Sulphide issue at Olkiluoto

Hydrogeochemical considerations

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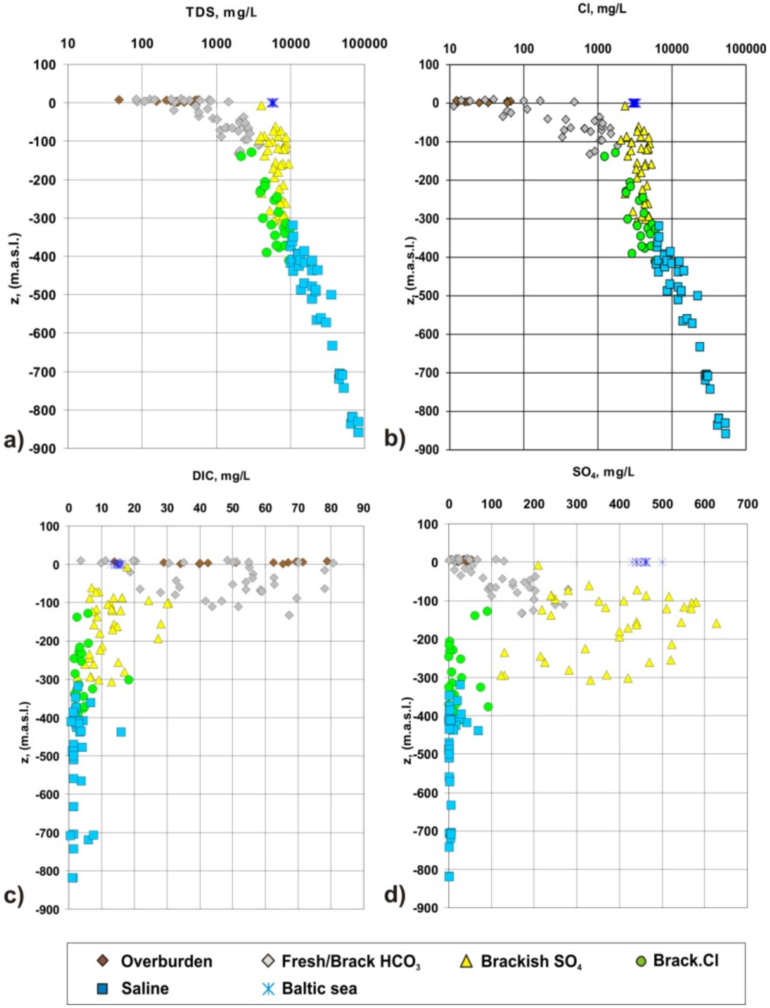
Background of sulphide issue

- Dissolved sulphide in groundwater is reduced from sulphate by bacteria (SRB) in low, ambient temperatures (< 20°C).
- Sulphide in steady state hydrogeochemical conditions is normally clearly below 1 mg/L, e.g. due to its insolubility with dissolved iron.
- Elevated mg/L level concentrations are observed occasionally.

- Sulphide corrodes copper, which will be used as outer cannister material of spent nuclear fuel.
- Normal sulphide concentrations in groundwater (< 1 mg/L) do not cause safety problems over long periods.
- Analyses show that several mg/L concentrations may result in remarkable number of cannister failures during long-term and are detrimental for the safety (*Performance Assessment 2012; POSIVA 2012-04*)

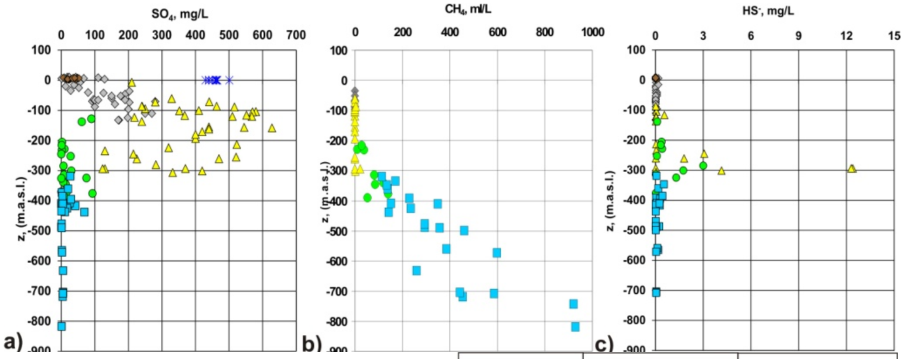
Hydrogeochemical conditions at Olkiluoto, salinity

- Salinity (TDS) varies from near surface fresh to highly saline (brine) grondwaters at 1000 m
- Classification of groundwater types is based on major anions, which reflect the origin of groundwater types
- Two rather separate groundwater systems:
    - Top meteoric carbonate-rich (DIC) with intermediate marine SO_4-rich groundwater in the upper part (post glacial)
    - and just Cl dominated, brine derived saline in deep groundwater system (pre glacial) below 300 m .
- *Site Description 2011 (POSIVA 2011-2)*

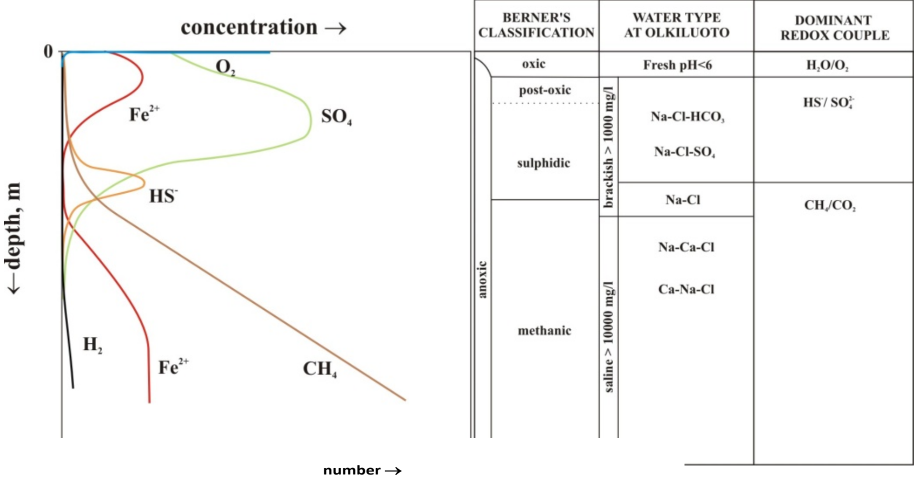


Hydrogeochemical conditions at Olkiluoto, redox

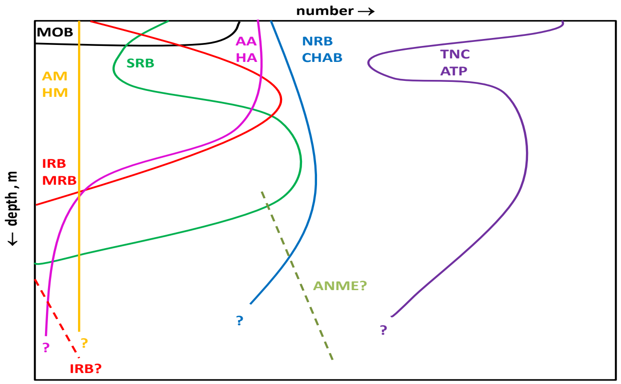
- Sulphate and methane divide the groundwater column at Olkiluoto
- Methane and hydrocarbons enriched below SO_4-rich gw in old groundwater system
- Elevated sulphide at SO_4- CH_4 transition zone



- Redox sensitive species in groundwaters form a sequential system with depth
- Mostly divided by sulphidic and methanic system (Berner's classification)



- Microbial groups, particularly SRB and IRB show similar sequential distribution *(Pedersen et al. POSIVA 2012-42)*
- TNC varies between 10^4 – 10^6 cells/mL, max. number of SRB and IRB about 10^3 cells/mL



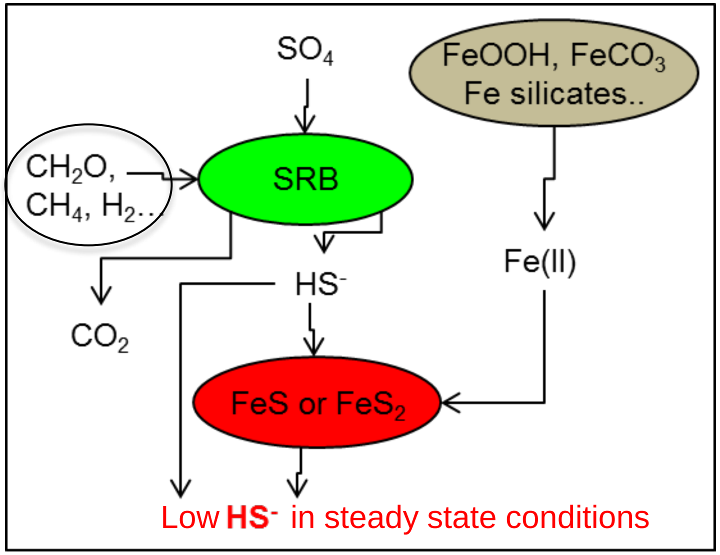
Sulphide in hydrogeochemical system at Olkiluoto

Formation

- High contents of SO_4 are able to buffer the amount of electron donors negligible in the upper groundwater system
- Deep groundwaters include potential electron donors for SO_4 reduction: CH_4, other short chain HC, hydrogen, carbohydrates.

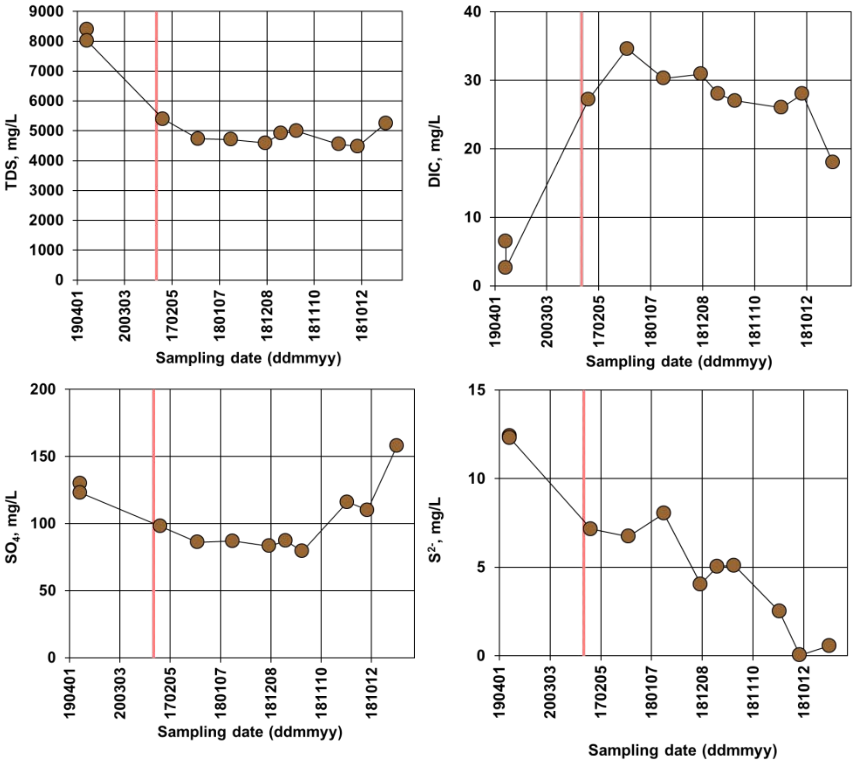
Sink

- Iron released from minerals potentially precipitates sulphide.
- The major source, silicates are kinetically slow
- First as metastable amorphous FeS, which is subsequently transformed to less soluble mackinawite and later insoluble pyrite (FeS_2)
- Pyrite is frequent fracture infilling and black iron sulphide precipitate has been observed
- *Wersin et al. POSIVA 2014-01*



Groundwater monitoring at the site

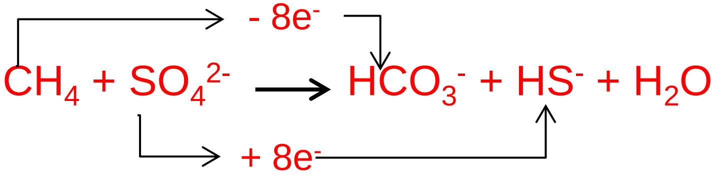
- Artificial transients caused by open drillholes and/or the ONKALO tunnel activate microbial SO_4 reduction as at the initial stage in OL-KR13 at 300 m depth (Figure)
- Input of shallower groundwater types indicated by dilution, and increased SO_4 and DIC results in sudden sulphide peaks in deep groundwater system
- After hydrogeochemical conditions have stabilised, e.g. drillholes closed by permanent parckers, sulphide concentrations tend to deplete
- Shortage of electron donor, suphide precipitation, dilution?



Electron donors and isotopic influence

- Depth distributions of redox sensitive species suggest that methane is used as an electron donor.
- SRB cannot use it, but coupled to anaerobic methane oxidation (AOM) could be possible.
- Required mass of other potential reducers DOC, H_2, short chain hydrocarbons is higher to conserve electron balance

- CH_4 has characteristically low $\delta^{13}C$ ratio, particularly at the SO_4- CH_4 transition zone (on left)
- Isotopic signal of CH_4 should be reflected in $\delta^{13}C$ (DIC) (mostly above -25‰, on right) or in precipitated fracture calcites (> -15‰, not shown) over long term
- Groundwater and fracture calcite isotopic data do not support AOM in general
- DOC has relatively constant (-25‰) and H_2 does not leave any signature at all.



$$CH_4 + SO_4^{2-} \longrightarrow HCO_3^- + HS^- + H_2O$$

- $8e^-$

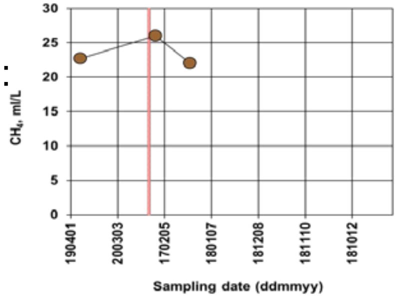
+ $8e^-$

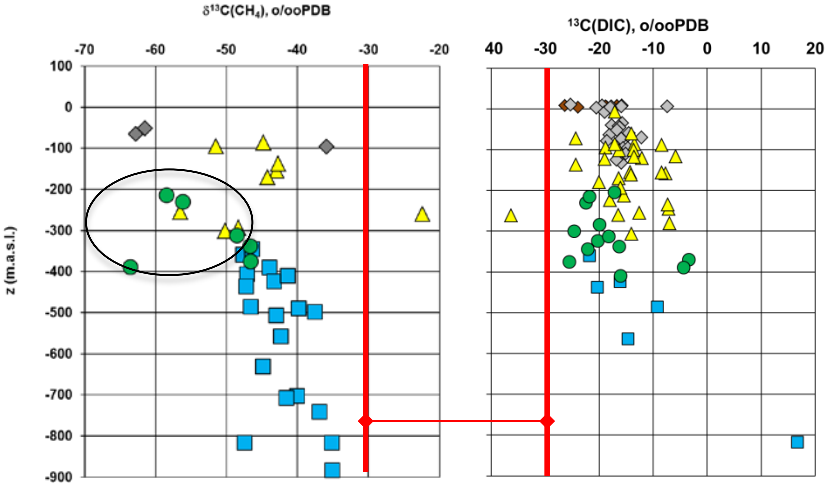
E.g., sulphide in OL-KR13:

8 mL/L CH_4,

9 mg/L DOC

34 mL/L H_2

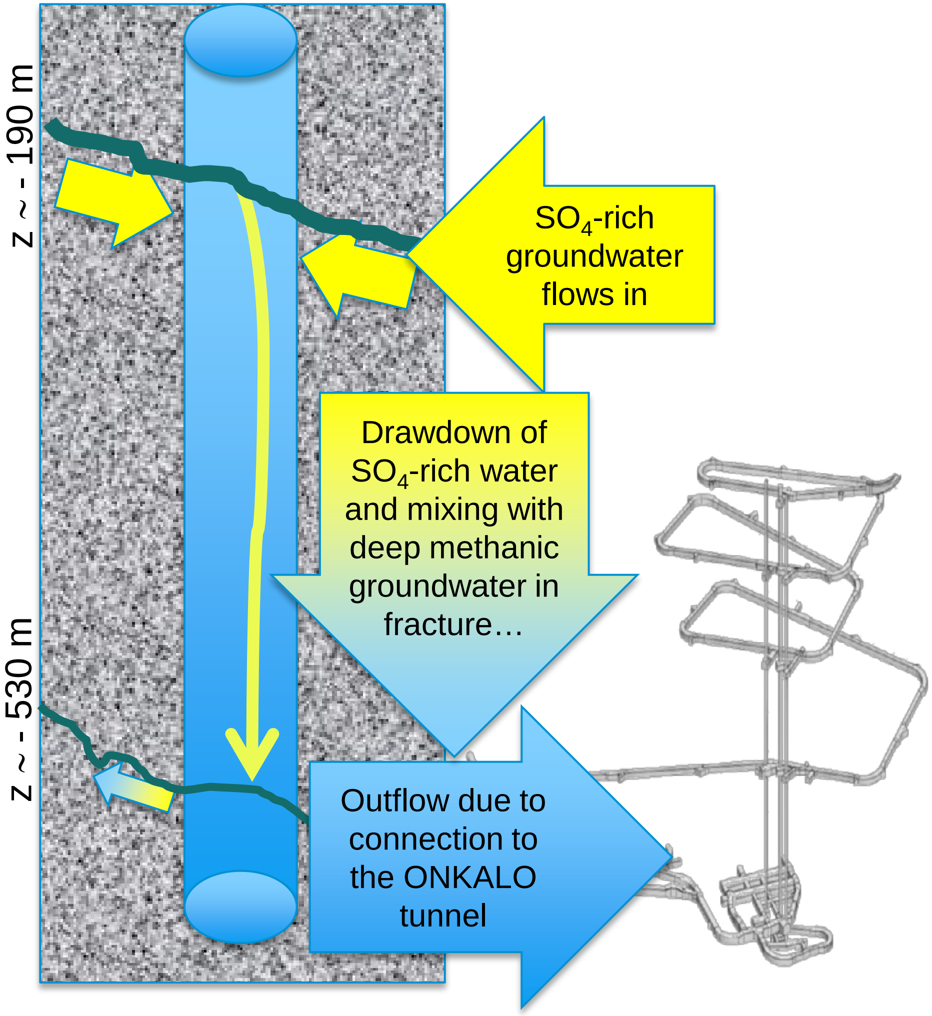




Indications of electron donors

- S^{2-} : 46 to 31 mg/L , i.e. 1.5 to 1 mmol/L in two different samplings
- HCO_3: 0.8 to 1.3 mmol/L rather low amount
- $^{13}C(DIC)$:-10.7 to -6.8‰ → too high compared to hydrocarbons,
- Organic carbon sources as a whole seem to be doubtful electron donors
- If hydrogen, such high sulphide needs rather significant source, i.e. 6 to 4 mmol/L H_2 (>100 ml/L of water)
- Do we have such amount H_2; current data do not fully support?

Open drillhole phenomenom in OL-KR46



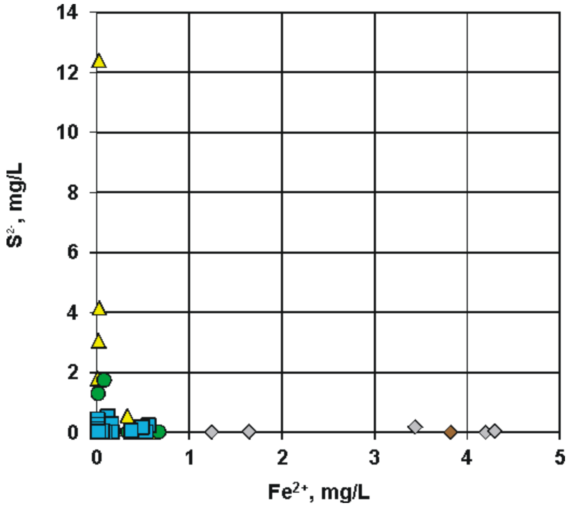
SO_4-rich groundwater flows in

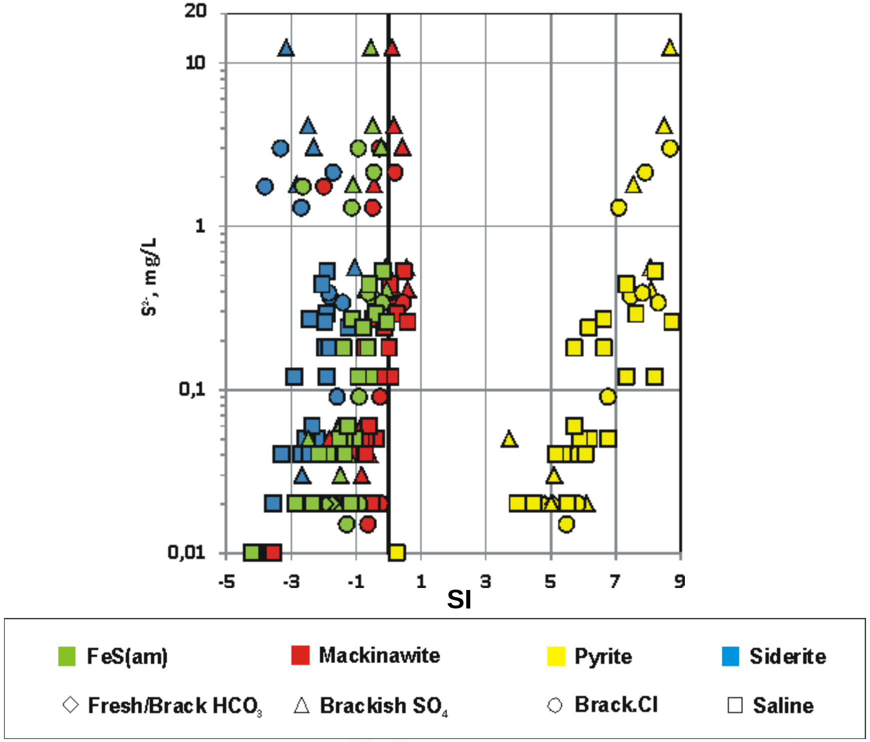
Drawdown of SO_4-rich water and mixing with deep methanic groundwater in fracture…

Outflow due to connection to the ONKALO tunnel

Role of iron to limit sulphide

- Dissolved sulphide and iron show an inverse relatioship (above)
- Poorly soluble FeS-phases control their solubility as also indicated by solubilty calculations (below)
- Saturation indices indicate equilibrium (SI=0) either with amorphous FeS or mackinawite in waters with measurable sulphide
- Insoluble pyrite may be in equilibrium in most of data, i.e. sulphide below detection limit (0.02 mg/L).
- Easily soluble Fe phases, e.g. ferric oxyhydroxides are lacking, and Fe release from silicate phases is poorly known, role of IRB?
- Life time of dissolved sulphide may be extended due to slow release of Fe from silicate phases





Summary and further studies

- Microbial sulphide reduction is activated by local hydrological transients mixing SO_4-rich and methanic groundwaters
- Dissolved sulphide tends to disappear after conditions are stabilised
- The decrease may due to several reasons, e.g.:
  - Depletion of electron donor, however, CH_4 seems not to be important, role of H_2?
  - Iron sulphide precipitation, the extension of high sulphide may result from slow release rate of iron from silicate phases
- More information is needed from availability of H_2 as an electron donor and iron as precipitating sulphide
  - Hydrogen low, mostly µl/L level in deep groundwater system, however, it could be easily lost during pumping samples. Matrix porosity in host rock may contain significant amounts H_2 accumulated over geologiacal time scales.
  - Ferric iron in silicates: biotite, chlorite, garnet etc. Microbes may activate the release of iron, IRB are general.

Kiitos

Thank you

Indications of electron donors

- OL-KR5 was open between 1998 and 2002
- Following the installation of multi-packers SO_4 decreased whereas sulphide increased at 450 m depth
- $\delta^{13}C$ remained rather stable in recent samples
- Low carbonate content (1.7 mg/L ~ 0.14 mmol/L) should be sensitive to anaerobic CH_4 oxidation.
- Increase in sulphide content (0.07 mmol/L) should decrease the ^{13}C level in DIC below -25 ‰ if similar mass of CH_4 (-43 ‰) is oxidised (even no fractionation included)
- Other electron donor seems probable