type water was the anomalous light stable isotope content, indicating recharge temperatures clearly below the present ones. Similar water type has also been observed at Olkiluoto. A plausible explanation for the origin of this water type is mixing between cold glacial melt water and sulphate-rich saline water of Litorina Sea (Pitkänen et al. 1996).

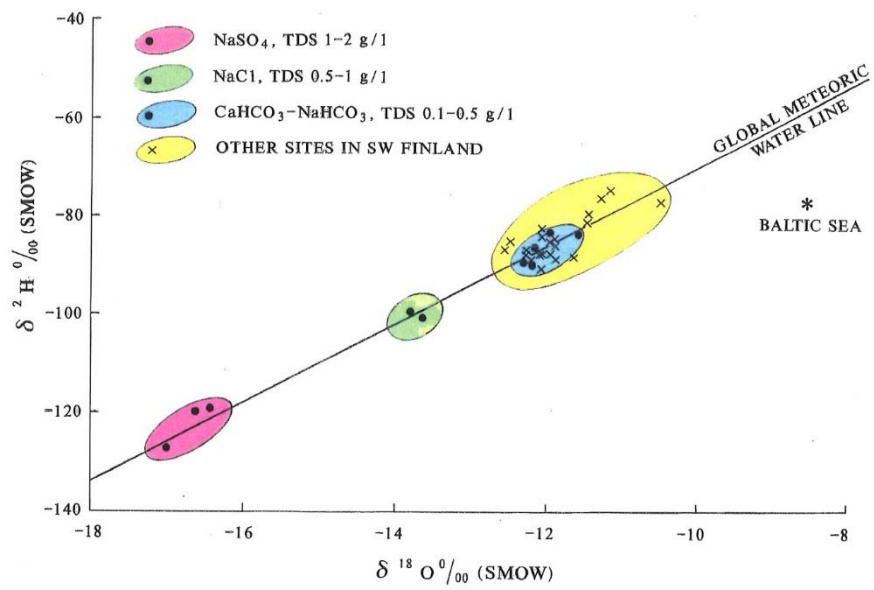


Figure 11. Stable isotopes of Palmottu groundwater (Blomqvist et al. 1995).

6 Discussion

The aim of MIND task 2.1. is to estimate the microbial sulphide production in the geosphere. In this context "geosphere" refers to the uppermost continental crust to the depth range relevant for considerations in geological disposal studies. In practice, geochemical sampling sites deeper than about 2.5 kilometres are very few. However, sampling sites reaching the depth of about 1 km are numerous, allowing fairly reliable general characterization of the hydrogeochemical conditions of the deep crystalline bedrock.

For the safety case, with respect to the long-term performance of the metals canister, sulphide concentration and supply around the repository are the key questions. Sulphide is generally considered as a dissolved species, for which a well-defined solubility constraint can be applied. Data presented in this report shows that sulphide concentration may be higher than that predicted by equilibrium solubility of iron sulphides. This is evidently due to sulphide production in sulphate reduction process in iron-deficient conditions. However, the process is a transient with respect to space, i.e. is manifested in a reduction zone.

Depth of the sulphate reduction zone varies in different localities in crystalline rock, but typically it lies within the uppermost hundreds of metres, as in Olkiluoto. However, in some conditions sulphate shows distinct stability in deep anoxic systems, existing together with high amounts of methane. This was observed to be more common in groundwaters hosted by basic rocks (e.g. gabbro), which are generally considered to be less permeable than common granites and gneisses. Anomalous, high sulphate/high methane groundwater type was found in Jotnian metamorphosed clay rock of Muhos formation. The formation may be considered more representative to a clay-rock environment than the typical crystalline environment.

Sulphate reduction requires the presence of a reducing compound, i.e. electron donor. Organic compounds are an essential component of the near-surface anoxic sedimentary systems, in which sulphate reduction typically takes place. Acetate and lactate are known to be effective electron donors that are frequently used in experimental studies of microbial sulphate reduction. A key question of sulphate reduction deep in the bedrock is the supply/replenishment of the reducing power: continuous supply of organic material or reducing power provided by inorganic compounds, mainly hydrogen and methane? Molecular hydrogen is a very strong electron acceptor, and generally considered as a very potential driving force of the deep life, but the observed concentrations are low compared to methane.

Considerable attention has been paid to the interaction between sulphate and methane. Oxidation of methane can reduce sulphate to sulphide, and microbes may be able to utilize the energy released in this anoxic oxidation of methane (AOM). However, present data indicates that sulphate and methane may coexist in deep fluids.

Study of the rock matrix fluid demonstrated the potential importance of the matrix porosity for biogeochemical processes. The otherwise reactive hydrogen may be formed and preserved in nano-scale pores.

7 Acknowledgement

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