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Further clarification and guidance to the discussion about redox conditions and related processes in the geosphere, SR-PSU

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1 Introduction

Determination of the effective redox processes in aquifers needs the integration of different type of data, including the analysis of some dissolved redox indicators and mineralogical and microbiological determinations. Organic matter degradation by different microbial metabolic groups, using dissolved species and mineral fases as terminal electron acceptors, represents a key concept in the understanding of the redox processes in aquatic systems (e.g., Stumm and Morgan, 1996, Appelo and Postma 2005).

The redox characterisation in the SFR reports (Gimeno et al. 2011, and summarised in Nilsson et al. 2011) is not only based on the hydrochemical characteristics of the groundwaters but has thoroughly integrated the available hydrochemical, isotopical, microbiological and mineralogical data from the SFR site. Therefore the oxidation of organic matter and the microbial sulfate reduction processes have been addressed in several different contexts throughout the two reports.

Chapter 2 below treats the oxidation of organic matter and the reduction of sulfate. Chapter 3 discusses the link between the measured redox potentials in the groundwater and the presence of redox-sensitive minerals such as iron oxides and clays in rock fractures. Both chapters give guidance to the different sections of the corresponding SKB-reports where detailed descriptions are given and also to other reports and publications that have been considered.

2 On the correlation between the oxidation of organic matter and reduction of sulfate in groundwater

2.1 Relevant hydrogeochemical information

Sulfide concentrations in the groundwaters at SFR have been and continue to be consistently very low, mostly close to or below the detection limit (from 0.006 to 0.02 mg/L). In contrast, iron and manganese contents are generally in the ranges 0.5 to 7 mg/L and 0.3 to 4 mg/L, respectively, suggesting that, iron-reducing bacteria (IRB) and manganese-reducing bacteria (MRB) are more active than the sulfate reducers (SRB, sulfate-reducing bacteria). The concentrations of total organic carbon (TOC) or dissolved organic carbon (DOC) are often quite low, in general between 1 and 2 mg/L, for depths between -20 and -400 m.a.s.l.

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The sulfur isotope ratio ($^{34}S/^{32}S$ in the sample related a standard expressed as $\delta^{34}S$) in sulfate may be used as an indication of sulfate reduction. SRB use preferably the light sulfur isotopes and therefore the residual sulfate shows an increase of the heavier isotope (resulting in higher $\delta^{34}S$). A comparison of $\delta^{34}S$ data between the SFR groundwater and the Baltic Sea is presented in Figure 1 which also shows the SO_4/Cl ratios of the groundwater samples compared with the marine ratios of the Baltic Sea. Groundwaters with low SO_4/Cl ratio and high $\delta^{34}S$ in the sulfate are interpreted as affected by sulfate reduction. This is most pronounced for samples of the brackish glacial type with the longest residence time. In contrast, the youngest waters, of the Baltic Sea type that has intruded in connection to the construction of the SFR facility, show only a small difference from the actual Baltic Seawater, indicating some minor influences from sulfate reduction.

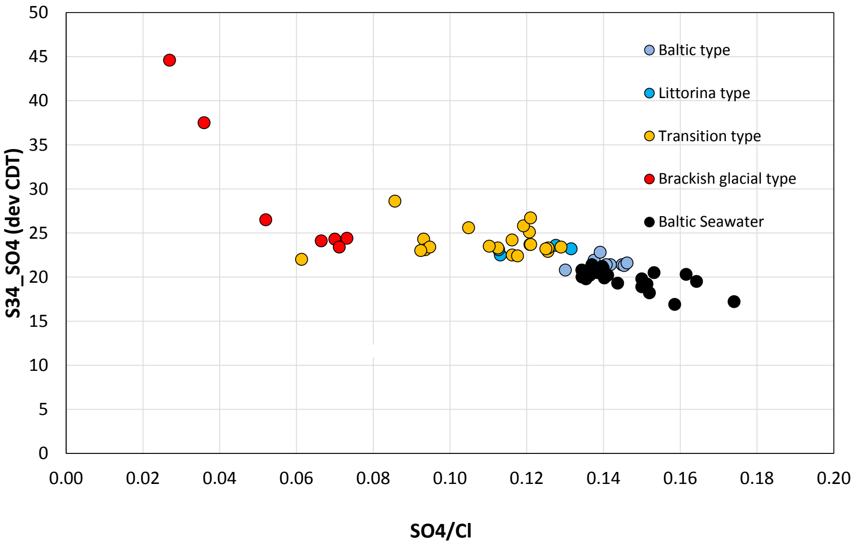

Figure 1. *$\delta^{34}S$ ‰ CDT (Canyon Diablo Troilite standard) in sulfate plotted versus the sulfate to chloride ratio. The data represents all groundwater samples and Baltic Sea water samples with $\delta^{34}S$ values. The colour code marks different groundwater types as well as seawater. Sulfate reduction is expected to decrease the groundwaterSO_4/Cl ratios and increase the $\delta^{34}S$ ‰ CDT in the remaining sulfate.*

2.2 Clarifications and guidance

In Gimeno et al. (2011), different aspects on oxidation of organic matter and reduction of sulfate are mainly treated in:

- Chapter 4 which deals with non-redox geochemical systems.
- Chapter 5 is dedicated to the redox geochemical systems and discusses the effects of biological degradation of organic matter, coupled to the available hydrochemical, mineralogical, isotopical and microbiological data from the SFR groundwaters. Continuous references to the possible effects of the different heterotrophic microorganism groups involved in the degradation of organic matter, including IRB, SRB, MRB, NRB (nitrate-reducing bacteria), acetogens and methanogens are given in the chapter.
- Section 5.3 (pp. 67 to 75), dedicated to the iron and sulfur systems, refers to the related heterotrophic microbial processes (by dissimilatory iron reducing bacteria, IRB and sulfate reducing bacteria, SRB) and explicitly indicates the representative reactions of these

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metabolisms (reactions 5.3 to 5.6, pp. 71). Sulfate reduction processes are exclusively driven by bacterial activities in low temperature systems and microbiological data are included in the discussion (pp. 71 and 72).

- Section 5.4 (pp. 76-79), dedicated to the manganese system, refers to the manganese reducing bacteria (MRB) and the representative reactions of this metabolism are also explicitly indicated (reactions 5-10 and 5-11).
- Section 5.5 (pp. 80-84), dedicated to the nitrogen system (nitrate, nitrite and ammonium), highlights the importance of heterotrophic microbial processes (the transformation between those nitrogen species is almost exclusively facilitated by microorganisms) and indicates that, under anaerobic conditions, nitrate is the most thermodynamically favored electron acceptor for the oxidation of organic substrates and that it may be used by nitrate reducing bacteria (NRB).
- Finally, section 5.6 (pp. 84-85) dedicated to the molecular hydrogen and methane, discusses the role of fermentative bacteria and heterotrophic acetogens in the degradation sequence of organic matter as they continuously produce biogenic molecular H_2 and simple organic molecules (e.g. acetate, pp. 84) which are quickly metabolised by other microorganisms (e.g. SRB).

The main results obtained by Gimeno et al. (2011) in Section 5 are summarised in Nilsson et al. (2011, section 5.6.3, pp. 113-118).

Microbial degradation of organic matter is also treated in Chapter 4 in Gimeno et al. (2011). These processes influence the carbonate system (producing carbon dioxide/alkalinity) and some of the involved metabolisms, like sulfate reduction bacteria, may participate in the control of other compositional systems like the sulfate system. Therefore, the effects of biological activity were also taken into account in section 4.1 which is dedicated to the carbonate system and section 4.2 which is dedicated to the sulfate system.

All the sampled groundwaters in the SFR have higher calculated pCO_2 than the atmospheric value (values higher than -3.5, Figure 4-4 in Gimeno et al. 2011, pp. 44 and 45). These conditions are usual in groundwaters recharged in the upper part of the bedrock in crystalline systems during the Holocene (usually derived from the soil zone where biogenic processes promote high concentrations of CO_2 in the waters), whereas deeper groundwaters, with longer residence times, clearly show lower pCO_2 values (promoted by calcite and aluminosilicate dissolution processes). This situation has been described, for example, in the Romuvaara, Kivetty and Olkiluoto groundwaters (Pitkanen et al. 1996, 1998, 1999 and 2004), and in the Forsmark and Laxemar groundwaters (Gimeno et al. 2008, 2009).

In the case of the SFR groundwaters, as they are under the seabed, the high pCO_2 (and HCO_3^-) values found in the groundwaters are most probably related with the biological activity in the seabed sediments (and not the soils) during the infiltration of the marine waters, although on-going microbial processes in the bedrock may also contribute. This aspect is discussed by Gimeno et al. (2011, p. 46, see also p. 40) and Nilsson et al. (2011, p. 101) in association to the present intrusion of Baltic Sea waters (due to drawdown related to the present SFR tunnel system) and to the past Littorina infiltration in the area. The high values are similar to those found in the site investigation (SR-Site) in Forsmark groundwaters at similar depths, and not as high as the concentrations found in some of the fresh and mixed groundwaters above 150 m depth in Forsmark boreholes related to the infiltration of meteoric waters in a calcite-rich overburden (Gimeno et al. 2008).

The identified and/or deduced microbial activities in the SFR groundwaters include most of the heterotrophic microorganisms involved in the oxidation of organic matter: indications of sulfate reduction, iron reduction, manganese reduction and nitrate reduction processes were identified associated to the present (Baltic) and past (Littorina) marine intrusions in the SFR area (see

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Gimeno et al. 2011, pp. 65-87). As stated in Gimeno et al. (2011, p. 71), microbial activity and organic matter decay in marine sediments may lead to complete redox sequences (from oxic to post-oxic, sulfidic and methanic environments and, then, involving most of the heterotrophic metabolisms) even at centimetre scales. As all these heterotrophic microorganisms (not only microbial sulfate reduction), in the sea sediments or in the bedrock, can increase the carbon dioxide contents of the waters (see Table 1 or reactions 5.2, 5.4 and 5.11 in Gimeno et al. 2011, pp. 71 and 78) a generic term, “biological activity”, has been frequently used in the context of the carbonate system in Gimeno et al. (2011) and Nilsson et al. (2011).

Table 1. *Reactions representing the sequence of heterotrophic metabolisms involved in the degradation of organic matter (from Stumm and Morgan, 1996).*

Aerobic respiration	$1/4CH_2O + 1/4O_2 + 1/4H^+ \rightarrow 1/4CO_{2(g)} + 1/4H_2O$
Denitrification	$1/4CH_2O + 1/8NO_3^- + 1/4H^+ \rightarrow 1/8NH_4^+ + 1/4CO_{2(g)} + 1/8H_2O$
Manganese reduction	$1/4CH_2O + 1/2MnO_{2(s)} + H^+ \rightarrow 1/2Mn^{2+} + 1/4CO_{2(g)} + 3/4H_2O$
Fermentation	$3/4CH_2O + 1/4H_2O \rightarrow 1/2CH_3OH + 1/4CO_{2(g)}$
Iron reduction	$1/4CH_2O + Fe(OH)_{3(s)} + 2H^+ \rightarrow Fe^{2+} + 1/4CO_{2(g)} + 11/4H_2O$
Sulfate reduction	$1/4CH_2O + 1/8SO_4^{2-} + 1/8H^+ \rightarrow 1/8HS^- + 1/4CO_{2(g)} + 1/4H_2O$
Methane fermentation	$1/4CH_2O \rightarrow 1/8CH_4 + 1/8CO_{2(g)}$

2.3 Conclusions

- High pCO_2 values have been found in many samples but the relation to bacterial sulfate reduction is not straightforward from data and interpretations. From the referenced redox modelling in Chapter 3 (below), iron and manganese reduction reactions by IRB and MRB are favoured. Nevertheless SO_4/Cl ratios and $\delta^{34}S$ measurements show that sulfate reduction has ocurred in these waters. The low sulfide contents measured in the SFR boreholes indicate that this sulfate reduction has taken place earlier or/and it takes place before the waters enter the bedrock, for example in the sea bed sediments. Another possibility is that the generated sulphide reacts with dissolved Fe and precipitates.
- A wider analysis considering microbial metabolisms involved in the degradation of organic matter was performed by Gimeno et al. (2011, Chapter 5). All the reactions described participate in the control of the redox conditions in the groundwaters, and influence the carbonate system.
- Microbial sulfate reduction processes are specifically addressed by Gimeno et al. (2011): in section 5.3, dedicated to the sulfur and iron redox systems (pp. 67-75) and in sections dealing with the carbonate (section 4.1, pp. 46-47) and sulfate systems (section 4.2, pp. 47-48 and 52) in the SFR groundwaters. These sections also treat available microbiological data.
- As all the identified/deduced heterotrophic metabolisms in the sea sediments or in the bedrock of the SFR can induce increments in the carbon dioxide contents, their influence on the carbonate system was discussed in terms of “biological activity” in Gimeno et al. (2011) and Nilsson et al. (2011).

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3 On measured redox potentials in the ground water and presence of redox-sensitive minerals

3.1 General

Iron and manganese concentrations are, as mentioned above in the introduction to Chapter 2, relatively high in the SFR waters and microbial activity of IRB and MRB use the easily available Fe(III) and Mn(IV) present in oxides/oxyhydroxides and potentially also in clay-minerals for the oxidation of organic matter. The evaluation of the redox system in SFR strongly suggests $Fe^{2+}/Fe(OH)_3$ as the most important redox couple. This is supported by the measurements and modelling published in the SFR PSU reports (Gimeno et al. 2011 and summarised in Nilsson et al. 2011, Auqué et al. 2013) and section 3.2 below gives a detailed guidance to the published material in reports and papers.

Related to the redox modelling is also the actual presence of different Fe-minerals along the conductive fractures and their relative distribution and content of Fe(II) and Fe(III). Additional information not included in the SFR-PSU has been and is presently being produced (see references and comments in section 3.3).

3.2 Clarifications and guidance.

The detailed analysis of the redox measurements and the subsequent modelling tasks performed by Gimeno et al. (2011) included:

- the screening stage for the selection of redox data (representative Eh and pH values and groundwater samples for redox modelling) summarised in section 5.1 (pp. 59-60)
- the evaluation on the significance of the potentiometric measured Eh values and the redox pair calculations (section 5.2, pp. 61-67)
- the evaluation of the main redox compositional systems: sulfur and iron (section 5.3, pp. 67-75), manganese (section 5.4, pp. 76-79), nitrogen (section 5.5, pp. 80-84), and molecular hydrogen and methane (section 5.6, pp. 84-85).

The evaluation of the redox systems covers a large part of the report by Gimeno et al. (2011), and it deals with the main processes controlling the redox characteristics of the groundwater, including the effects of biological degradation of organic matter as the main driving force. This is the part that includes the highest level of integration of microbiological, mineralogical, hydrochemical and isotopic data. When necessary, specific subsections were included on these subjects (e.g. sections 5.3.2 and 5.4.2 to discuss the mineralogical data related to the iron-sulfur and manganese systems, respectively; or section 5.3.3. to discuss the microbiological data available for the nitrogen system, p. 83). Redox data and results for the SFR groundwaters were compared with the Forsmark Site groundwaters and with those from the other sites studied in Sweden and Finland (pp. 63 to 85 in Gimeno et al. 2011).

With respect to the potentiometric measurements, the limitations and uncertainties related to their use as the only redox indicator is widely explained in Gimeno et al. (2011) and Nilsson et al. (2011). They can be influenced by technical and interpretative problems and at the base of all the problems is the typical redox disequilibrium among the different redox pairs in natural waters, which promotes that an overall Eh value for a groundwater is often impossible to assign (see Gimeno et al. 2011, for detailed references to other authors). That is why redox potentials calculated from redox couples are usually considered the only way to approach accurate Eh values in natural waters, see Gimeno et al. (2011, section 5.2.2., pp. 63-67 and more specifically in pp. 65-67). However, the comparison between potentiometrically measured Eh values and those obtained by different redox couples can be very helpful to identify the most probable redox pairs

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involved in the control of the measured Eh. The use of the Fe^{2+}/ $Fe(OH)_3$ redox pairs (some of the very few clearly electroactive redox pairs) is also very helpful to deduce the type of iron oxyhydroxide that may control these measured values. This methodology has been successfully used in previous works in the field (e.g. Grenthe et al. 1992, Banwart, 1999, Trotignon et al. 2002, Gimeno et al. 2008, 2009) and in the laboratory (e.g. Macalady et al. 1990, Bonneville et al. 2004).

Gimeno et al. (2011) performed a thorough study including different redox pair among which the following heterogeneous iron couples were included:

- For the Fe^{2+}/ $Fe(OH)_3$ pair Gimeno et al. (2011) used three different sets of log K values for the solid component of the couple (cf. p. 63): 1) for the amorphous-microcrystalline hydrous ferric oxides (Nordstrom et al. 1990), 2) for a crystalline phase (such as hematite or goethite; Grenthe et al. 1992), and 3) for an iron phase representative of intermediate crystallinity (Banwart, 1999, Figure 2).
- The other iron couple was the Fe(III)-clay/Fe(II)-clay (Banwart, 1999, results from the "Large-Scale Redox Experiment" carried out in Äspö). This redox pair is based on the reversible one-electron transfer between oxidised and reduced smectites and, therefore, can also be clearly electroactive. For this reaction, the conditional redox potential (Eh, V) as a function of pH at 10°C is defined by the equation: Eh = 0.280 –0.056 pH.

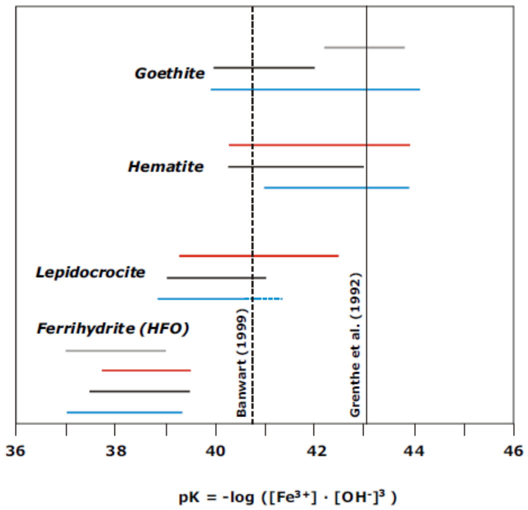

Figure 2. Reported solubility ranges at 25°C for the main ferric oxyhydroxides. Blue lines represent the ranges obtained by Langmuir (1969; 1997); black lines correspond to the values suggested by Appelo and Postma (2005) from an analysis of Cornell and Schwertmann (2003) data; red lines represent the ranges reported in Bonneville et al. (2004); and, finally, grey lines represent the range of values proposed by Nordstrom et al. (1990). The most recent solubility ranges obtained by Majzlan et al. (2004) for 2-line and 6-line ferrihydrite (HFO: hydrous ferric oxyhydroxides; values between 37.5 and 39.5) coincide with the ranges shown in the plot for this phase. The values reported by Macalady et al. (1990) for goethite (pK=44.15) and hematite (pK=44.0) are in agreement with the less soluble extreme of the range shown in the plot for these minerals. Empirical values deduced by Grenthe et al. (1992; pK=43.1) and Banwart (1999, pK = 40.8) for different Swedish groundwaters are also indicated. From Figure C.1 in Gimeno et al. (2009).

The obtained results (including redox calculation) provide reasonable justifications for the Eh values measured in SFR. High Eh values (from +30 to +110 mV) were measured in some of the analysed borehole sections. The redox pair calculations would support a control by amorphous

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Fe(III)-oxyhydroxides (Table 5-3 in Gimeno et al. 2011 and 5.9 in Nilsson et al. 2011). As indicated in both reports (page 65 in Gimeno et al. 2011 and page 110 in Nilsson et al. 2011), oxygen intrusion in reducing media usually induces the precipitation of amorphous Fe(III)-oxyhydroxides and it would support the reliability of the oxidising Eh measurement.

In the case of the measured low Eh values (from −140 to −190 mV), redox pair calculations would support a control by the $Fe^{2+}/Fe(OH)_3$ redox pair using the equilibrium constant proposed by Banwart (1999) (Gimeno et al. 2011, p. 64 and Nilsson et al. 2011, p. 109) that is, with the iron phase of intermediate crystallinity referred to above. The Fe(III)-clay/Fe(II)-clay redox couple, also provides good agreement with the reducing Eh values. This coincidence in the results from the two redox pairs was not found in the SR-Site (Forsmark) and the Laxemar-Simpevarp groundwaters (Gimeno et al. 2011, pp. 64 and 67), but it is similar to the observations from the “Large-Scale Redox Experiment” by Banwart (1999). These results are also supported by the fact that mixed layer clays (poorly ordered smectite/illite) are the most abundant minerals in the fracture fillings from water conducting fractures and the presence of hematite and other unclassified iron oxyhydroxides has also been identified (see section 3.3). Based on all that, Gimeno et al. (2011, p. 67) suggest that more data on those phases, especially, on the type and particle size (crystallinity), would be needed to fully verify their findings.

3.3 The relative importance of mixing as compared with reactions

Assuming the feasible control of the reducing Eh values by the Fe(III)-clay/Fe(II)-clay redox pair, some inorganic or microbial involving reactions with respect to sheet silicates would be on-going and they would contribute with solutes, in addition to reduced iron, to the groundwaters (apart from the contribution from mixing or from other heterogeneous processes). However, the precipitation of reduced smectites was already examined and discussed by Banwart (1999) in the context of the mixing processes effective in the “Large-Scale Redox Experiment” and he found that there was not much evidence of clay mineral precipitation as the contents of Ca, Na, Mg and K (chemical elements that would be affected by aluminosilicate dissolution/precipitation) were explained well by mixing or mixing + calcite +cation exchange reactions (Banwart, 1999, p. 2926). But most important, the formation of reduced smectites (necessary for the Fe(III)-clay/Fe(II)-clay redox pair), can also occur by reduction of structural Fe(III) in existing mineral phases, without any important contribution to the groundwater, both inorganic and microbially mediated (Rozenson and Heller-Kallai, 1978, Stuck and Lear, 1990, Banwart, 1999, Gimeno et al. 2009, p.185, and references therein, Gorski et al. 2012a, 2012b, 2013, Neumann et al. 2013, Pentráková et al. 2013).

Other possible contribution to dissolved elements could come from the weathering of other iron sheet silicates, such as biotite or chlorite. However, weathering reactions of these mineral phases usually take place through incongruent dissolution processes minimising, at least in part, their net contribution to the groundwaters. Furthermore, kinetically faster reactions, like cation exchange, can play a much more prominent role in the control of dissolved cations, especially in systems affected by present marine intrusions like the SFR.

The possible influence of heterogeneous reactions on Na, Ca, Mg and K contents were indicated in Nilsson et al., (2011) even for elements that are clearly controlled by mixing with marine end-members like K and Mg (see pages 71-74 in Nilsson et al., 2011).

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3.4 Additional mineralogical/geochemical information

To link the measured Eh value in the groundwater in a specific borehole section with observed occurrences of redox-sensitive minerals in the fractures in the same section is not an easy task. The measure of Eh is very complex and it is associated with several technical and conceptual problems (e.g. Auqué et al. 2008, Lindberg and Runnels 1984, Wikberg, 1991), which further complicates any linking between the Eh and the observed fracture minerals. Nevertheless the knowledge of the general presence of different redox sensitive minerals along the flow paths is very helpful to understand the ongoing processes and the available redox buffer capacity.

Generally Fe-minerals (and to some extent also Mn-minerals) together with sulfide minerals make up the mineralogical redox buffer along the flow routes. The most reactive minerals are the Fe and Mn-oxyhydroxides, providing easily available Fe(III) and Mn (IV) for the IRB and MRB but the clay minerals can act as Fe(III) source as well (see section 3.3 above). Pyrite which provides reducing capacity in terms of Fe(II) and of sulfide is one of the most sensitive minerals to oxic conditions and constitutes an important buffer against oxygen intrusion. Going from surface towards depth the presence of Fe-oxyhydroxide is usally reflected by the absence of pyrite. Deeper down the situation is the reverse (no Fe-oxyhydroxide but pyrite). The zone were the switch occurs has been called the redox transition zone (Tullborg et al 2008, Drake et al 2009, Sidborn et al. 2010 and references therein). It has also been shown that clay minerals like smectites, mixed layer clays and corrensites together with chlorite, host Fe^{3+} and Fe^{2+} (Sandström et al. 2014 and ongoing measurements at Linneaeus University) some of them probably easily available as ion exchangeable or, in the case of Fe^{3+}, as terminal electron acceptor. The knowledge about the minerals present along the hydraulic pathways is, therefore, an important input to the evaluation of the Eh values.

The presence of reactive fracture minerals providing redox capacity and pH buffering in the flowing fractures, Posiva Flow Log-structures (PFL), is compiled in Nilsson et al. 2011 (see Figure 3). From this plot it is evident that chlorite together with clay minerals are very common and present in all flow anomalies. Mixed layer clays of illte/smectite type were also found in all but one of the measured sections. Fe-oxyhydroxides, although more limited to the near surface fractures, have also been found in a few deeper fractures (Sandström et al. 2011) of which two correspond to sections with potentiometric Eh measurements (ca -60 and -135 m elevation).

The fracture mineral data in Sicada database are collected during ocular drill core mapping and it is often difficult to visually distinguish between Fe-oxyhydroxide and iron rich clay minerals and hematite-stained minerals. Therefore 61 apparent occurrences of Fe(III)-hydroxides were revisited and analysed by Sandström et al. (2014), in addition to the previously analysed sections studied for redox (Sandström et al. 2011) . This study (Sandström et al. 2014) included only samples from the new boreholes KFR102B, KFR103, KFR104 and KFR106 because these represent triple tube drillings and the story of storage of the cores was also known. The occurrences in these boreholes represent all depths down to –325 m.a.s.l. After detailed fracture mineralogical identification, only two of the fractures studied were inferred to potentially contain iron hydroxide. The minerals most often mistaken for Fe-oxyhydroxide in these drill cores are iron-rich mixed layer clay, uranium-minerals and hematite-stained adularia and albite. A few fractures mapped as iron hydroxide-bearing contained rust-coloured metallic iron from the drilling process.

Thirteen fracture mineral samples with clay minerals from the SFR drill cores were used for Mössbauer analyses and determination of iron oxidation state. The Fe(II)/Fe(tot) ratio varied between 0 and 0.79% (Sandström et al. 2014).

In addition, redox sensitive minerals in Forsmark are presently being investigated at Linnaeus University. This study was initiated to identify and quantify the redox states and mineralogy of Fe in fresh and altered rock as well as in a number of fractures coatings by the use of a large variety

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of analytical techniques, including Scanning Electron Microscope (SEM), X-ray absorption spectroscopy (XAS), whole-rock chemical analyses (ICP-MS) together with additional Mössbauer spectroscopy analyses. The latter results and interpretations are not available yet. In any case, the results obtained so far give some variation in Fe(II)/Fe(III) between methods but indicate the presence of a 94% to 15% of Fe(II)/Fe(tot) in the clay mineral rich samples (personal communication Henrik Drake, Linnaeus University, 2017).

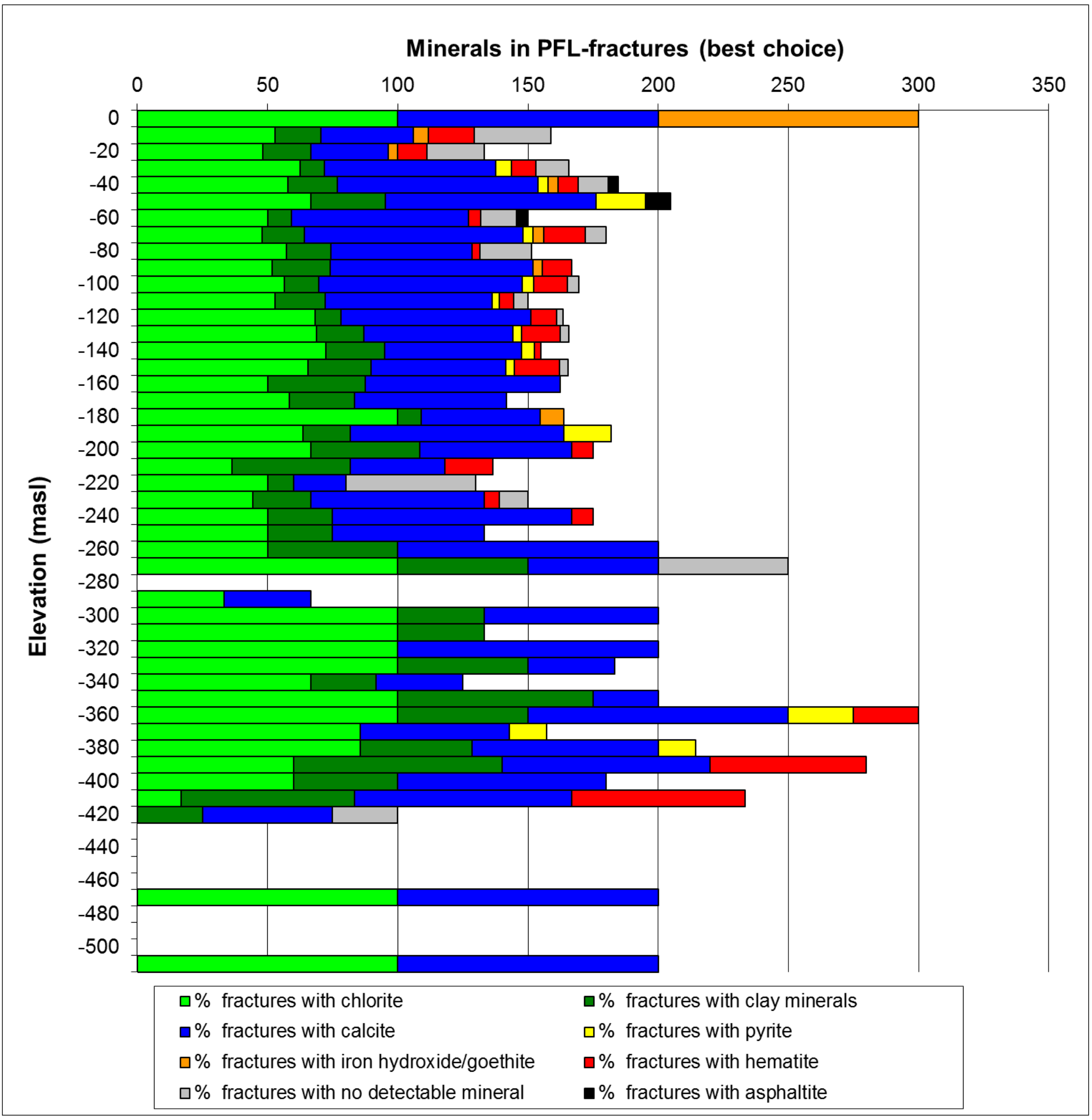

Figure 3. Depth distribution of the fracture mineralogy in water conductive fractures (PFL-anomalies best choice) at SFR. Figure from Nilsson et al., 2011.

It is important to keep in mind that the presence of Fe-oxy-hydroxides in the upper part of the bedrock, interpreted as an indication of infiltration of oxygenated waters in the fracture system, may not be the result of ongoing precipitation in the groundwater. Instead, the presence of Fe-oxyhydroxides is used as an indication of possibly recent (<2 Ma) infiltration of oxygenated waters (cf. Sidborn et al. 2010; Sandström et al. 2014).

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3.5 Conclusions

- It is important to emphasise that the analysis of the redox conditions involves more information and methodologies than the potentiometric measurement of the Eh. A weight-of-evidence approach is necessary in order to properly evaluate redox conditions in groundwater.
- The rationale and data used for the performed redox pair calculations are stated, based on previous reviews, studies and results, and referenced in Gimeno et al. (2011) and Nilsson et al. (2011). First, the relatively high values of measured Eh (from +30 to +110 mV) seem to be controlled by amorphous Fe oxyhydroxides. Then, the Fe oxyhydroxide of intermediate crystallinity participating in the $Fe^{2+}/Fe(OH)_3$ redox couple and the Fe^{3+}-clay/Fe^{2+}-clay redox pair, are unambiguously defined (Gimeno et al. 2011, section 5.2.2, p.63 and Nilsson et al. 2011, section 5.6.2., p.109) as the most probable controlling pairs for lower Eh values (from −140 to −190 mV) in the SFR groundwaters,
- Despite the described role of sheet aluminosilicates (Fe(III)-clay/Fe(II)-clay redox pair) in the control of some measured Eh values in the SFR system, the contribution to solutes in addition to reduced iron, to the groundwaters is not necessarily important. The redox control can also occur by reduction of structural Fe(III) in clay minerals. Even if precipitation of ferrous smectites was involved, the effects on the contents of major cations would be minor compared with the effects of mixing and other heterogeneous processes (Banwart, 1999, Gimeno et al. 2011, pp. 64, 67 and Nilsson et al. 2011, p. 110).
- Correlation between flow anomalies and drill core mapping shows that clay and chlorite is common in all flowing structures (eg. Öhman et al. 2011). In most of the sections measured for Eh, detailed studies show the presence of mixed-layer clay of illite/smectite type and in two sections Fe-oxyhydroxide is identified (Sandström et al. 2011). Furthermore redox state measurements and chemical analyses (Sandström et al. 2014), supported by ongoing studies at Linnaeus University (personal communication Henrik Drake, 2017), show that clay and chlorite provides both Fe(II) and Fe(III) in the fracture coatings. No depth trend can be seen regarding Fe(II)/Fe(III) in these minerals.

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