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Proterozoic to Quaternary events of fracture mineralisation and oxidation in SE Sweden

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The figure on the cover is a back-scattered electron image of a scalenohedral calcite crystal from an open fracture. The sample is from drill core KLX03 (Laxemar, SE Sweden), at 662.33-662.65 m borehole length.

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ABSTRACT

Fracture minerals and altered wall rock have been analysed to reveal the low-temperature evolution, especially regarding redox conditions, of the Simpevarp area, SE Sweden. This area is one of the two areas in Sweden investigated by the Swedish Nuclear fuel and Waste Management Co. (SKB) in order to find a potential geological repository for spent nuclear fuel. The 1.8 Ga granitic to dioritic rocks in the area are generally un-metamorphosed and structurally well-preserved, although low-grade ductile shear zones and repeatedly reactivated fractures exist. Investigations of cross-cutting fractures along with a wide variety of fracture mineral analyses, such as stable isotopes and $^{40}Ar/^{39}Ar$ geochronology, have been used to distinguish a sequence of fracture filling generations. The characteristics of these generations indicate the low-temperature evolution of the area, including information of e.g. fluid origin, formation temperature, paleo stresses and relation to known geological events. Knowledge of the fracture mineral evolution is important for the conceptual geological and hydrogeochemical understanding of the site and supports predictions of future scenarios in the safety assessment. The fracture mineral generations identified have been formed at widely varying conditions starting in the Proterozoic with formation from inorganic hydrothermal fluids, continuing in the Paleozoic with formation from lower temperature brine type fluids with organic influence, and ranging into minerals formed from waters of varying salinity and with significant organic influence at conditions similar to the present conditions. However, the amount of potentially recent precipitates is very small compared to Proterozoic and Paleozoic precipitates. The fracture mineral parageneses have been associated, with varying confidence, to far-field effects of at least four different orogenies; the Svecokarelian orogeny (>1.75 Ga), the Danapolonian orogeny (~1.47-1.44 Ga), the Sveconorwegian orogeny (~1.1-0.9 Ga) and the Caledonian orogeny (~0.5-0.4 Ga). The fracture minerals related to the Danapolonian orogeny were mainly formed in relation to the intrusion of two granites nearby. Periods of extension and influence from overlying sedimentary successions have also been indicated in the fracture mineral record.

Demonstration of long term preservation of stable reducing conditions at repository depth is an important task in the safety assessment of a nuclear waste repository. This is because oxygen may harm the copper canisters and may cause increased mobility of some radionuclides in case of canister leakage. It is therefore important to demonstrate the extent of past oxygen intrusion in the bedrock, i.e. the position of the redox front, at which originally present oxygen have been reduced along the fractures. It is also important to obtain information on the available reducing capacity (mainly Fe^{2+}) of the wall rock, especially regarding the widespread hydrothermally altered, red-stained and supposedly oxidised wall rock. The results from two comprehensive studies on these tasks are satisfying and robust and can be summarised as: 1) The recent redox front is indicated to be located in the uppermost twenty meters of the bedrock, as shown by the depth distribution of redox sensitive minerals pyrite and goethite, Ce-anomalies and U-series nuclides, and 2) red-stained wall rock still has a high reducing capacity, which is largely similar to that of the unaltered rock.

Keywords: fracture minerals, low-temperature evolution, paleohydrogeology, redox front, wall rock alteration, stable isotopes, geochemistry, Ar-Ar dating, fluid inclusions, Mössbauer spectroscopy, U-series disequilibrium, Simpevarp, Laxemar, SE Sweden, nuclear waste repository.

PREFACE

This doctoral thesis includes the following papers:

Paper I **Palaeohydrogeology: A methodology based on fracture mineral studies.** E-.L. Tullborg, H. Drake, B. Sandström, Applied Geochemistry, vol. 23, 7, 1881-1897.

Tullborg wrote the paper in collaboration with Drake and Sandström, Drake contributed with results from the Simpevarp area, figures, tables and discussion.

Paper II **Red-staining of the wall rock and its influence on the reducing capacity around water conducting fractures.** H. Drake, E-.L. Tullborg, H. Annersten, Applied Geochemistry, vol. 23, 7, 1898-1920.

Drake carried out planning, sampling, sample preparation, microscopy and SEM-EDS, interpretations and writing. Tullborg contributed with planning and discussion and Annersten with Mössbauer spectroscopy analyses and discussion.

Paper III **Paleohydrogeological events recorded by stable isotopes, fluid inclusions and trace elements in fracture minerals in crystalline rock, Simpevarp area, SE Sweden.** H. Drake, E-.L. Tullborg, Applied Geochemistry, in press.

Drake carried out planning, sampling, sample preparation, microscopy and SEM-EDS, fluid inclusion analyses, interpretations and writing. Tullborg contributed with planning, sampling and discussion and additional analyses.

Paper IV **Detecting the near surface redox front in crystalline bedrock using fracture mineral distribution, geochemistry and U-series disequilibrium,** H. Drake, E-.L. Tullborg, A.B. MacKenzie, submitted to Applied Geochemistry.

Drake carried out planning, sampling, sample preparation, microscopy and SEM-EDS, interpretations and writing. Tullborg contributed with planning, sampling and discussion and MacKenzie with U-series analyses and discussion.

Paper V **Distinguished multiple events of fracture mineralisations related to far-field orogenic effects in Paleoproterozoic crystalline rocks, Simpevarp area, SE Sweden.** H. Drake, E-.L. Tullborg, L. Page, submitted to Lithos.

Drake carried out sampling, sample preparation, microscopy and SEM-EDS, interpretations and writing. Tullborg contributed with planning and discussion and Page with $^{40}Ar/^{39}Ar$ *analyses and discussion.*

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1. Introduction

The bedrock in the Simpevarp area in south-eastern Sweden consists mainly of Paleoproterozoic, c. 1.80 Ga, granitic to dioritic rocks belonging to the Transscandinavian Igneous Belt (Gaàl and Gorbatschev, 1987; Wahlgren et al., 2008). This area is one of the two areas in Sweden that has been investigated by the Swedish Nuclear fuel and Waste Management Co. (SKB) in order to find a potential geological repository for spent nuclear fuel (SKB, 2000; Ström et al., 2008). The Simpevarp area is divided into two investigation subareas; the Simpevarp subarea and the Laxemar subarea. SKB have put forward the KBS-3 method for the repository design (SKB, 1983; SKB, 2006b). In this method, spent nuclear fuel is contained in copper canisters with a cast iron insert. The canisters are surrounded by bentonite clay and deposited at approximately 500 m depth in granitic rock (Fig. 1). The life time of the repository will be at least 100,000 years, and to predict future scenarios which may influence the stability of the repository it is crucial to have good knowledge about the present geological conditions and the geological evolution of the site (SKB, 2006b). The site investigations are comprehensive geo-scientific investigations, including measurements from the ground surface and in boreholes (SKB, 2001).

This thesis is focused on two major topics of importance in the planning of a repository for spent nuclear fuel: 1) the low-temperature evolution of the Simpevarp area based on fracture mineral studies, and 2) evolution of redox conditions in fracture coatings and in the wall rock.

1.1 The low-temperature evolution of the area

The rocks in the area are generally un-metamorphosed and structurally rather well-preserved and can be considered to have been quite stable throughout their geological history. However, low-grade ductile shear zones and fractures formed and reactivated during several events of deformation occur. These structures, and especially their mineral infill, but also wall rock alteration, can be used to gain information about the low- to moderate temperature evolution of the area from the Paleoproterozoic until the Quaternary. Information of the low-temperature evolution has been one of the major focuses in this thesis (Papers I, III and V) and is of importance for the site investigations because it contributes to the conceptual geological understanding of the site. This information will also give input to other investigation programmes at the site investigations, such as hydrogeochemical modelling and will provide input of evolutionary aspects of importance for the safety assessment and predictions of future scenarios of the site. Additionally, results from these studies have been important support to the drill core mapping at the site investigations.

The basis for these investigations is detailed examinations of cross-cutting relations of fracture mineralisations of different generations (Fig. 7), by which a relative sequence of fracture minerals can be distinguished (Papers I and V). Formation temperatures, crystal morphologies and chemical variations of the fillings have also been used to separate the generations. Furthermore, analyses of stable isotopes (C, O, S and Sr), fluid inclusions and trace element compositions of the fracture minerals can be used to reveal paleohydrogeological information (e.g. Gehör et al., 2002; Whelan et al., 2002; Tullborg, 2003; Blyth et al., 2004; Gascoyne et al., 2004; Milodowski et al., 2005). This information includes indications of formation temperatures, fluid chemistry, organic or microbial influence, and will aid to distinguish hydrothermal from low-temperature precipitates and indicate the origin of the fluids (Papers I and III). Radiometric dating and analysis of preferred fracture orientations of the different fracture filling generations provides time constraints and indications of the stress field at the time of formation (Paper V). This may enable interpretations of to which geological event each fracture filling generation is related, such as far-field effects of orogenies or sedimentary loading and unloading cycles. Fracture minerals and wall rock alteration features can also be used to reveal past and present redox conditions. This is for example shown by the distribution of Fe^{2+}-bearing pyrite, which is dissolved during oxidising conditions and the Fe^{3+}-bearing goethite and hematite which are formed during oxidising conditions.

1.2 Evolution of redox conditions

An important task in the safety assessment of a potential repository for spent nuclear fuel in crystalline bedrock is to demonstrate that reducing conditions can be maintained for a long period of time (Gascoyne, 1999; Puigdomenech et al., 2001). This is because oxygen may harm the copper canisters that host the nuclear waste and oxidising conditions may increase the mobility of some radionuclides, in case of canister failure. Normally, oxidising conditions prevail in surface waters and near-surface groundwaters, but are changed to reducing conditions at greater depth. Oxygen will be introduced into the repository during the construction phase. Dissolved oxygen originally present will be consumed through inorganic (mainly Fe^{2+}) and organic reactions along the flow paths (Puigdomenech et al., 2001). Fracture minerals and the wall rock participate in these reactions (e.g. Rivas-Perez et al., 2003) and studies of these can reveal past and present redox conditions, and the reducing capacity remaining. A scenario which may introduce oxygenated water to great depth in the bedrock is glacial melt-water intrusion (cf. Boulton et al., 2001). Such water can be assumed to contain more dissolved oxygen than the present recharge water and furthermore the organic buffer may be severely reduced below the ice (Puigdomenech et al., 2001).

Two different studies with focus on Precambrian as well as recent redox features in the fractures and in the wall rock are included in this thesis:

1. Wide-spread hydrothermally altered, red-stained (supposedly oxidised), wall rock have been compared to fresh rock nearby, and differences in mineralogy, mineral and whole rock chemistry and especially in reducing capacity, have been determined (Paper II). The main objective was to demonstrate the reducing capacity (mainly present in the form of Fe^{2+}) of fresh as well as altered wall rock.

2. Detection of the position of the recent near surface redox front has been investigated based on mineralogical, geochemical and U-series disequilibrium analyses of mineral coatings along open fractures (Paper IV, methodology outlined in Paper I). The main objectives were to locate the redox front and to determine its stability over time.

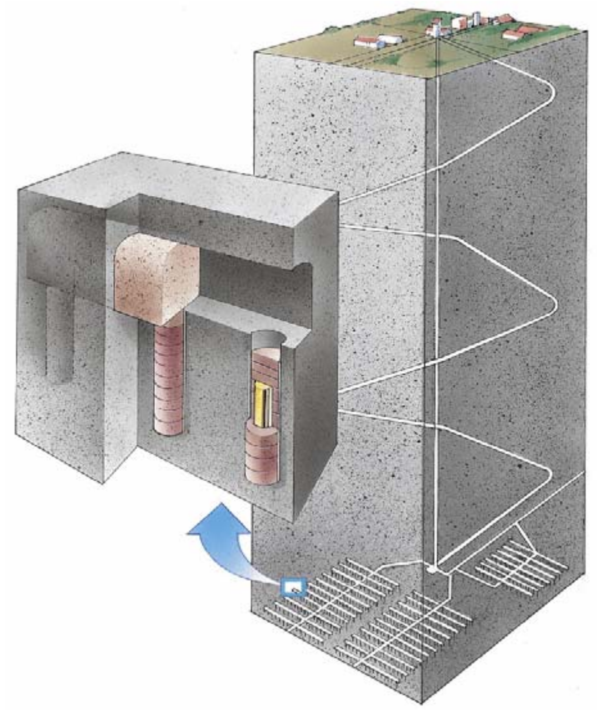

Fig. 1. Illustration of the KBS-3 method. ©SKB.

2. Geological setting

The bedrock in the Simpevarp area is dominated by a suite of c. 1.80 Ga rocks of variable composition (granite to quartz monzodiorite to diorite-gabbro) (Wahlgren et al., 2006) of the Transscandinavian Igneous Belt (TIB) (Gaàl and Gorbatschev, 1987) (Fig. 2). TIB makes up an area between the older

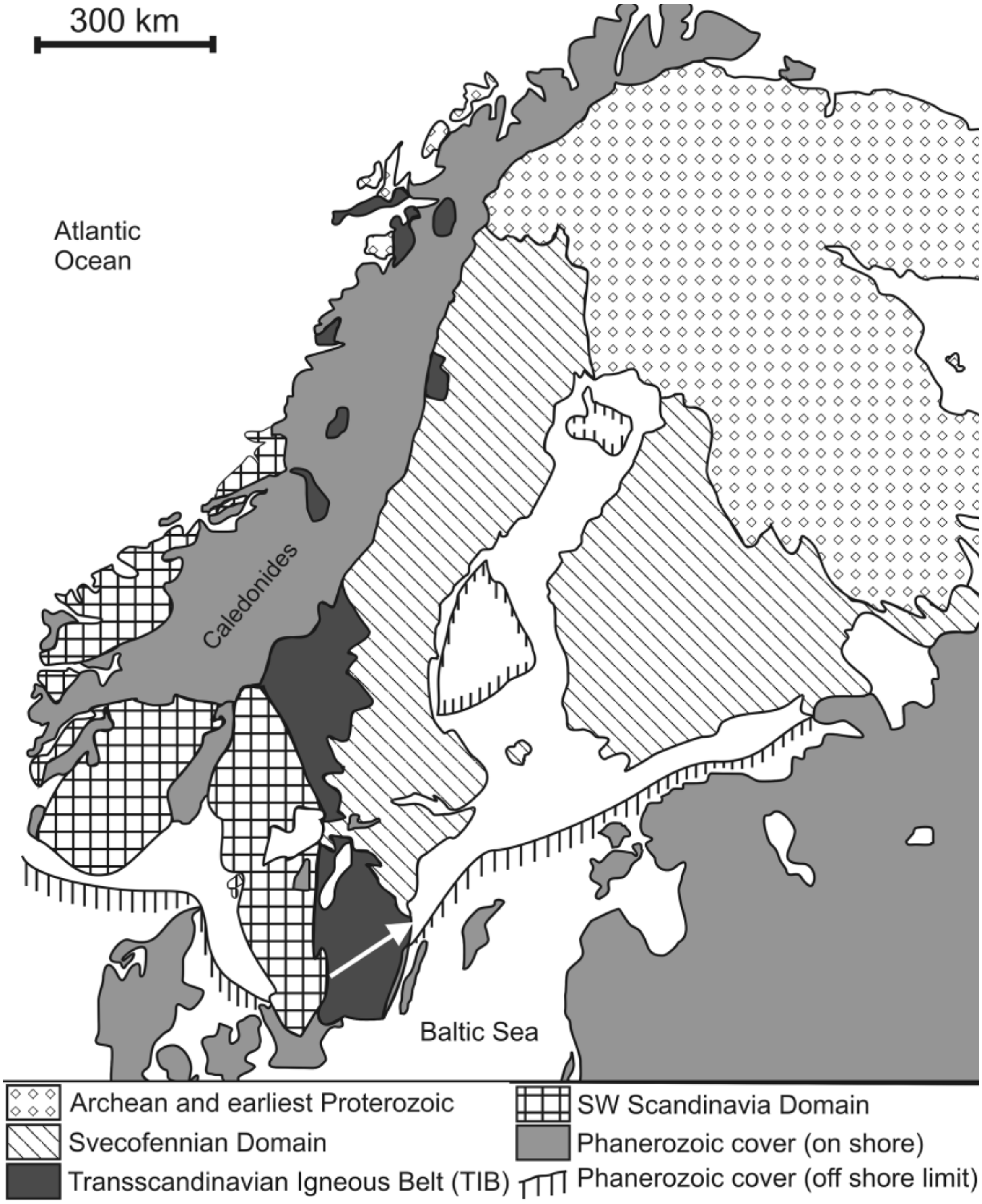

Fig. 2. Geological map showing the major units of the Baltic shield and surrounding areas (modified after Koistinen et al., 2001). The arrow indicates the location of the Simpevarp area.

Svecofennian crust to the north and the younger, SW Scandinavia domain in the west and was formed during several pulses of magmatism between 1.85 and 1.66 Ga with the younger of these rocks to the west (e.g. Larson and Berglund, 1992; Åhäll and Larson, 2000). The TIB rocks in south-eastern Sweden were formed towards the end of the Svecokarelian tectonic cycle at 1.83-c. 1.79 Ga (Stephens and Wahlgren, 2008). The major rock types within the site investigation area are Ävrö granite (quartz monzodiorite to granodiorite), quartz monzodiorite and fine-grained dioritoid (Fig. 3), in order of abundance. These rock types have overlapping mineralogical and chemical compositions and are mainly distinguished texturally. Minor rock types include dykes of fine-grained

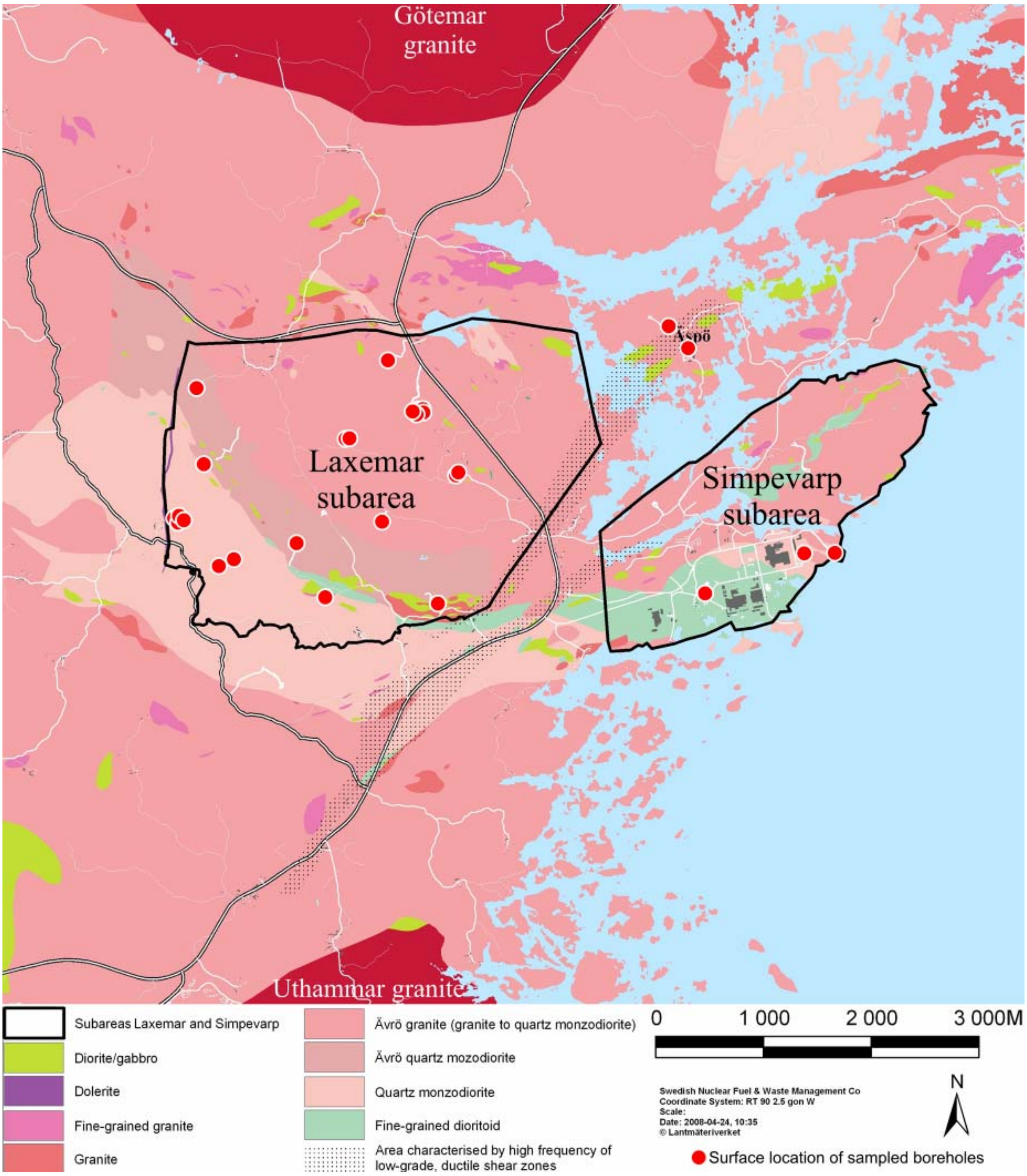

Fig. 3. Geological map of the Simpevarp area with Laxemar subarea and Simpevarp subarea indicated along with the surface locations of the cored boreholes sampled.

granite and dolerite. The TIB rocks in the Simpevarp area cooled through 500°C at 1,799-1,773 Ma and through 300°C at 1,620 Ma (Söderlund et al., 2008). Two granitic intrusions at Götemar and Uthammar (c. 1.45-1.44 Ga) crop out 2-3 km from the site investigation area (Kresten and Chyssler, 1976; Åberg et al., 1984; Kornfält et al., 1997; Åhäll, 2001). Recent studies indicate that they are associated to the Danapolonian orogeny in the south (Čečys and Benn, 2007; Bogdanova et al., 2008; Brander and Söderlund, 2008). The $^{40}Ar/^{39}Ar$ system in both biotite and amphibole within the site investigation area were reset in response to these intrusions (Söderlund et al., 2008).

The Sveconorwegian orogeny affected western Sweden at 1.1-0.9 Ga (e.g. Bingen et al., 2005). This orogeny was succeeded by development of a sedimentary foreland basin in eastern Sweden (Larson et al., 1999). During the end of the Sveconorwegian, N-S striking 978-946 Ma dolerite dykes (Söderlund et al., 2005b) intruded the TIB-rocks in southern Sweden, related to E-W extension. After erosion in the late Proterozoic the sub-Cambrian peneplain was created (Lidmar-Bergström, 1996) and the presently exposed bedrock surface largely corresponds to this peneplain. Cambrian to Early Silurian transgression and marine sedimentation resulted in deposition of Paleozoic sequences of mainly sandstone, alum shale and limestone, which covered large parts of the Baltic Shield. Remnants of these are currently mainly found off shore (Koistinen et al., 2001). The Scandinavian Caledonides in the northwest formed at ~510-400 Ma, with the main collision event at c. 430-400 Ma (e.g. Gee, 1975; Fossen and Dunlap, 1998; Roberts, 2003) (Fig. 2). In the south, amalgamation of Avalonia onto Baltica occurred at about 443 Ma (Torsvik and Rehnström, 2003), during formation of the North German-Polish Caledonides (Ziegler, 1985). Various thermal indicators, e.g. fission track analyses (Zeck et al., 1988; Larson et al., 1999; Cederbom, 2001), show that Caledonian foreland basin sediments had a thickness of c. 2.5-4 km during the Late Paleozoic. Mainly Permian to Triassic erosion, reduced the thickness of the sedimentary cover considerably (Zeck et al., 1988; Larson et al., 1999; Cederbom, 2001; Söderlund et al., 2005a). The sedimentary cover was finally eroded away during the Tertiary and the sub-Cambrian denudation surface was re-exposed (Lidmar-Bergström, 1996).

Several glaciations have influenced the area during the last 2 Ma. The resulting groundwater evolution is characterised by injection of glacial water into the bedrock fractures due to high hydraulic heads beneath the ice, followed by marine-brackish conditions with Baltic Sea influence causing density intrusion. Later interplay between meteoric recharge and glacial rebound (SKB, 2006a) has occurred. Thus, a combination of meteoric-brackish sea water and glacial melt water, and old, highly-saline, brine type waters is presently found at varying depths (SKB, 2006a).

3. Methods and material

More than 430 drill core samples have been collected from 38 cored boreholes of variable length (≤1000 m) from the Simpevarp area (Fig. 3), mainly from the Laxemar subarea. The triple-tube core drilling technique (e.g. Ask, 2006) has facilitated sampling of well-preserved fracture minerals.

For analyses of altered wall rock, sample pairs of altered and relatively unaltered reference rock were analysed. Thin sections were investigated using petrographic microscope and scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS) to trace mineralogical changes. ICP-AES/QMS analyses and Mössbauer spectroscopy analyses were carried out to trace element mobility and the degree of oxidation, respectively. Porosity and density were measured in a minor number of samples, using water-saturation technique.

Brief presentations of the different methods applied to fracture minerals are listed below. More detailed method descriptions are included in the specific papers.

3.1 Microscopy, SEM-EDS and X-ray diffraction

Thin sections and fracture surface samples from more than 300 fractures (about 120 thin sections and 185 fracture surface samples) have been analysed using petrographic microscope and SEM-EDS, which has enabled identification of minerals, as well as their crystal morphologies and chemical compositions. X-ray diffraction

(XRD) has mainly been applied to identify clay minerals, especially in water conducting fractures.

3.1 Stable isotopes

Stable isotope analyses of $\delta^{13}C$ ($^{13}C/^{12}C$) and $\delta^{18}O$ ($^{18}O/^{16}O$) in calcite, $\delta^{34}S$ ($^{34}S/^{32}S$) in pyrite, barite and gypsum and $^{87}Sr/^{86}Sr$ in calcite and gypsum have been carried out. The $\delta^{18}O$ value in calcite reflects the $\delta^{18}O$ of the groundwater from which it precipitated as well as the formation temperature (e.g. Veizer, 1983) and the $\delta^{18}O$ value in the formation fluid reflects its origin, e.g. marine or meteoric. However, water-rock interaction may also have an influence on the $\delta^{18}O$ value, especially under hydrothermal conditions (e.g. Truesdell and Hulston, 1980). In contrast to $\delta^{18}O$, $\delta^{13}C$ fractionation is not very temperature sensitive and influence from interaction with the crystalline wall rock is generally insignificant. Instead, the $\delta^{13}C$ in calcite generally reflects the $\delta^{13}C$ of the carbon sources involved, e.g. organic or inorganic (Ohmoto and Rye, 1979). The $\delta^{34}S$ value in sulphides and sulphates can, for instance, be used to separate hydrothermal/ magmatic sulphide from sulphide formed during bacterial sulphate reduction (e.g. Hoefs, 2004). The $^{87}Sr/^{86}Sr$-ratios in calcite and gypsum can be used to distinguish between different fracture filling generations. This is because $^{87}Sr/^{86}Sr$-ratios in the groundwater are mainly controlled by water-rock interaction and, therefore, by the $^{87}Sr/^{86}Sr$-ratios of the wall rock, which increase over time in response to ^{87}Rb decay (Faure, 1986; McNutt, 2000).

3.2 Fluid inclusions

Fluid inclusions in calcite and quartz have been analysed using a freezing-heating device mounted to an optical microscope. Temperatures of ice melting and fluid inclusion homogenisation have been obtained and provide information of the formation temperature, salinity and fluid compositions.

3.3 Trace element compositions

The trace element composition of calcite has been obtained by ICP-MS-analyses of calcite leachates. Trace elements of special interest are Sr, Mn and rare earth element (REE). The Sr content can be used to distinguish hydrothermal from possible low temperature precipitates. Mn contents can indicate redox conditions during formation but possibly also microbial Mn reduction of organic material (Tullborg, 2003; Milodowski et al., 2005). REE contents can provide information about redox conditions (Ce-anomalies) and the fluid composition (Möller and Morteani, 1983).

3.4 Calcite crystal morphology

Calcite crystal morphology can give information of the salinity of the water from which it precipitates (Folk, 1974; Milodowski et al., 2002; Milodowski et al., 2005). c-axis elongated calcite (e.g. scalenohedral crystals) has been correlated with formation from saline water, whereas c-axis flattened crystals indicate precipitation from fresh water. Equant crystals indicate precipitation from brackish water or a transition zone of fresh and saline water.

3.5 $^{40}Ar/^{39}Ar$ geochronology

Adularia and muscovite from fractures and altered wall rock from the Simpevarp area have been dated with $^{40}Ar/^{39}Ar$ dating. In summary, this method is based on formation of ^{39}Ar by irradiation of ^{39}K in K-bearing minerals. ^{39}Ar represents the original K-content of the mineral and is measured along with the radiogenic ^{40}Ar (produced by decay of ^{40}K in the mineral) released during step-heating of the mineral. The age is obtained from a plateau of similarly aged steps which reflects the $^{40}Ar/^{39}Ar$-ratio in the mineral. Closure temperatures for argon diffusion, below which ^{40}Ar is retained in the mineral, are ~350°C for muscovite and ~125-350°C for K-feldspar, although these temperatures may vary with e.g. grain size and deformation (Lovera et al., 1989; Hames and Bowring, 1994; Warnock and Zeitler, 1998; McDougall and Harrison, 1999; Reddy et al., 2001).

3.6 U-series disequilibrium

The uranium decay series nuclides (^{238}U, ^{234}U and ^{230}Th) can be applied to study recent redox conditions because the mobility of uranium is increased when oxidised (e.g. MacKenzie et al., 1992; Gascoyne et al., 2002). Basically, disequilibrium (activity ratio $\neq 1$) between the nuclides in the uranium decay series indicates mobilisation of uranium (removal or deposition) during the last 1 Ma.

3.7 Fracture orientations and mineral distribution

Fracture minerals have been routinely mapped by on-site geologists for each borehole during the site investigations. Fracture orientations have been measured during the drill core mapping, using Borehole Image Processing System (e.g. Gustafsson and Gustafsson, 2007), a method used for borehole wall imaging. Mapping data used in this thesis has been extracted from the SKB database Sicada and fracture orientations visualised in stereographic plots.

4. Summary of papers

Paper I
Palaeohydrogeology: A methodology based on fracture mineral studies. E-.L. Tullborg, H. Drake, B. Sandström, *Applied Geochemistry, vol. 23, 7, 1881-1897.*

The objective of this paper was to describe the methodology applied for paleohydrogeological studies used within the site investigations. Special focus has been put on investigations for detection of the near surface redox front and the variation of the saline/fresh water interface over time. The paper includes early and preliminary results from the site investigations in the Simpevarp area as well as at Forsmark. In addition, examples from studies in other areas, e.g. earlier SKB studies at adjacent Äspö Hard Rock Laboratory (Wallin and Peterman, 1999; Landström et al., 2001; Tullborg, 2003; Milodowski et al., 2005) are included. Prerequisites for paleohydrogeological investigations are described in detail. These include high quality drill core material and groundwater samples, as well as good background information and conceptual understanding of the site; both geological and hydrogeological. A scheme of step-by-step procedures is presented with a special aim to gain as much paleohydrogeological information as possible from the often very limited sample volumes, although the choice of methods is site specific. Preferred minerals are calcite and redox sensitive pyrite and Fe-oxyhydroxide. Calcite is preferred mainly because it is common and may precipitate during a wide range of temperatures as a response to physiochemical changes. Furthermore, the paleo groundwater conditions can be indicated by fluid inclusion analyses and the isotopic and chemical composition of calcite.

It is concluded that fracture mineral studies can be used successfully to outline the paleohydrogeological record in crystalline rock. Essential information to understand the stability or evolution of the groundwater system over a time scale that is relevant to performance assessment for a nuclear waste repository is likely to be obtained using the suggested methodology. It is also shown to be a good complement to hydrochemical investigations.

Similar methodology has been used at both Simpevarp and Forsmark, although some site specific differences exist, mainly depending on minor mineralogical differences and slightly diverse post-glacial evolution. Both sites are situated in Paleoproterozoic crystalline rocks which have suffered repeated fracture reactivation and formation of several fracture filling generations. The present water conductive fractures have often been conductive at several periods but the amounts of potential low temperature precipitates are small compared to hydrothermal and warm brine precipitates. The evolution of the Quaternary hydrology of both areas has been influenced by glaciation cycles and the evolution of the Baltic Sea, which have resulted in groundwater with varying compositions through time. These varying conditions can be traced by the different calcite types precipitated.

This methodology has been used in Papers III and IV, and to some degree in Paper V. The methodology is also suggested to be valid for other sites, especially in areas of crystalline bedrock, although site specific modifications are expected.

Paper II

Red-staining of the wall rock and its influence on the reducing capacity around water conducting fractures. H. Drake, E.-L. Tullborg, H. Annersten, *Applied Geochemistry, vol. 23, 7, 1898-1920.*

Red-stained, hydrothermally altered, rock is common adjacent to fractures in the Simpevarp area, and borders about 50% of the sealed fractures. Red-stained rock has commonly been interpreted to represent a distinct zone of altered, oxidised rock but analyses to reveal the degree of oxidation have seldom been performed. Red-stained wall rock from drill core samples from different depths have been compared to relatively fresh reference rock nearby in order to detect differences in mineralogy, mineral- and whole rock chemistry and especially in reducing capacity, in this case dominantly Fe^{2+} available, determined by Mössbauer spectroscopy. This is of importance because the safety assessment in the planning of a nuclear waste repository needs to show that Fe^{2+} (or another reductant) is available in the bedrock and along the fractures in order to provide enough reducing capacity, e.g. in a glacial scenario when oxygenated water may descend to great depths (e.g. Puigdomenech et al., 2001).

The red-stained rock adjacent to the fractures displays major changes in mineralogy compared to fresh rock; biotite, plagioclase and magnetite have been altered and chlorite, K-feldspar, albite, sericite, prehnite, epidote and hematite have been formed (Fig. 4), in accordance with earlier studies at Äspö (Eliasson, 1993; Tullborg, 1995). Moderate alteration in the macroscopically fresh reference rock shows that the hydrothermal alteration reaches further from the fracture than the red-staining. The changes in chemistry are however moderate; e.g. K-enrichment, Ca-depletion but constant Fe_{tot}. The Fe^{3+}/Fe_{tot} ratio in the oxide phase is higher in the red-stained samples whereas the Fe^{3+}/Fe_{tot} ratio in the silicate phase is largely similar in the altered rock as in the reference samples. Because most of the Fe is hosted in the silicate phase, the decrease in reducing capacity, if any, in the red-stained rock is very small and not as high as macroscopic observations suggest. Instead, formation of minute hematite grains in porous secondary minerals in pseudomorphs after plagioclase has caused the red-staining. The change in Fe^{2+} contents is generally insignificant and the average value for all of the samples shows a very small depletion (0.03 wt.%) in the red-stained rock. This small decrease is mainly related to the replacement of magnetite by hematite and the generally slightly higher epidote content in the red-stained rock but is probably also partly related to the replacement of biotite by chlorite. The average Fe^{2+}-content is considerably higher in quartz monzodiorite (3.8 wt.%) and fine-grained dioritoid (3.7 wt.%) than in Ävrö granite (1.7 wt.%), which has lower Fe-Mg silicate contents and higher epidote contents. Increased porosity is also characteristic for the red-stained rock and may result in enhanced retention of radio-nuclides due to an increased sorptivity and diffusion close to the fracture.

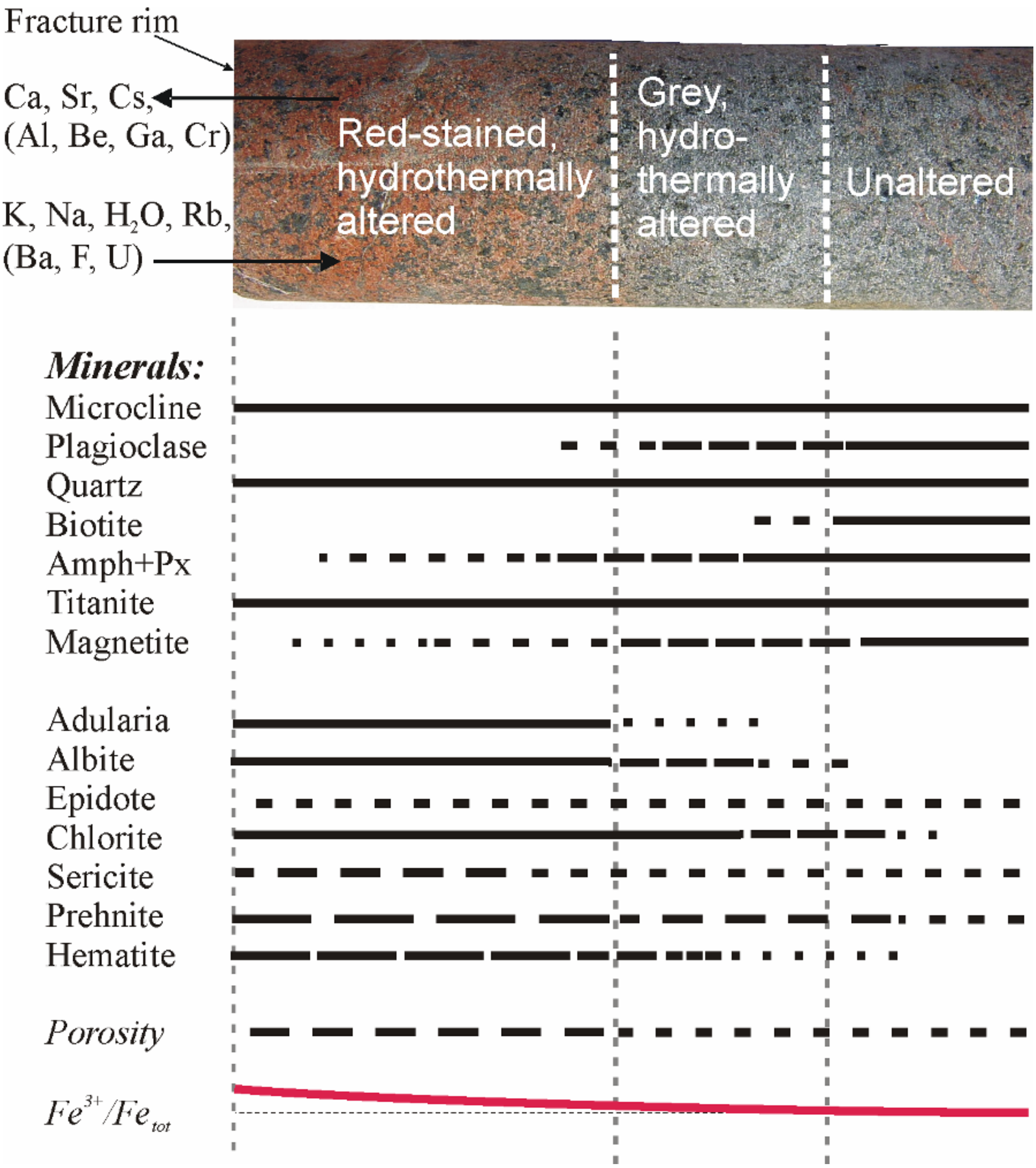

Fig. 4. Tentative illustration of the major features of the red-stained wall rock compared to the reference rock nearby, which is either partly altered but not red-stained, or unaltered. Arrows indicate elements enriched or depleted in the red-stained rock compared to the reference rock. The horizontal lines (partly stippled) show the mineral distribution adjacent to the fracture, as well as the difference in porosity. The lowermost line illustrates the change in Fe^{3+}/Fe_{tot} relative to a reference line.

Paper III
Paleohydrogeological events recorded by stable isotopes, fluid inclusions and trace elements in fracture minerals in crystalline rock, Simpevarp area, SE Sweden. H. Drake, E.-L. Tullborg, *in press, Applied Geochemistry.*

The objective of this paper was to gain information of the paleohydrogeological evolution of the Simpevarp area. Such information is essential to understand the stability or evolution of the groundwater system over time scales relevant to the

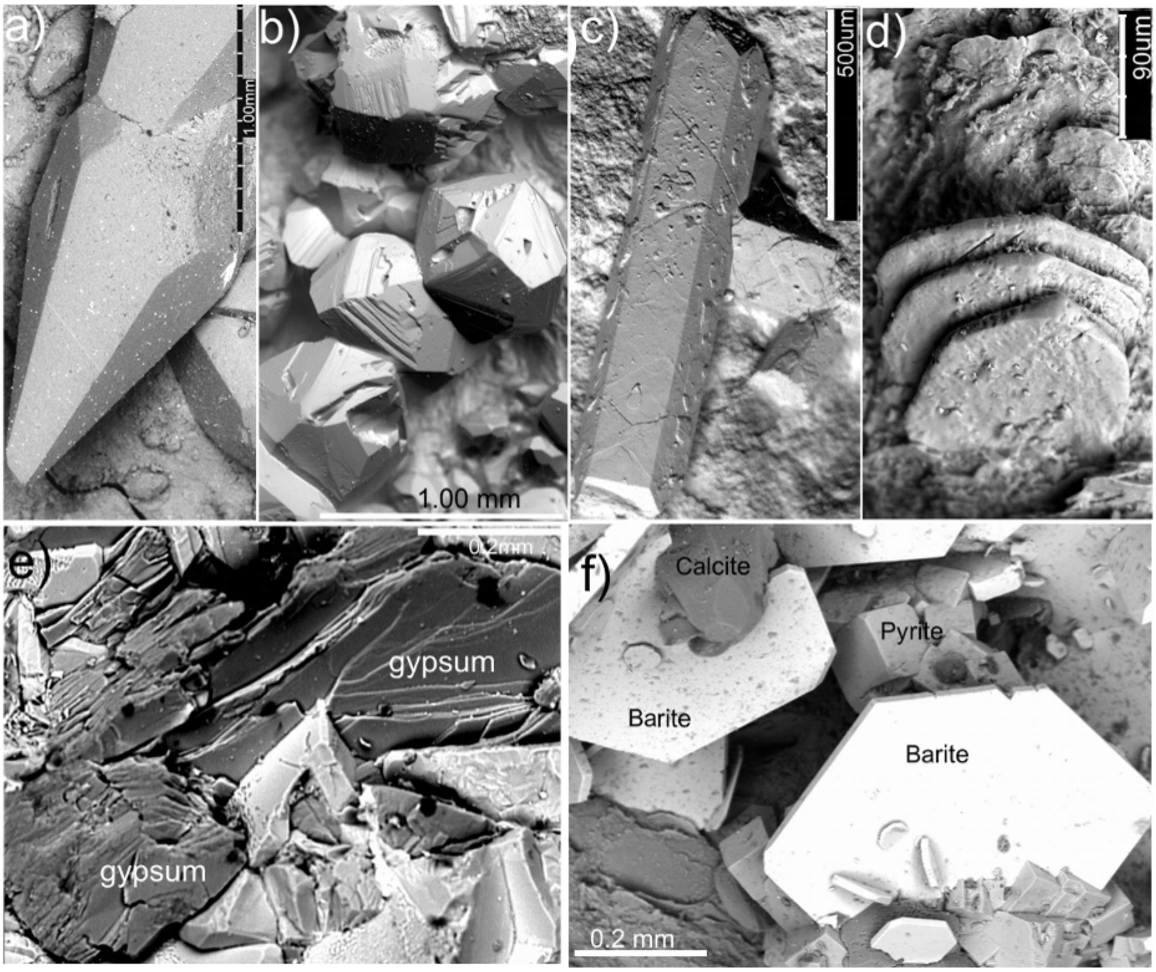

Fig. 5. Back-scattered SEM-images of (a) scalenohedral (c-axis elongated) calcite, (b) equant (short c-axis/round) calcite, (c) needle-shaped (very elongated c-axis) calcite, (d) nailhead-shaped (very short c-axis) calcite, (e) gypsum, and (f) euhedral barite, calcite and pyrite, from open fractures.

performance assessment for a spent nuclear fuel repository. Fracture minerals calcite, pyrite, gypsum, barite and quartz (Fig. 5), formed during several events, from the Proterozoic possibly to the Quaternary, have been analysed for stable isotopes; $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$, trace element chemistry and fluid inclusions. This methodology has been successful to separate the different generations and to characterise their formation conditions. Proterozoic calcite and pyrite show inorganic and hydrothermal/magmatic stable isotope signatures and varying formation temperatures (c. 200-360°C) and salinities (0-24 wt.% eq. $CaCl_2$). The Paleozoic fracture minerals precipitated from brine-type fluids with organic influence at 80-145°C. Late Paleozoic to recent, possibly Quaternary, minerals have probably formed during different events at gradually lower temperatures. Some precipitates are formed from organic-rich fluids partly modified by microbial activity in situ. However, overlapping isotope signatures complicate chronological separations of these minerals. They are common in the same fracture systems indicating that water conducting structures have been intermittently conductive from the Paleozoic and onwards. The low-temperature calcite shows $\delta^{18}O$ values and crystal morphologies (Fig. 5a-d) indicating formation from a wide range of water types; fresh to brackish and saline and that the fresh-saline water interface has changed considerably over time. $^{87}Sr/^{86}Sr$-ratios in calcite show that Sr isotope ratios in the groundwaters have mainly been determined by in situ water-rock interaction processes.

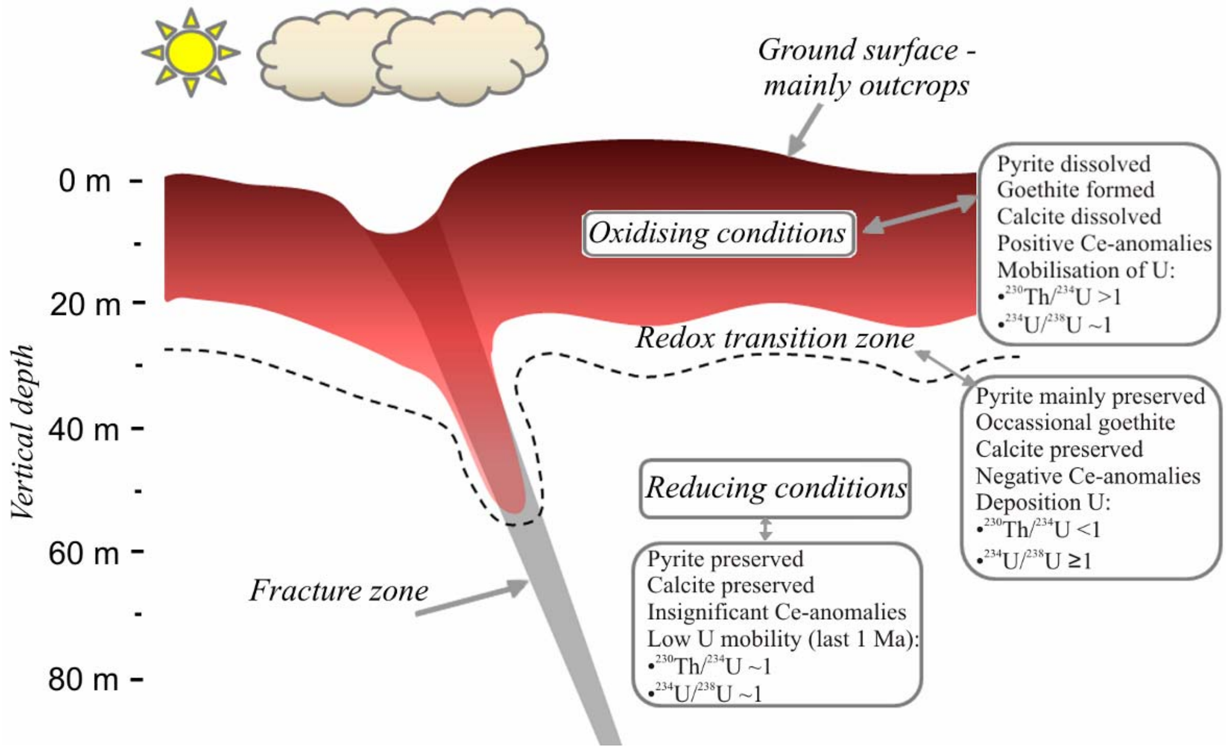

Fig. 6. Tentative sketch model of the near-surface redox front in the Laxemar subarea. The different fields represent the depth intervals where mineralogical, geochemical and U-series analyses of fracture coatings indicate recent oxidising condition, reducing conditions or a transition zone between these.

Paper IV
Detecting the near surface redox front in crystalline bedrock using fracture mineral distribution, geochemistry and U-series disequilibrium, H. Drake, E-.L. Tullborg, A.B. MacKenzie, *submitted to Applied Geochemistry.*

The redox front marks the change from oxidising conditions in surface waters and near-surface groundwaters to reducing conditions in deeper groundwaters. The oxygen is reduced through organic and inorganic reactions along the flow paths and these reactions involve fracture minerals, which can be used to trace the redox front. The focus of this paper was to locate the near surface redox front in the Laxemar subarea, and to determine its stability over time. This is of importance for the safety assessment of a nuclear waste repository, e.g. because oxygen may harm the copper canisters (cf. Chapter 1).

A combination of different methods, such as detailed mapping and investigation of redox sensitive minerals, geochemical analyses and U-series measurements of fracture coatings from eleven, closely spaced, near surface cored boreholes, have been used to detect the recent redox front in the site investigation area. Although penetration of glacial waters to great depths has been confirmed in the area (SKB, 2006a), this study indicates that these glacial waters were not oxidising at repository depth. Instead, oxygen in the recharge water has generally been consumed within the upper tenths of meters or at slightly greater depth in fractures/crush zones with increased transmissivities ($\geq 1 \cdot 10^{-7}$ m^2/s). Fig. 6 outlines the signatures used to locate the redox front position. These include a shift from mainly pyrite in fractures below the redox front to mainly goethite in fractures above the redox front. Fracture coatings close to the surface also show positive Ce-anomalies and clear signs of bulk U removal, indicative of oxidising conditions. The U-series measurements indicate that the observed redox front corresponds to recent conditions.

Paper V
Distinguishing multiple events of fracture mineralisations related to far-field orogenic effects in Paleoproterozoic crystalline rocks, Simpevarp area, SE Sweden. H. Drake, E-.L. Tullborg, L. Page, *submitted to Lithos*

The aim of this paper was to outline the low-temperature evolution of the Simpevarp area from 1.8 Ga to present, mainly by distinguishing a relative chronological sequence of fracture filling generations related to local or regional events of deformation. The different fracture filling generations have been distinguished using microscope investigations (mainly SEM-EDS) of cross-cutting fractures (Fig. 7). Results from analyses of stable isotopes, trace elements and fluid inclusions (Paper III) have also added to the subdivision of the different generations. Chronological constraints of the different generations have been gained by $^{40}Ar/^{39}Ar$-dating of muscovite and adularia from fractures and altered wall rock. Preferred fracture orientations of the different generations have been obtained using data from the drill core mapping.

Fracturing and formation of different fracture mineral parageneses during at least four different orogenies have been indicated; the Svecokarelian orogeny (>1.75 Ga), the Danapolonian orogeny (~1.47-1.44 Ga), the Sveconorwegian orogeny (~1.1-0.9 Ga) and the Caledonian orogeny (~0.5-0.4 Ga). Fracture minerals and greisen of presumed Danapolonian origin were mainly formed in relation to the intrusion of two indicatively Danapolonian-related granites nearby. Late Sveconorwegian dolerite intrusions (Wahlgren et al., 2007) and fractures filled with Cambrian sandstone indicate periods of extension in the area (cf. Munier and Talbot, 1993; Röshoff and Cosgrove, 2002). Fracture minerals formed from the late Paleozoic until recently, possibly Quaternary, show influence of loading and unloading cycles of sediments and subsequent glaciations and the youngest fracture minerals may have been precipitated from waters of similar composition as the present groundwater.

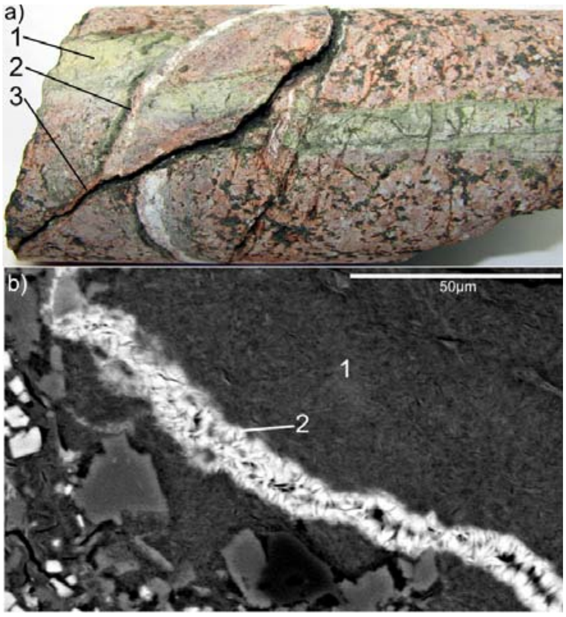

Fig. 7. Examples of cross-cutting fractures of different generations. (a) Photograph of three fracture generations in a drill core sample; 1) epidote-filled fracture, 2) fracture filled with calcite, adularia and laumontite, and 3) open fracture coated by clay minerals. (b) Back-scattered SEM-image of two generations of fracture fillings containing Mg-rich chlorite, adularia and apatite (1), cut by a fracture filled with Fe-rich chlorite (2).

5. Discussion

Detailed and comprehensive investigations of fracture minerals in cross-cutting fractures have resulted in the establishment of a sequence of fracture filling generations. The characteristics of each generation indicate potential association to specific geological events. Most of the fracture fillings in the area are very old (Proterozoic to Paleozoic) and only small amount of the fracture minerals might be Quaternary. Important characteristics, including redox conditions, of each generation in the chronological sequence of fracture mineralisations are discussed below:

- Many of the deformation zones in the area include mylonite. These are dominated by fine-grained epidote and quartz, ± muscovite, chlorite and albite, and represent the first mineralisation in the area. Formation in response to N-S to NNW-SSE directed maximum compressive stress in the late stages of the Svecokarelian orogeny (>1,750 Ma) has been suggested based on micro-structures of the mylonites and cooling ages of the TIB-rocks (Lundberg and Sjöström, 2006; Wahlgren et al., 2006; Stephens and Wahlgren, 2008; Söderlund et al., 2008). $^{40}Ar/^{39}Ar$-dating of muscovite in mylonite yielded a plateau age of c. 1,406 Ma, which is much younger than expected and does probably not represent the ductile deformation. Instead, the age probably represents resetting of the $^{40}Ar/^{39}Ar$-system in muscovite in relation to the intrusions nearby.

- Cataclasite is very common in deformation zones, often in reactivated ductile shear zones. Several varieties exist and these can be divided into at least two main types. The semi-ductile features observed suggest formation close to the brittle-ductile transition at about 300-350°C. A reasonable age estimate is formation prior to 1,620 Ma, when the rock initially cooled below 300°C but younger than 1,773 Ma, when the rock cooled below 500°C (Söderlund et al., 2008). Formation in relation to later events is also possible.

- A sequence of fracture mineral parageneses and associated wall alteration (greisen, red-staining and sericitisation), is interpreted to be related mainly to the intrusion and post-magmatic circulation of the granites at Götemar and Uthammar, as indicated by $^{40}Ar/^{39}Ar$ dating of muscovite in red-stained wall rock and in greisen. These granites seem to be related to the Danapolonian orogeny in the south (Čečys and Benn, 2007; Bogdanova et al., 2008; Brander and Söderlund, 2008). Consequently, these fillings have formed as a far-field effect of this orogeny, although the features of this orogeny are still rather poorly known. This sequence of fillings formed at gradually lower formation temperatures, as suggested by the stability temperatures of the dominant Ca-Al-silicates (in chronological order); epidote, prehnite, and laumontite, as well as by fluid inclusion homogenisation temperatures which range from c. 370°C down to 195°C. The assumption that the fillings in this sequence are fairly coeval and formed at similar conditions is based on stable isotopes in calcite ($\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$) and pyrite ($\delta^{34}S$), as well as on gradual mineral replacements during the sealing of the fractures. However, some of these fillings are probably older than the Götemar and Uthammar granites. The stable isotopes $\delta^{18}O$, $\delta^{13}C$ and $\delta^{34}S$ indicate formation from hydrothermal fluids without organic influence and fluid inclusions show large salinity variations. The characteristic red-staining wall rock alteration related to these fractures show major mineralogical differences but small changes in chemistry and reducing capacity compared to fresh wall rock. Although the red-stained rock appears to be oxidised, the reducing capacity is generally unchanged. This is important for the safety assessment of the repository since a high reducing wall rock capacity aids to maintain long-term reducing conditions in the repository.

- Sveconorwegian effects in the area are intrusion of N-S oriented, c. 0.9 Ga dolerites indicating E-W directed extension during a late stage of this orogeny (Wahlgren et al., 2007). Thin sealed fractures filled with mainly calcite, adularia, laumontite, chlorite, quartz, illite, and hematite may also be related to far-field effects of the Sveconorwegian orogeny, as indicated by an $^{40}Ar/^{39}Ar$ age of adularia of c. 989 Ma. Alternatively, this age represents resetting of the adularia during this orogeny. Based on the mineralogy and appearance only, these fillings are not easily distinguished from older fillings in the absence of cross-cutting relations. However, stable isotope ratios and fluid inclusion signatures indicate formation from hydrothermal fluids at slightly lower temperatures than older calcite. Fluid inclusion homogenisation temperatures of mainly >200°C suggest formation prior to 710±78 Ma, when the rock temperatures cooled below c. 200°C, as shown by titanite fission track ages (Tullborg et al., 1996). Although this paragenesis may be largely Sveconorwegian, it is not very distinct and not as widespread as the other fracture mineral parageneses.

- The occurrence of Cambrian sandstone in a few sub-vertical, near-surface fractures in the Simpevarp area indicates that the bedrock surface is close to the sub-Cambrian peneplain. According to Röshoff and Cosgrove (2002), the sandstone textures indicate downward injection of fluidised sediments. The high pressure needed may have been built up in the Cambrian sediments due to the load of overlying Paleozoic sedimentary successions covering southern Sweden. The sediments were injected into sub-vertical, bedrock fractures when these were re-activated during early Paleozoic tectonic events. Cambrian sandstone fractures in the coastal region around Simpevarp generally follow the orientation of the basement fracture sets with dominant directions in NNE-ENE (Nordenskjöld, 1944; Kresten and Chyssler, 1976; Munier and Talbot, 1993; Alm and Sundblad, 2002; Röshoff and Cosgrove, 2002). These directions may indicate relation of the sandstone fractures to NW-SE directed extension associated to the opening of the Iapetus Ocean, as proposed by Munier and Talbot (1993).

- Fracture fillings dominated by calcite, adularia, chlorite, fluorite, hematite, quartz, pyrite, sulphates, clay minerals, apophyllite, zeolites and REE-carbonate are interpreted to be formed in relation to far-field effects of the Caledonian orogeny. Stable isotopes, trace elements and fluid inclusions of these fillings show that they were mainly formed at 80-145°C from highly saline (brine type) fluids with organic influence. This indicates influence from descending fluids from overlying, organic-rich, Cambrian-Silurian sediments, as evidenced by asphaltite in Paleozoic fillings at Forsmark, central Sweden (Sandström et al., 2006). Adularia from sealed fractures yielded $^{40}Ar/^{39}Ar$ ages of c. 401, 426 and 444-448 Ma. These adularia ages overlap in time with both the Scandinavian Caledonian orogeny in the northwest (e.g. Roberts, 2003) and the North German-Polish Caledonian orogeny in the south (Ziegler, 1985; Torsvik and Rehnström, 2003). The dominant fracture orientations of these fractures correlate with formation in relation to the maximum compressive stress of the Scandinavian Caledonides. Similar orientations have been documented for post-Ordovician fractures at Öland nearby (Milnes and Gee, 1992) and fractures cross-cutting Cambrian sandstone dykes in SE Sweden (Nordenskjöld, 1944).

- Fracture fillings of similar mineralogy as the Caledonian fracture fillings were precipitated intermittently in open bedrock fractures from the late Paleozoic during gradually lower temperatures following the uplift related to erosion of the Paleozoic sediments, and ranging into ambient temperatures similar to the present conditions. Late Paleozoic minerals are difficult to separate from potential recent precipitates using stable isotopes due to overlapping and similar signatures. Calcite and pyrite show organic and closed system microbial influence, which infer temperatures below 110°C (Jørgensen et al., 1992). $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values show that some of the calcites may have formed from fluids in equilibrium with waters similar to present groundwaters at ambient temperatures. A combination of calcite $\delta^{18}O$ values and crystal morphologies indicate formation from waters with different $\delta^{18}O$ values and salinities, such as fresh and brackish water, in accordance with Tullborg (2003) and Milodowski et al. (2005). Presently water conducting fractures are mostly related to deformation zones and often consist of loose and clayish coatings, calcite, chlorite, and wall rock fragments. In the upper part of the bedrock, dissolution of pyrite and formation of goethite is evident. This shift in mineralogy is generally located at 15-25 m depth and marks the change from oxidising conditions in groundwater near the surface to reducing conditions at greater depth. This extent of oxygen intrusion is also indicated by positive Ce-anomalies and U-series analyses. The latter show that the observed redox front corresponds to recent conditions. This also shows that descending oxygenated waters, e.g. glacial meltwater, generally have had their oxygen load reduced within the upper tenths of meters by organic and inorganic reactions. These observations are highly important for the safety assessment in the planning of a nuclear waste repository.

6. Conclusions

This thesis has resulted in detailed information on the low-temperature evolution, including paleohydrogeology and implications of past and present redox conditions, of the Simpevarp area, based on a combination of several methods. The methodology used has successfully added to the understanding of the geological and hydrogeological/hydrogeochemical evolution of the site. Furthermore, important information for the safety assessment in the planning of a repository for spent nuclear fuel has been gained regarding redox conditions.

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Appendix

Other related contributions by the author not included in the thesis:

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