Stable isotope composition of mineral proxies as a record of fluid evolution in fractured bedrock, the Olkiluoto site, Finland

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Cover photo: Zoned pyrite grains. Back cover photo by P. Niinikoski.

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Abstract

Fluid evolution in fractured bedrock at the Olkiluoto site in Finland was investigated by examining the stable oxygen and carbon isotope composition of secondary calcite and sulfur isotope composition of secondary sulfide minerals, analyzed from bulk material by traditional techniques and *in situ* by secondary ion mass spectrometry (SIMS). The application of in situ analyses allowed for great spatial resolution to be obtained for the stable isotopic variation in the samples. The results of this study clearly demonstrated a high variability in isotopic composition of mineral grains within a few tens of micrometers.

The study site is located on the western coast of Finland, hosts the Olkiluoto nuclear power plant and is the planned site for the geological disposal of spent nuclear fuel. Due to these reasons, the evolution of the deep bedrock groundwaters at the site is of special interest. The aim of this work was to characterize the latest fracture fillings and increase our knowledge of the hydrogeochemical evolution in deep fractured bedrock. In order to achieve this, drill core material was collected from water conducting fractures, concentrating on hydraulically active zones along which the infiltration of surface waters is most active. Calcite bearing fracture fillings were selected from numerous drill cores available from the site.

Fracture filling calcites were grouped according to calcite morphology, mineral associations and their relative position in the fracture sequence into five groups. The latest fracture fillings were identified from the surfaces of open fractures as clear, platy or euhedral fillings (Group 1) which occasionally contained minor amount of silicate inclusions (Group 2). A low formation temperature of the late-stage fillings was confirmed by fluid inclusion studies. Massive, older calcite fillings were separated into three groups all representing high temperature fluid circulation. The massive fillings were broadly comparable by their morphology, mineral associations and stable oxygen and carbon isotope composition to the results obtained in earlier studies, which characterized hydrothermal circulation at the site. Group 3 fillings preceded the late-stage calcite fillings and are interpreted to be associated with a Paleozoic (541-252 Ma) thermal event caused by the uplift and erosion of the Caledonian nappes, affecting large parts of the Fennoscandian Shield. Analyses of cogenetic pyrite grains by SIMS showed highly variable sulfur isotope compositions indicative of bacterial sulfate reduction (BSR) in the fracture fillings of Groups 1, 2 and 3. Detailed analysis of the carbon isotope composition of the Group 3 calcite indicated degradation of organic matter as the electron source in BSR. Group 5 and Group 4 fillings represent the earliest hydrothermal events in the bedrock, likely related to the rapakivi granite and diabase intrusions of Mesoproterozoic (1600-1000 Ma) age. Variations in the oxygen and carbon isotope compositions of Group 4-5 fillings indicate evolution of the hydrothermal system and possible re-equilibration of the calcite fillings with later fluid flow.

A characteristic feature of the late-stage fillings (Group 1, 2) is small-scale variations in stable isotope compositions, indicating the influence of microbial processes on groundwater conditions. Furthermore, a comparison with the groundwater data showed that the late-stage fillings are generally not in isotopic equilibrium with the current groundwaters. Based on the results obtained in this work, the following characteristics of the paleogroundwaters representing Group 1-2 mineralizations can be identified: Transitions between geochemically distinct environments can be identified in the shallow bedrock, at depths <100 m. The upper ca. 30 m has been characterized by BSR. Organic matter has been the electron donor and sulfate derived from infiltrating waters has been the electron acceptor. The depth range of 34-54 m has been characterized by microbial oxidation of methane, although the scarcity of calcite with methanotrophic signature suggests that most of the carbon was derived from degradation of organic matter. At depths >54 m the increase in the $\delta^{13}C$ values of late-stage calcite shows distinct evidence for methanogenesis. After the precipitation of calcite in Groups 1-2, the methanic environment in the depth range of ~60-300 m has been replaced by sulfidic conditions. Most likely the chance occurred by the infiltration of SO_4^{2-}-rich waters into the bedrock during the Littorina Sea stage or an unspecified earlier marine stage of the Baltic Sea. BSR in the fractured bedrock has been characterized by restricted SO_4^{2-} input, causing highly variable sulfur isotopic signatures in the precipitating pyrite grains. The age of the late-stage fillings is difficult to constrain, but they are likely associated with the infiltration events related to deglaciation events and glacioisostatic land movements, which have occurred repeatedly during the Quaternary period (<2.58 Ma).

Tiivistelmä (in Finnish)

Tässä työssä tarkasteltiin kallioperän raoissa kiertäneiden fluidien kehitystä Olkiluodossa käyttäen hyväksi rakovyöhykkeisiin kiteytyneiden sekundääristen kalsiitti ja sulfidimineraalien stabiilien happi, hiili ja rikki-isotooppien koostumusta. Mineraalien isotooppikoostumus määritettiin perinteisin menetelmin, sekä käyttäen sekundääri-ioni massaspektrometriä (SIMS), jonka ansiosta mineraalien isotooppisuhteiden vaihtelu mineraalirakeiden sisällä voitiin määrittää tarkasti. Tutkimus osoitti että mineraalien isotooppikoostumuksissa on laajaa vaihtelua jo muutamien kymmenien mikrometrien sisällä.

Tutkimuskohde sijaitsee Suomen länsirannikolla Olkiluodon saaressa, jossa sijaitsee Olkiluodon ydinvoimala ja joka suunniteltu loppusijoituspaikka käytetylle ydinpolttoaineelle. Tämän vuoksi kohteen syvien pohjavesien kehitys on erityisen kiinnostava tutkimuskohde. Tämän tutkimuksen tarkoituksena oli karakterisoida viimeisimmät raontäytteet ja niitä hyväksi käyttäen selvittää alueen kalliopohjavesien hydrogeokemiallista kehitystä. Tutkimukseen valittiin alueelta saatavilla olevasta kairasydänmateriaalista raontäytteitä vettä johtavista raoista, keskittyen erityisesti hydraulisestä tärkeisiin vyöhykkeisiin kallioperässä. Kalsiittipitoisia raontäytteitä valittiin lukuisista kairasydämistä, joita on saatavilta tutkimuskohteesta.

Raontäytteet luokiteltiin viiteen ryhmään kalsiittien morfologian, mineraaliseurueiden ja suhteellisen aseman perusteella raontäytteessä. Viimeisimmät raontäytteet esiintyivät avoimilla rakopinnoilla läpikuultavina laattamaisina tai omamuotoisina kalsiittikiteyminä (ryhmä 1), joista osassa oli pieniä määriä silikaattimineraalisulkeumia (ryhmä 2). Fluidisulkeumatutkimukset osoittivat niiden syntyneen alhaisissa lämpötiloissa. Massiiviset, vanhemmat rakokalsiittitäytteet jaettiin kolmeen ryhmään ja ne vastaavat korkean lämpötilan fluidien kiertoa tutkimuskohteessa. Perustuen niiden morfologiaan, mineraaliassosiaatioihin ja stabiilien happi- ja hiili-isotooppien koostumukseen, massiiviset raontäytteet vastaavat pääpiirteiltään aikaisemmissa tutkimuksissa karakterisoituja hydrotermisiä kalsiittirakotäytteitä. Ryhmän 3 täytteet edeltävät viimeisimpiä kalsiittikiteymiä, ja niiden tulkittiin liittyvän Paleotsooiseen (541-252 Ma), Fennoskandian kilven alueella laajalti vaikuttaneeseen termiseen tapahtumaan, jonka aiheutti Kaledonien vuorijonon kohoaminen ja rapautuminen. Ryhmien 1-3 kalsiitin kanssa kiteytyneen pyriitin rikki-isotooppianalyysit SIMS menetelmällä osoittivat rikki-isotooppisuhteiden voimakkaan vaihtelun, mikä viittaa bakteerien välittämään sulfaatin pelkistykseen. Ryhmän 3 kalsiittien hiili-isotooppianalyysit puolestaan osoittavat, että bakteerit käyttivät orgaanista materiaalia elektronien lähteenä sulfaatin pelkistyksessä. Ryhmän 4 ja 5 raontäytteet edustavat alueen varhaista hydrotermistä kiertoa, ja liittyvät todennäköisesti Mesoproterotsooisiin (1600-1000 Ma) rapakivigraniitti ja diabaasi intruusioihin. Ryhmän 4-5 kalsiittien hiili- ja happi-isotooppikoostumuksien vaihtelut viittaavat hydrotermisen systeemin kehitykseen ja mahdolliseen rakojen uudelleen aktivoitumiseen ja siihen liittyvään isotooppikoostumusten uudelleen tasapainottumiseen myöhempien fluidien kanssa.

Myöhäisimpien kiteymien (ryhmät 1-2) tyypillinen piirre on voimakas vaihtelu stabiilien isotooppien suhteissa, mikä viittaa mikrobien

toiminnan vaikutukseen pohjavesissä. Vertailu nykyisten pohjavesien ja viimeisimpien kiteymien välillä osoittaa myös, että viimeisimmät kalsiittikiteymät eivät ole tasapainossa nykyisten pohjavesien kanssa stabiilien happi- ja hiili-isotooppien koostumuksen suhteen vaan ne vastaavat joitain aiempia pohjavesiolosuhteita. Tämän tutkimuksen perusteella ryhmien 1-2 mineralisaatioita vastaavien paleopohjavesien piirteistä voidaan todeta seuraavaa: Geokemialtaan erilaisten ympäristöjen välistä vaihtelua on tapahtunut maan pinnan läheisissä (<100 m) kalliopohjavesissä. Ylimmässä 30 m vallitsevana prosessina on ollut bakteerien välittämä sulfaatin pelkistys, jossa bakteerit ovat käyttäneet energialähteenään pintalähtöisten vesien mukanaan tuomaan sulfaattia ja orgaanisia yhdisteitä. Syvyysvälillä 34-54 m on tapahtunut jonkin verran mikrobien välittämää metaanin hapettumista, joskin bakteerit ovat pääsääntöisesti käyttäneet prosessissa elektronien lähteenä orgaanisen aineksen hajottamista. Yli 54 m:n syvyydellä kalsiittien δ^{13}C arvojen nousu viittaa mikrobien metaanin tuottoon. Syvyydellä ~60-300 m tämä kalsiittien viittaaman metanogeneettinen ympäristö on myöhemmin korvautunut sulfaattia pelkistävällä. Tämä muutos on todennäköisesti seurausta sulfaattirikkaiden vesien virtauksesta kallioperään joko Litorina merivaiheen tai sitä edeltävän aikaisemman merivaiheen aikana. Olkiluodon kallioperässä bakteerien välittämään sulfaatinpelkistykseen liittyvä erityispiirre on voimakkaasti vaihtelevat rikki-isotooppisuhteet, jotka ovat seurausta sulfaattia pelkistävien bakteerien rajoitetusta sulfaatin saannista. Viimeisimpien rakomineralisaatioiden syntyikää on vaikea haarukoida, mutta ne oletettavasti liittyvät jäätiköiden perääntymisvaiheita seuraaviin maankuoren liikkeisiin ja pintavesien suotautumistapahtumiin, joita alueella on jaksoittain tapahtunut Kvartäärikauden (<2,58 Ma) aikana

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List of original publications

This thesis is based on the following publications:

I Sahlstedt, E., Karhu, J.A. and Pitkänen, P. 2010. Indications for the past redox environments in deep groundwaters from the isotopic composition of carbon and oxygen in fracture calcite, Olkiluoto, SW Finland. Isotopes in Environmental and Health Studies, vol. 46 (3), p. 370-391

II Sahlstedt, E., Karhu; J.A., Pitkänen, P. and Whitehouse, M. 2013. Implications of sulfur isotope fractionation in fracture-filling sulfides in crystalline bedrock, Olkiluoto, Finland. Applied Geochemistry, vol. 32, p. 52-69.

III Sahlstedt, E., Karhu, J.A., Pitkänen, P. and Whitehouse, M. Carbon isotope records of microbial sulfate reduction in crystalline bedrock fractures. Submitted to Applied Geochemistry.

The publications are referred to in the text by their roman numerals.

Author's contribution to the publications:

I The study was planned by J. Karhu and P. Pitkänen. The analyses were conducted by E. Sahlstedt and the results were jointly interpreted by E. Sahlstedt and J. Karhu. E. Sahlstedt had the main responsibility of preparing the manuscript, which was commented on and edited by the other authors.

II The study was planned by J. Karhu and E. Sahlstedt. E. Sahlstedt had the main responsibility of selecting the samples, sample preparation and analyses. The SIMS analyses were conducted by E.Sahlstedt with the help of M. Whitehouse. Sören Fröjdö at the Åbo Akademi University conducted bulk sulfur isotope analyses. The results were jointly interpreted by E. Sahlstedt and J. Karhu. E. Sahlstedt prepared the manuscript, other authors commented and edited the paper.

III The study was planned by J. Karhu and E. Sahlstedt. The samples were prepared and bulk isotope analyses of carbonate fillings were conducted by E. Sahlstedt. E. Sahlstedt conducted the SIMS analyses with the help of M. Whitehouse. The results were interpreted by E. Sahlstedt and J. Karhu. E. Sahlstedt prepared the manuscript, which was commented on and edited by the other authors.

Abbreviations

AOM	anaerobic oxidation of methane
bsl	below sea level
BSR	bacterial sulfate reduction
DIC	dissolved inorganic carbon
SIMS	secondary ion mass spectrometry
TDS	total dissolved solids
VCDT	Vienna Canyon Diablo Troilite
VPDB	Vienna Peedee Belemnite

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1. Introduction

In the upper parts of bedrock, fluid flow is contained in fractures and fracture networks which are variably interconnected. Along these fractures, groundwaters transport dissolved species from the surface to the fractured rock, imparting subtle, but nevertheless important changes to the deep environment. Several infiltration events may be superimposed on one another (e.g. Douglas et al., 2000; Laaksoharju et al., 1999; Pitkänen et al., 2004), although evidence for all of them is not necessarily preserved in the fractures. At best, a partial record of the fluid history may be preserved in mineral precipitates, which can serve as proxies for past geochemical conditions.

The importance of fracture mineral proxies has been recognized especially in studies investigating the suitability of geological repositories for radioactive waste disposal (Bath et al., 2000). Fracture minerals can be used to reconstruct the composition of paleofluids and thus constrain past changes in the natural environment (Bath et al., 2000; Tullborg et al., 2008). The barriers designed to insulate radioactive waste from the surrounding environment can then be considered from the point of view of possible natural changes which may occur in the repository (e.g. Pitkänen et al., 2004). Tullborg et al. (2008) noted that calcite is especially useful in these studies because it is a common secondary mineral in bedrock fractures, forms at both high and low temperatures and its chemical analysis is often straight forward. It is no wonder then that many investigators have utilized fracture filling calcite to reconstruct paleohydrogeochemical conditions in sites located in northern Europe (e.g. Blyth et al, 2000;, Blyth 2004; Clauer et al., 1988; Drake and Tullborg, 2009; Sandström and Tullborg, 2009; Tullborg, 1989; Wallin and Pederman, 1999), central Europe and England (Fourcade et al., 2002; Milodowski et al., 1998), in Yucca Mountain (U.S.A.) and in Canada (e.g. Bottomley 1987; Bottomley and Veizer, 1992; Vaniman and Chipera, 1996; Whelan et al., 2002; Wilson et al., 2003) and Japan (Iwatsuki et al., 2002; Lee et al., 2003).

Part of the usability of fracture mineral studies especially concerning carbonate minerals comes from the utilization of the stable isotopes of oxygen and carbon (e.g. Tullborg, 1989). In addition, sulfur containing minerals can be used in paleofluid investigations because sulfur is cycled through variable reactions both at low and high temperatures (e.g. Hoefs, 2009). Variation in the $^{18}O/^{16}O$-, $^{13}C/^{12}C$- and $^{34}S/^{32}S$-ratios in compounds containing these elements follows from the preferential distribution, i.e. fractionation, of the isotopes between reacting phases in physicochemical reactions (Urey, 1947). The fractionation of the isotopic composition of oxygen, carbon and sulfur in different naturally occurring reactions have been widely studied and can therefore be used in reconstructing environmental conditions usually with great confidence (e.g. Hoefs, 2009). In fractured rock, the isotopic composition of secondary calcite has been used, for example, to demonstrate reactivation of fractures and circulation of meteoric waters (Bottomley and Veizer, 1992; Tullborg, 1989; Iwatsuki et al., 2002) and indicate carbon cycling related to microbial processes (Budai et al., 2002; Clauer et al., 1988; Drake et al., 2012). Sulfide minerals have been investigated especially in studies related to deposits with potential economic value (e.g. Bawden et al., 2003; Eldridge et al., 1988) and in marine environments where sulfur cycling plays an important role (e.g. Habicht and

Canfield, 2001). Pyrite in bedrock fractures has been used to provide evidence for e.g. biogenic signals (e.g. Drake et al., 2013, 2015a; Pedersen et al.,1997).

This work focuses on the past deep groundwater environment at the Olkiluoto planned nuclear waste repository site. The Olkiluoto site is located on the western coast of Finland, and the fracture groundwaters bear evidence for a complex evolution characterized by multiple infiltration events (e.g. Pitkänen et al, 2004). Previous studies have characterized early hydrothermal circulation events at Olkiluoto (e.g. Blyth et al., 2000), showing that stable isotope composition of fracture minerals can serve as important proxy for the composition of paleofluids. This thesis concentrates on investigating variations in the geochemistry of paleofluids, focusing on the most recent mineralizations. Specifically, the stable isotope compositions of calcite and pyrite were utilized to characterize the fluids from which they precipitated. The reactions of carbon and sulfur are especially important in biogenic reactions, and therefore, variations in carbon and sulfur isotope compositions of calcite and pyrite are potential records of biogeochemical reactions. Identifying these reactions helps to constrain natural variations in the geochemical conditions of fractured bedrock. The results will, on a local scale, benefit the safety assessment of the planned nuclear waste repository at Olkiluoto, and on a larger scale, help to understand an environment with restricted connection to the dynamic processes of the surface of the Earth.

1.1. Stable isotope geochemistry of water-mineral reactions

1.1.1. Definitions

The stable isotopic composition of a mineral phase is analyzed in mass spectrometry as isotope ratios (e.g. Hoefs, 2009) and expressed using the conventional δ-notation, defined as:

$$\delta = (R_{sample} - R_{standard})/R_{standard} \times 10^3 ‰$$

where R denotes the isotope ratio, for example $^{13}C/^{12}C$, $^{18}O/^{16}O$ or $^{34}S/^{32}S$. The isotopic composition of the unknowns are reported relative to internationally recognized reference standards, which allows for comparison between data obtained by different research groups. For carbonate analyses (both $^{13}C/^{12}C$ and $^{18}O/^{16}O$), the results are reported relative to the VPDB (Vienna Peedee Belemnite) standard and for sulfur analyses relative to the VCDT (Vienna Canyon Diablo Troilite) standard.

1.1.2. Stable isotope compositions of mineral phases as environmental tracers

The study of stable isotope systematics of mineral phases is wide in scope both with respect to the minerals used in these studies and the variability of the geochemical environments (e.g. Faure and Mensing, 2005; Hoefs, 2009). Further, the geochemistry of the precursor phases of the minerals and their behavior in the studied environment must also be considered. Therefore, the following discussion is limited to the stable isotope systematics of carbon and oxygen in calcite and sulfur in pyrite, as they pertain to the objectives of the research presented in this thesis.

Oxygen

Carbonate minerals provide two major components for the study of stable isotope systematics; oxygen and carbon. Both of these elements carry information on the source water compositions, but with certain restrictions. Classical use of the oxygen isotope composition of calcite has been to interpret the marine carbonate record, where variations in the $\delta^{18}O$ values of calcite reflect the isotopic and temperature variations in the ocean water due to global glaciations (e.g. Emiliani, 1966; Emiliani and Shackleton, 1974). O'Neil et al. (1969) determined the equilibrium fractionation factors for oxygen isotope exchange between calcite and water over a temperature range of 0-500°C. The results of O'Neil et al. (1969) have been closely reproduced by later experimental and computational methods (e.g. Chacko et al., 1991; Chacko and Deines, 2008; Kim and O'Neil, 1997). The isotope composition of the fluid can be calculated by using the equilibrium fractionation factors and the oxygen isotope composition of the calcite, provided that the temperature of precipitation is known or can be independently determined, for example, by fluid inclusion studies. At low temperatures, however, determination of the exact precipitation temperature may be difficult, which will lead to uncertainties on the order of few per mille in the calculated water compositions. Although temperature and the oxygen isotope composition of the water have a strong control on the isotope composition of calcite (O'Neil et al., 1969; Kim and O'Neil, 1997), also solution speciation (e.g. Horita et al., 1993a,b; Zeebe, 1999) can affect isotope fractionation.

Carbon

The equilibrium fractionation factors between different dissolved carbon species and between dissolved carbon species and calcite have been determined by many research groups (e.g. Bottinga 1968, 1969; Mook 1986; Romanek et al., 1992). In most low temperature environments the sources and cycling of carbon can be traced by the isotopic fingerprints of dissolved inorganic carbon (DIC) (Clark and Fritz, 1997). In near neutral to alkaline conditions (pH > 6.5), most of the carbon in solution occurs as HCO_3^- or CO_3^{2-} ions and the fractionation between calcite and DIC is small, ~1 ‰ (Mook, 1986; Mook et al., 1974; Romanek et al., 1992). In addition, at low temperatures the temperature effect on fractionation is small to negligible (Mook, 1986; Mook et al., 1974; Romanek et al., 1992). Fractionation between CO_2 and calcite, on the other hand, is larger, ~10-13 ‰ (at 10-25 °C, Bottinga, 1968), which means that a decrease in pH will increase fractionation between DIC and calcite, due to the increase in the fraction of CO_2 in solution (cf. Clark and Fritz, 1997). However, decrease in pH will also increase calcite solubility, and therefore, calcite precipitates in near neutral to alkaline conditions, where HCO_3^- and CO_3^{2-} species dominate. Accordingly, the $\delta^{13}C$ values of calcite can usually be used as a tracer for the carbon source in DIC (cf. Clark and Fritz, 1997). Carbon isotopes in calcite in fractured rock have been used to indicate, for example, biogenic activity (Pedersen et al., 1997) and to identify the source waters in calcite precipitation (Iwatsuki et al., 2002).

Certain processes which cause kinetic fractionation may also be recognized by their carbon isotopic signatures. A distinct isotopic signature is associated with reactions related to methane production and consumption. Methanogenesis occurs at low temperatures in anaerobic environments by the activity of methanogenetic microbes and at high temperature environments by cracking of large hydrocarbon compounds (thermogenic CH_4) or abiogenically from inorganic compounds (abiogenic CH_4). These methane producing pathways are associated with distinct carbon isotopic signatures (e.g. Schoell, 1988; Wang et al., 2015; Whiticar, 1999). Methane is enriched in the lighter ^{12}C isotope in such a way that microbial methane tends to have $\delta^{13}C$ values <-50 ‰ and thermogenic and abiogenic methane $\delta^{13}C$ values >-50 ‰ (e.g. Whiticar, 1999). In environments where microbial methanogenesis occurs, the DIC pool is enriched in ^{13}C by the preferential use of the lighter isotope by microbes to the extent that $\delta^{13}C$ values of calcite precipitating in this environment can be positive (e.g. Clark et al., 2004; Irwin et al., 1977). Reversal of this isotopic signature occurs in environments where methane is oxidized, which leads to low $\delta^{13}C$ values in DIC depending on the source of the CH_4 and the amount which is oxidized. If microbial methane is transferred to the DIC-pool, calcite with anomalously low $\delta^{13}C$ values may precipitate (Drake et al., 2015b). Enrichment of ^{13}C in calcite may also occur in certain specific environments by inorganic reactions, where carbon is lost by sudden outgassing of CO_2, initiating calcite precipitation (Clark and Lauriol, 1992; Lacelle, 2007).

The carbon isotope composition of precipitating calcite in hydrothermal systems has been shown to be dependent on variables such as pH, ionic strength of solution, temperature and carbon concentrations, as well as the isotopic composition of the carbon source (Ohmoto, 1972). Further, processes such as mixing of waters, temperature changes and changes in carbon concentrations in solution (due to calcite precipitation or CO_2 degassing) can cause significant changes in the $\delta^{13}C$ values of precipitating calcite (e.g. Blyth et al., 2004; Zheng, 1990; Zheng and Hoefs, 1993a). Zheng (1990) and Zheng and Hoefs (1993a) have shown how the $\delta^{13}C$ and $\delta^{18}O$ values of the calcite can be used in combination to trace the evolution of fluids in hydrothermal systems.

Sulfur

The sulfur isotope variation in pyrite and other sulfide minerals has been extensively studied in both hydrothermal (e.g. Ohmoto, 1972; Ohmoto and Goldhaber, 1997) and low temperature processes (e.g. Canfield, 2001a). In low temperature environments microbes use sulfur species in energy production via oxidation-reduction reactions, which may lead to the precipitation sulfide minerals (Rickard and Morse, 2005). The most notable of these processes is bacterial sulfate reduction (BSR), which occurs in anaerobic marine settings as well as other environments where SO_4^{2-} is available (Megonigal et al., 2005). The sulfur isotopic composition of the precipitates in these cases is dependent on the isotopic composition of sulfate source, the extent of kinetic fractionation and the possible reservoir effects (e.g. Canfield, 2001a). By far the largest reservoir of SO_4^{2-} used in BSR is marine water, which currently has a $\delta^{34}S$ value of +19 ‰, but which has changed over the geological history (Paytan et al., 1998, 2004). BSR causes kinetic fractionation of sulfur isotopes due to the preferential use of the lighter ^{32}S isotope by the bacteria, in a reaction which transfers SO_4^{2-} into S^{2-} over variable metabolic pathways (e.g. Canfield, 2001a). The extent of the isotope fractionation between SO_4^{2-} and product S^{2-} has been found to be dependent on the rate of reaction in such a way that a high reaction rate results in lower fractionation of around 20 ‰ or less (Canfield, 2001b), and low reaction rates can result in fractionation of up to about 66 ‰ (Sim et al., 2011). Biogenic pyrite is thus variably depleted in ^{34}S and usually has negative $\delta^{34}S$ values (e.g. Habicht and Canfield, 2001; Virtasalo et al., 2010). Cases where biogenic pyrite has positive $\delta^{34}S$ values may signify a reservoir effect caused by Rayleigh fractionation (e.g. McKibben and Riciputi, 1998). In this fractionation process, restricted SO_4^{2-} input results in the evolution of the $\delta^{34}S$ value of residual sulfate to increasingly higher values as BSR proceeds. At the same time, the $\delta^{34}S$ value of sulfide will increase, and eventually reach the $\delta^{34}S$ value of the original SO_4^{2-}. If the sulfide is continuously removed from the solution, the $\delta^{34}S$ value of the sulfide will continue to increase, eventually surpassing the $\delta^{34}S$ value of the original SO_4^{2-}. The isotope effect of the Rayleigh fractionation can be calculated according to the equation (Rayleigh, 1896):

$$R = R_0 f^{(\alpha-1)}$$

Where R is the $^{34}S/^{32}S$-ratio of the reactant SO_4^{2-}, R_0 is the $^{34}S/^{32}S$-ratio of the sulfate at the beginning, f is the fraction of SO_4^{2-} remaining and α is the sulfate-sulfide fractionation factor. Estimating the effect of this reaction may be difficult based on the $\delta^{34}S$ values of pyrite, because it requires knowledge on both the sulfate source as well as the extent of kinetic fractionation in BSR. Furthermore, solute transport in the system may be more complex than simple closed or open system as shown for fractured bedrock by Drake et al., (2015b) and the complexity of microbial reaction pathways and associated reaction kinetics may require a modified Rayleigh fractionation equation to accurately describe fractionation in BSR (e.g. Van Breukelen, 2007). Nevertheless, Rayleigh reactions can usually be recognized in trends of sulfide $\delta^{34}S$ values in individual grains (Drake et al., 2013; Ferrini et al., 2010; McKibben and Riciputi, 1998; Paper II).

Sulfate reduction may proceed without biocatalytic reactions at high temperatures (Krouse et al., 1988). The fractionation associated with thermocatalytic sulfate reduction is up to about 20 ‰ (Kiyosu and Krouse, 1990). Calculations by Ohmoto (1972) show that sulfur speciation in solution is an important factor controlling the S isotope composition of the precipitating sulfide phase. Increase in the fraction of SO_4^{2-} in the solution increases the fractionation between solution and precipitating sulfide phase, because ^{34}S is preferentially enriched in SO_4^{2-} compared to sulfide phases (Ohmoto and Lasaga, 1982). The sulfur isotope systematics in hydrothermal solutions is thus related to multiple variables, including sulfur concentration, oxygen fugacity, temperature, pH, isotope composition of sulfur sources and ionic strength of the solution (Ohmoto, 1972). Furthermore, the isotope composition may be modified by reservoir effects caused by, for example, precipitation of sulfur containing minerals (Ding and Rees, 1984; Zheng and Hoefs, 1993b). It is important to notice that sulfides precipitating via inorganic processes may also have variable S isotope compositions (cf. Ohmoto, 1972). Hoefs (2009), however, notes that irregular variations at a small scale (i.e. within individual grains) could be used to distinguish between bacterial and thermochemical sulfate reduction.

1.2. Fracture mineral studies at Olkiluoto

Geological studies which aimed to investigate the suitability of Olkiluoto as a potential site for the disposal of spent nuclear fuel started at the end of 1980’s. As a part of these preliminary investigations, characterization of fracture filling minerals were conducted by a research group led by the Geological Survey of Finland (Blomqvist et al., 1992). One branch of this mineralogical study, which was conducted on the drill core OL-KR1 material, was to characterize and analyze the stable isotopic composition of fracture filling calcite (Frape et al., 1992). The characteristics of the paleo fluid flow at Olkiluoto were further constrained by combining stable isotope and fluid inclusion studies of the OL-KR1 fissure fillings (Blyth et al., 1998, 2000; Blyth, 2004). Later studies on fracture fillings were conducted as a part of the EQUIP project (Evidence for Quaternary Infils for Palaeohydrogeology), which had the specific aim of investigating calcite bearing fissure fillings (Bath et al., 2000). This later study used the multiple drill cores available from Olkiluoto at the time (Gehör et al., 2002). In addition, closed and open fracture structures and the fissure fillings were routinely mapped and recorded, in order to provide data for the geological model of the site (Aaltonen et al., 2010). Key results from the previous work are summarized in the following.

Fracture fillings from the OL-KR1 drill core were divided into three groups by Frape et al. (1992), which, based on cross cutting relationships, characterized three precipitation events. However, results from fluid inclusion studies indicated that the calcite fillings in the drill core were precipitated by four different fluids (Blyth et al., 2000; Blyth, 2004). The three calcite types occurring in the OL-KR1 were: crystalline, crystalline with clay and platy grey calcite (Frape et al., 1992, Blyth et al. 1998, 2000; Blyth, 2004). The following briefly describes the calcite types and their possible formation fluids according to the results presented in Blyth et al. (2000) and Blyth (2004). The characteristics of these calcite fillings are presented in Table 1. The oldest calcite type in the fissures was crystalline calcite occurring as closed veins, together with pyrrhotite and zeolite (laumontite). Fluid inclusion data indicated a possible dilute basinal brine or altered meteoric water as the source of the fluid. In OL-KR1, this calcite type occurs in closed veins at depths >500 m (Blyth et al. 2000). The second calcite type was associated with clays, typically kaolinite or illite, and the source water was likely magmatic or metamorphic. This calcite type occurred at depths <500 m in the drill core in closed veins (Blyth et al. 2000). Third calcite type crystallized as platy grey coverings in the fractures. This calcite type occurs through the studied depth range on open fracture surfaces. Two types of fluids were responsible for this calcite type. The so called platy a-type calcite was precipitated from a fluid equilibrated with magmatic rock. The second type, platy b calcite likely precipitated from a basinal brine. The salinities of the fluids for platy a and platy b fillings were distinctly different. Fluid associated with platy a calcite had low salinities of <16 wt% ($NaCl_{eq}$) compared to the fluids associated with platy b fillings, with salinities varying from 23 to 32 wt% ($NaCl_{eq}$) with a significant $CaCl_2$-component (Blyth et al. 2000). The results (Blyth et al., 2000; Blyth 2004) indicate a sequence of events that precipitated calcite; the first two or three events in a temperature range of 100-250 °C from a $NaCl$-H_2O-type fluid of varying salinity, followed by a high salinity, moderate temperature (~70-100 °C) fluid of a probable $NaCl$-$CaCl_2$-H_2O composition. The platy a and b calcite types may have formed by a dissolution-precipitation process that consumed some

Table 1. Calcite types and fluids from drill core OL-KR1 fillings (Blyth et al. 2000; Blyth, 2004). According to cross cutting relations, crystalline-type represents the earliest and platy grey-type the last hydrothermal cycle.

calcite type	T_h	salinity ($NaCl_{eq}$), Fluid type	calcite $\delta^{13}C$ (VPDB) / $\delta^{18}O$ (VPDB)	water $\delta^{13}C_{CO2}$ (VPDB) / $\delta^{18}O_{H2O}$ (VSMOW)
Crystalline	151-224 °C	<10 %, $NaCl$-H_2O	-21.0 to -13.9 ‰ -18.0 to -17.3 ‰	-20.7 to -14.2 ‰ -0.3 to +4.6 ‰
Crystalline with clay	92-210 °C	<25 %, $NaCl$-H_2O	-2.6 to +3.8 ‰ -11.1 to -9.9 ‰	-2.1 to -0.1 ‰ +2.6 to +11.5 ‰
Platy grey a	95-238 °C	<16 % $NaCl$-H_2O	-12.2 to -3.8 ‰ -15.5 to -10.9 ‰	-13.9 to -6.5 ‰ +0.1 to +11.7 ‰
Platy grey b	67-98 °C	23-32 %, $NaCl$-Ca_2Cl-H_2O	-13.0 to -6.2 ‰ -15.3 to -10.4 ‰	-16.8 to -10.4 ‰ -3.8 to +2.3 ‰

material from older calcite types (Blyth et al., 2000). Certain trends of fluid evolution, such as cooling and fluid mixing, were also suggested based on microthermometric data (Blyth, 2004, Blyth et al., 2009).

Characterization of the fracture fillings in the multiple drilled cores have shown that calcite is ubiquitous in Olkiluoto fractures, with bulk of the vein calcite being of hydrothermal origin (Aaltonen et al., 2010), which is in line with the earlier findings of Blyth et al., (1998, 2000). The occurrence of the calcite fillings have shown that calcite is typically the last mineral phase which precipitated from the hydrothermal fluids (Aaltonen et al., 2010) and possibly also later at low ambient temperatures (Gehör et al., 2002).

In a study concentrating on calcite bearing fracture fillings, Gehör et al. (2002) noted that the latest calcite precipitates occur as thin, scaly coatings or idiomorphic crystals on open fracture surfaces. This late calcite type corresponds to the description of a calcite filling mentioned in the Blyth et al. (2000) study, which they, however, excluded from their study due to limitations on available material for analyses (Blyth et al., 2000; Blyth, 2004). The results of Gehör et al. (2002) showed that the calcite types were variable and likely presented a long period of precipitation, estimated to extend from present day to ~1000 Ma. Further, microthermometric measurements obtained from the more massive parts of the fillings were overall comparable to the data presented by Blyth et al. (2000) and Blyth (2004), but with slightly larger variation in homogenization temperatures (~60-300 °C). Unfortunately, only a few isotope analyses were made from these fillings, all representing the latest calcite precipitates (Karhu, 1999, 2000). The δ^{13}C values ranged from -10.3 ‰ to +12.3 ‰, and the δ^{18}O values from -9.1 ‰ to -14.8 ‰ and suggested precipitation from water similar to the present-day groundwaters (Karhu, 1999, 2000).

Overall, the research conducted at Olkiluoto has revealed that calcite precipitation has been an important part of the hydrothermal circulation of the site (Aaltonen et al., 2010; Blyth et al., 2000, Blyth 2004). Furthermore, based on these studies it is likely that calcite precipitation has continued at least sporadically at the site in a low temperature environment (Gehör et al., 2002), which is typical feature in fractured crystalline bedrock environment (Tullborg, 1989; Bottomley and Veizer, 1992; Blyth 2004). However, although the hydrothermal system is reasonably well characterized, systematic investigation of the late-stage precipitates which includes stable isotope studies, has so far not been conducted at Olkiluoto.

1.3. Aims of the study

Our knowledge on the last precipitates on fracture surfaces at Olkiluoto is limited. Characterization of these late-stage precipitates could offer important information on the paleohydrogeological evolution of the site and especially on the events which took place after the cessasion of hydrothermal fluid circulation and establishment of the current groundwater regime. Furthermore, late-stage precipitates potentially are an important repository of information on biogeochemical reactions, which can have a strong influence on the chemical composition of groundwaters. The aims of this thesis are:

i) to characterize the latest precipitates on fracture surfaces, with special interest on calcite fillings. The selection of calcite precipitates is justified by noting that studies conducted at Olkiluoto have found this mineral phase to be the most common last precipitate on fracture surfaces. Hydrogeochemical conditions are interpreted using the isotopic composition of oxygen and carbon in calcite (Paper I)

ii) to use detailed, in situ measurements of $^{34}S/^{32}S$-ratios in pyrite to study the process of sulfur cycling in bedrock fractures (Paper II)

iii) to use detailed, in situ measurements of $^{13}C/^{12}C$-ratios in calcite to investigate the sources of carbon and the processes of carbon cycling in bedrock fractures, especially where they relate to sulfur cycling (Papers I, III)

iv) to reconstruct the paleohydrogeochemical environment based on the bulk and in situ stable isotope records from fracture minerals (Papers I-III)

2. Geological background

2.1. Bedrock

The Olkiluoto island is situated on the western coast of Finland, about 15 km north of the town of Rauma (Fig. 1). The area of Olkiluoto belongs to the Paleoproterozoic Svecofennian Domain, and the bedrock at Olkiluoto is mainly composed of metamorphosed supracrustal rocks now encountered as migmatitic mica gneisses. The supracrustal rocks took part in the Svecofennian orogeny culminating around 1.89-1.87 Ga (Vaasjoki, 1996), but a secondary thermal event took place 1.86-1.81 Ga ago, resulting in the formation of potassium granitic melts (Paulamäki et al. 2002). Olkiluoto is surrounded by Mesoproterozoic sedimentary and intrusive rocks cutting and covering the Svecofennian rocks (Fig. 1). The Laitila rapakivi batholith covers a roughly arc shaped area from south to west of Olkiluoto. A smaller Eurajoki rapakivi stock is located 4 km from Olkiluoto. The main phase of the rapakivi magmatism occurred at 1583 ± 3 Ma ago (Vaasjoki, 1996). The Eurajoki stock is slightly younger, dated to 1570 ± 10 to 1573 ± 8 Ma (Vaasjoki, 1977). Rapakivi related greisen veins have also been found at Olkiluoto, cutting the migmatitic gneisses (Aaltonen et al., 2010). A wedge shaped Satakunta sandstone formation is located adjacent to the northern parts of the Laitila rapakivi batholith. The sandstone formation is estimated to be ca. 1600 Ma old (Klein et al., 2014). The rapakivi granite and sandstone formations were cut by olivine diabase intrusions having ages from 1258 ± 13 to 1264 ± 12 Ma (Suominen, 1991). A younger set of diabase dykes, cutting the olivine diabase dykes of the area have been inferred from magnetic anomalies (Koistinen et al. 1996). Diabase dykes are also encountered at the Olkiluoto island, where they form a few tens of centimeters wide veins. The diabase dykes are strongly altered and cut the host rocks sharply (Paulamäki, 2007). The age of these dykes is assumed to be similar to the rapakivi granite (~1670-1540 Ma, Mänttäri et al., 2006).

2.2. Hydrogeochemical characteristics of the groundwaters

The chemical and isotopic composition of Olkiluoto groundwater has been extensively analyzed and interpreted with the aid of geochemical and hydrological modeling (e.g. Pitkänen et al., 2004; Posiva, 2013). The variations in groundwater composition can, in general, be connected to specific infiltration events and water-rock reactions in the overburden and bedrock. In the following, the general characteristics of the present-day groundwaters are outlined, following the data and interpretations presented in Posiva (2013). The depths mentioned are given as m below sea level (bsl).

The chemical and isotopic composition of groundwater at Olkiluoto tends to change systematically with depth, resulting in a distinct vertical chemical stratification (e.g. Pitkänen et al. 2004, Posiva, 2013, Fig. 2 in Paper I).

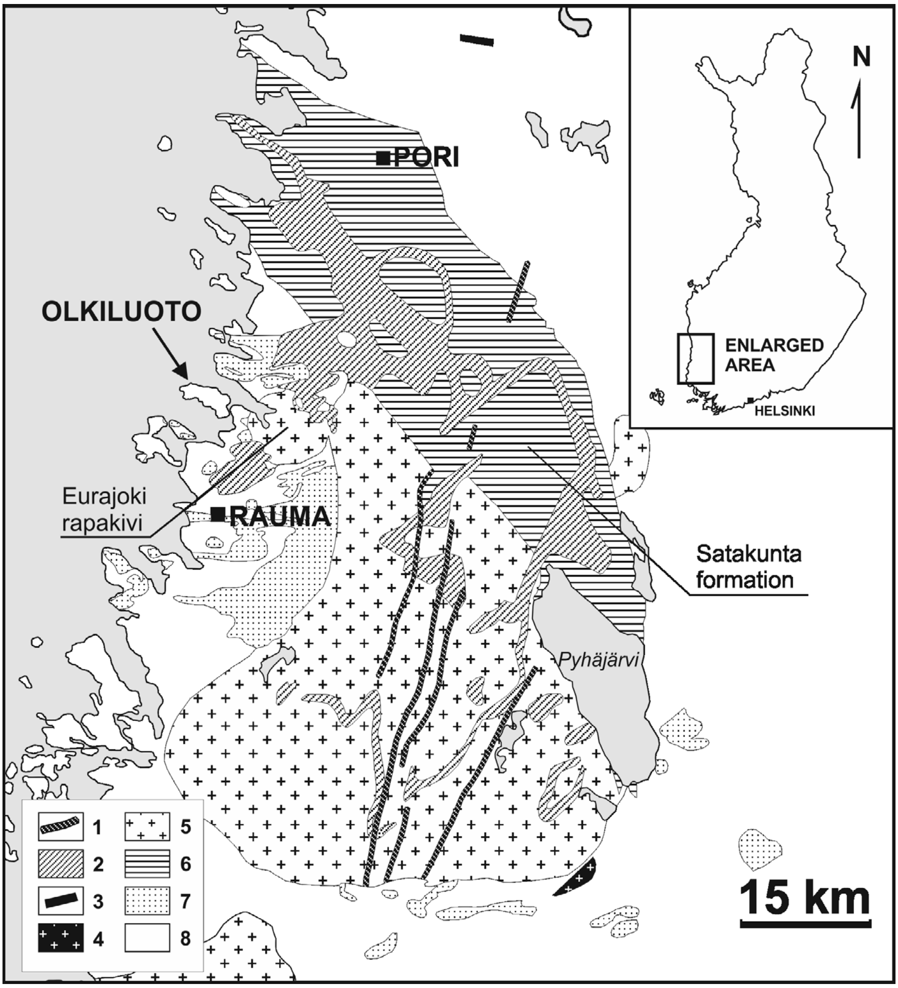


Figure 1. The bedrock of Olkiluoto is composed of high grade metamorphic rocks belonging to the Svecofennian bedrock domain. To the east are located the Eurajoki rapakivi granite stock and Laitila batholith, Satakunta sandstone formation and olivine diabase dykes, all Mesoproterozoic in age. 1) diabase (age unknown), 2) diabase (ca. 1.27 Ga), 3) diabase (ca. 1.65-1.57 Ga), 4) gabbro, 5) rapakivi granite, 6) sandstone, 7) Svecofennian late orogenic granites, 8) Svecofennian supracrustal and plutonic rocks (modified after Korsman et al., 1997).

Salinity, measured as total dissolved solids (TDS), increases with depth. Fresh groundwaters (TDS<1 gL^{-1}) are encountered in the upper tens of meters in the bedrock, brackish (1<TDS<10 gL^{-1}) at depths of 30-400 m and saline (10<TDS <100 gL^{-1}) at depths of 400 m to about 900 m (Posiva, 2013). Even higher groundwater salinity is predicted for greater depths, where electrical conductivity measurements indicate the presence of brine (TDS>100 gL^{-1}). The most dominant dissolved species are Ca^{2+}, Na^{+} and Cl^{-}, which increase with increasing depth so that at 800 m, Ca^{2+} concentration is 11-19 gL^{-1}, Na^{+} is 7-13 gL^{-1} and Cl^{-} is 41-53 gL^{-1}. Elevated concentrations of Mg^{2+} and SO_4^{2-} are found at the depth range of approximately 100-300 m, up to about 250 mgL^{-1} and 600 mgL^{-1}, respectively. K^{+} concentration has a peak at 100-300 m (up to about 20-30 mgL^{-1}), after which it drops to about 10 mgL^{-1} and then start to increase steadily with increasing depth to about 30 mgL^{-1} at 800 m. Dissolved inorganic carbon concentration is highest closest to the ground surface (up to about 80 mgL^{-1}), and decrease with increasing depth so that at depths >300 m the concentration of DIC is typically <10 mgL^{-1}. The groundwaters are divided into different types according to the characteristic dissolved species and salinities (Fig. 2 in Paper I); groundwaters from surface to about 100 m are the so called *fresh to brackish* HCO_3^--type, at depths of 100-300 m *brackish* SO_4^{2-}-type, at depths 300-400 m *brackish* Cl^--type and at depths >400 m *saline*-type.

All the water types mentioned above are mixtures of different water sources, but they usually have one distinct contributor. For the *fresh and brackish* HCO_3^--type, major contribution comes from relatively recent fresh water infiltration, which started to seep into the bedrock as the land mass rose above the sea level approximately 3-2.5 ka ago (Eronen and Lehtinen, 1996). In addition, Baltic Sea water contributes in the upper parts of the bedrock mainly by increasing groundwater salinities slightly (Posiva, 2013). The chemical evolution of this groundwater type is characterized by the following important processes: microbially mediated organic matter decay, mineral weathering and carbonate dissolution. Pitkänen et al. (2004) estimated that the influence of oxic waters (i.e. containing dissolved O_2) is mainly limited to the overburden, where dissolved O_2 is used in microbial reactions, plant matter degradation and oxidation of iron and sulfide phases, among others. The acidification produced by organic matter degradation is quickly consumed by weathering reactions, including dissolution of carbonates, which is seen in the quick rise of pH values to 7 or greater by the depth of 20 m (Pitkänen et al., 2004, Posiva, 2013). Degradation of organic matter and weathering of silicate minerals and calcite in the overburden and shallow bedrock cause the increase in DIC concentration of the infiltrating groundwater. The $\delta^{13}C_{DIC}$ values of the recharge are -27 ‰ to -24 ‰, and increases to about -15 ± 5‰ in the overburden and shallow bedrock.

The main contributor of salinity to the underlying *brackish* SO_4^{2-}-type groundwater is Littorina Sea water (Posiva 2013). The Littorina Sea represents a comparably high salinity stage of the Baltic Sea which started around 9-8.5 ka ago (Björk, 2008). During the Littorina Sea stage the salinity in the Bothnian Sea was 10-13 ‰, compared to the present day level of 4-5 ‰ (Widerlund and Andersson, 2011). The Littorina influence in the Olkiluoto groundwaters is seen as elevated concentrations of SO_4^{2-}, Mg^{2+} and K^+, high $\delta^{18}O$ values of groundwater (up to -8.8 ‰), and it is reflected in the marine Br^-/Cl^--, SO_4^{2-}/Cl^--, and Mg^{2+}/Cl^--ratios (Posiva, 2013). The $\delta^{13}C$ values of DIC in the brackish SO_4^{2-}-type groundwater tends to vary from -25 ‰ to -5 ‰, with values in the upper end of the range indicating a high proportion of a marine DIC component and the low $\delta^{13}C$ values reflecting the input from organic matter mineralization (Posiva, 2013). The SO_4^{2-} concentration is on average 356 mgL^{-1} and the mean $\delta^{34}S$ value of SO_4^{2-} is +25.8 ‰ (Pitkänen et al., 2004). The high $\delta^{34}S$ values of SO_4^{2-} in the Littorina-derived groundwater indicate that the isotopic composition of SO_4^{2-} was modified by bacterial sulfate reduction, which is presumed to have occurred already in the sea bottom sediments prior to the infiltration of these waters into the fractured bedrock (Pitkänen et al., 1999). In addition, low $\delta^{18}O$ values, down to about -15.8 ‰, are found in the brackish SO_4^{2-}-type waters, indicating that Littorina Sea water mixed with older glacial meltwater residing in the bedrock (Posiva 2013).

At the depth of approximately 300 m, SO_4^{2-} concentration drops, and CH_4 concentration starts to rise. This boundary defines the transition from *brackish SO_4^{2-}-type* groundwater to *brackish Cl^--type* groundwater. The main component of brackish Cl^--type groundwater is the saline or brine groundwater of the deep bedrock. The highly saline water was diluted by glacial melt water or meteoric water from a colder time period, as suggested by the low $\delta^{18}O$ values (Pitkänen et al., 2004; Posiva, 2013). The effect of recent dilution decreases with depth, and the concentrations of Na^+, Ca^{2+} and Cl^- steadily increase (Posiva, 2013).

The *brackish Cl^--type* groundwater changes to *saline*-type at a depth of approximately 400 m. The origin of the highly saline deep groundwater is still somewhat unclear, but chemical and isotopic evidence suggest that it has formed over a long time period, possibly at elevated temperatures (Posiva, 2013). High Br/Cl^--ratios in the saline groundwaters suggest a possible evaporitic brine source, but $\delta^{18}O$ and δ^2H values above the global meteoric water line as well as the Ca-Na-Cl composition are atypical for evaporitic brines. These data indicate that the original brine has been altered by water-rock interaction (Posiva, 2013).

Variations in the stable isotope composition of dissolved CH_4 have been used to investigate the source of CH_4 in the deep groundwaters (Posiva, 2013). The $\delta^{13}C$ values of CH_4 vary from -63.5 ‰ to -22.4 ‰ (Pitkänen and Partamies, 2007). The $\delta^{13}C_{CH4}$ values tend to increase with increasing CH_4 concentration and thus also with depth (Pitkänen and Partamies, 2007). The $\delta^{13}C_{CH4}$ values have the greatest variation at low CH_4 concentrations (Pitkänen and Partamies, 2007). Low $\delta^{13}C$ values of CH_4 are indicative of biogenic (i.e. microbially produced) methane (e.g. Whiticar, 1999). A notable increase in the $\delta^{13}C$ values of CH_4 up to -22‰ at low CH_4 concentrations can be explained by methanotrophic oxidation (Pitkänen and Partamies, 2007) which depletes the CH_4 pool in ^{12}C (Whiticar, 1999). With an increasing concentration of CH_4 the $\delta^{13}C_{CH4}$ and δ^2H_{CH4} values increase and the molecular ratios of CH_4 to longer chained hydrocarbons (C_1/C_{2+}) decrease (Pitkänen and Partamies 2007). These characteristics are similar to the CH_4 found in other shield areas at depth, and may be attributed to CH_4 formation via non-biogenic pathways at high temperatures from inorganic components (e.g. Sherwood Lollar et al., 1993). Thermogenic breakdown of higher hydrocarbons to produce CH_4 cannot be completely ruled out as a CH_4 source at Olkiluoto (Pitkänen and Partamies, 2007), although the existence of such a hydrocarbon reservoir at the site is questionable. Pitkänen and Partamies (2007) provide an estimate for the contribution of biogenic vs. non-biogenic CH_4 in the groundwaters based on mixing calculations which use the C_1/C_{2+} evolution as a function of $\delta^{13}C_{CH4}$. Based on these calculations the contribution of biogenic methane may be over 50 % in the brackish waters (Pitkänen and Partamies, 2007).

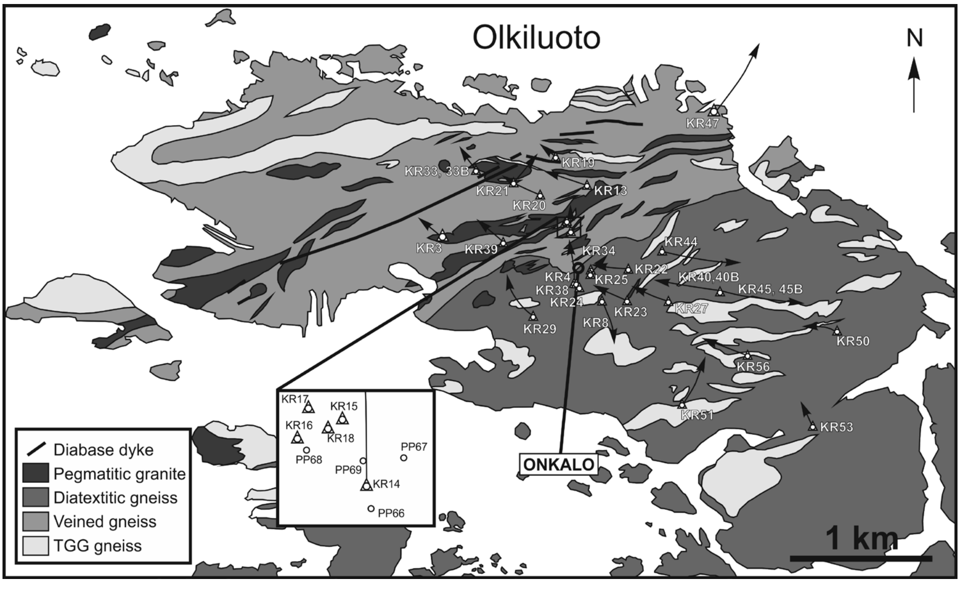
The descriptions above allow a rough generalization of the hydrological system. The groundwater environment can be separated into a dynamic upper bedrock zone of the first ~300 m and a comparatively stagnant deep groundwater environment at depths >300 m (Posiva, 2013). The upper part is dominated by several infiltration events from the last deglaciation to the present day (Pitkänen et al., 2004). The penetration depth of an infiltration is not only dependent on groundwater chemistry (i.e. density difference resulting from differences in salinity) or pressure, but also on the distribution of fractures in the bedrock. Fracture density is higher closer to ground surface and highly transmissive fractures are more common (Posiva, 2013). Infiltrating water tends to progress deeper in highly transmissive zones in the bedrock, and in reverse, older groundwater persists longer in less transmissive areas of the bedrock. As a result, boundaries of different groundwater types deviate from horizontal along these highly transmissive zones (Posiva, 2013).

Two important redox zones are identified in Olkiluoto. The first is close to ground surface, at the depth where dissolved O_2 is consumed from the groundwater, and the second is located at the boundary between the brackish SO_4^{2-}-type and brackish Cl^--type groundwaters (Pitkänen et al., 2004; Posiva, 2013). Both redox boundaries are characterized by increased microbial activity, which is dependent of the characteristics of the specific sampled drill holes (Pedersen et al., 2012, Posiva 2013). In the near surface level of <20 m, O_2 is consumed quickly in microbial and mineral reactions (Pedersen et al., 2012; Posiva 2013). Based on geochemical and microbiological data, anaerobic iron and sulfate reductions start quickly after the consumption of dissolved O_2 (Posiva, 2013; Pedersen et al., 2012). The second level of increased microbial activity occurs at depths of 200-400 m, in fracture groundwaters where both SO_4^{2-} and CH_4 are present (Posiva, 2013). This boundary is also characterized by elevated HS^--concentrations (Pitkänen et al., 2004), and it features the highest level of sulfate reducing bacteria (Pedersen et al., 2012), suggesting that sulfate reduction is connected to anaerobic CH_4 oxidation (Pedersen et al., 2012; Pedersen, 2013; Posiva, 2013). Also, microbes capable of anaerobic methane oxidation have been identified in the deep bedrock at Olkiluoto (Bomberg et al., 2015).

3. Materials and methods

The material for this study was collected from the drill cores available from the Olkiluoto site (Fig. 2). The drill holes are mostly located around the middle of the Olkiluoto island, in the area

Figure 2. Geological map of the Olkiluoto island showing the main rock units and locations of drill holes from which the drill core material used in this thesis was obtained. Not shown on the image are drill holes located in the ONKALO tunnel (the approximate center of the ONKALO access tunnel system is marked in the figure), which include the following drill cores: ONK-PH2, ONK-PH10, ONK-PH11, ONK-PH13, ONK-PH14, ONK-PH17, ONK-KR13, ONK-PVA5, ONK-PVA8, ONK-PP274 (modified after Posiva, 2013).



where the final repository, ONKALO (Finnish for "cavern"), is being built. Recently, core drillings have been concentrated on the eastern side of the island (for example, drill holes OL-KR53 and OL-KR50 in Fig. 2). In addition, drill core material was obtained along the ONKALO tunnel prior to the excavation (ONK-PH cores), and through the tunnel floors and walls (ONK-KR, ONK-PVA, ONK-PP cores). These core drillings intercept various alteration zones and hydrologically active fractures and fracture networks (e.g. Posiva, 2013). Open, water conducting fractures in hydrologically important zones are the most likely candidates to include recent mineral precipitates. Previous work on the fracture filling calcite has indicated that the latest calcite precipitates occur as thin layers on open fracture surfaces, sometimes showing euhedral crystal faces (Blyth et al. 2000; Blyth 2004; Gehör et al. 2002). Accordingly, water conducting, open fractures were targeted for study in this thesis (Papers I-III). The drill core material was compared to the drill hole loggings, which indicated the positions of water conducting fractures along the hole. Special attention was paid to the hydrological zones HZ19 and HZ20 which are important conducts for infiltrating waters (Posiva, 2013). In total, calcite bearing fracture surfaces were collected for this study from 51 drill cores at Olkiluoto.

The sample material was characterized by optical microscopy of hand samples and by a thin section study with a standard petrological microscope and an electron microprobe. Back scattered electron imaging was used to detect possible internal zoning of the fillings and mineral separates (Papers I-III). Calcite composition was semi-quantitatively determined by electron dispersive spectroscopy (EDS, Paper I).

Based on optical observation of the fracture fillings in hand samples and in thin section studies, sub-samples of calcite were carefully separated from the filling using either a hand held drilling equipment or a steel blade. The small sample size required for isotope analyses, ca. 100-150 µg, enabled a detailed analysis of different calcite phases of the fracture surfaces. The oxygen and carbon isotope ratios were measured using a ThermoFinnigan Gas Bench II coupled to a Delta Plus Advantage mass spectrometer in a continuous flow mode at the Department of Geosciences and Geography, University of Helsinki (Papers I-III). Some additional samples were analyzed in the Laboratory of Chronology of the Finnish Museum of Natural History, University of Helsinki using a ThermoQuest Finnigan DeltaPlusXL mass spectrometer coupled with GasBench II (Paper III, unpublished data). At the department of Geosciences and Geography, the measurements were conducted by reacting approximately 90-150 µg of sample aliquots with a concentrated phosphoric acid at 70 °C for a minimum of 1 h to liberate the CO_2 gas. The measured $^{18}O/^{16}O$- and $^{13}C/^{12}C$-ratios were normalized against an in-house working standard, which is calibrated against the NBS-19 calcite standard. The results are given as δ-values in per mille (‰) relative to the Vienna Peedee Belemnite (VPDB) standard. The external precision of the measurements, based on multiple analysis of an in-house quality standard was ±0.1 ‰ for $\delta^{13}C$ values and ±0.2 ‰ for $\delta^{18}O$ values. At the Laboratory of Chronology, calcite material was reacted with >100 % phosphoric acid for 24 h at 25 °C. The measured isotope ratios were normalized against an in-house working standard and the international L-SVEC carbonate standard. The reproducibility was ±0.1 ‰ for $\delta^{13}C$ values and ±0.3 ‰ for $\delta^{18}O$ values, determined from multiple analyses of a reference calcite sample.

The isotope composition of pyrite measured from bulk material was analyzed at the Åbo Akademi University (Paper II). The pyrite (with minor marcasite) was separated from the fracture fillings, and reacted with 10 % acetic acid to remove traces of calcite. In the $^{34}S/^{32}S$ ratio measurements, 6.4-26.8 mg of pyrite were used. The sample aliquots were converted to SO_2 gas by burning with Cu_2O at 1000°C for 15 minutes (Robinson and Kusakabe, 1975). The $^{34}S/^{32}S$ ratios were measured using a Micromass MM602 dual inlet gas source mass spectrometer. The standards used for calibration were PbS with $\delta^{34}S$ = -3.2 ‰ and CdS with $\delta^{34}S$ = +10.8 ‰ and the analytical error is estimated to be ±0.3‰. In addition, sphalerite from a greisen vein was analyzed by EA-IRMS at the Iso-Analytical laboratory in Crewe, Chesire, in England (Paper II). Each separate was analyzed in duplicate, and the variations between duplicate analyses were less than 0.1 ‰. The precision of the analysis is ±0.3 ‰ or better, based on duplicate analysis of sample and standard material. The results of bulk sulfur isotope compositions are given as δ-values in per mill against the Vienna Canyon Diablo Troilite (VCDT) standard.

Analysis of isotope ratios with secondary ion mass spectrometry allows for excellent spatial resolution in isotopic data. The $^{34}S/^{32}S$ ratios of sulfide grains (Paper II) and the $^{13}C/^{12}C$ ratios of calcite fillings (Paper III) were measured *in situ* using a Cameca IMS1280 ion microprobe (SIMS) of the Nordsim laboratory at the Museum of Natural History, in Stockholm, Sweden. The spot size for both sulfur (Paper II) and carbon (Paper III) isotope analysis was ca. 10 µm. For sulfur isotope measurements (Paper II), the samples were prepared by separating sulfide grains from the fracture surfaces and fixing the collected grains on epoxy mounts together with grains of sulfide standards. Details of the analytical settings can be found in Paper (II). Typical precision on a single $\delta^{34}S$ value obtained by SIMS was ±0.3-0.4 ‰ (SD). The results are reported using the δ-notation with respect to the VCTD standard.

In order to determine the $^{13}C/^{12}C$-ratios in calcite fillings *in situ*, rock cuttings containing the fracture filling sequence was prepared (Paper III). The subsamples contained a cross section of the sample filling, cut perpendicular relative to the fracture surface. The analytical conditions are those described in Paper (III). The external precision of a single $\delta^{13}C$ value was <0.3 ‰ (SD).The results are reported against the Vienna Peedee Belemnite (VPDB) standard.

Fluid inclusion studies conducted for selected samples were made using a THMS 600 heating-freezing stage by Linkam with a standard optical microscope by Leica at the University of Helsinki (Papers I-II). Due to thin zones and small crystals, calcite was gently separated from the fracture surface. In the case of massive fillings, the surface of calcite was gently polished using a micro drill and water as coolant to avoid heating of the sample. Calcite chips were examined under a standard polarizing microscope. The stage was calibrated at -56.6, -21.2, -10.7, 0.0 and 374.1 °C using synthetic fluid inclusions by Syn Flinc. The precision for calibration was ±0.1 °C for the melting temperatures and ±3 °C for the triple point of water (374.1 °C). Homogenisation temperatures were obtained first by heating the sample slowly until the vapour bubble disappeared. The freezing run was performed after the heating run, by cooling the inclusion until it froze. Then the inclusions were slowly heated until the temperature of the first melt T_e was observed. T_e was difficult to observe in most inclusions due to low amounts of first melt and repeated measurements indicated a precision of ±4°C or better for T_e. Slow heating was continued and the temperature T_m, where last the ice disappears, was recorded to indicate the salinity of the fluid. The precision of T_m measurements was ±0.3 °C or better.

4. Review of the original papers

4.1. Carbon and oxygen isotope compositions of fracture calcite as tracers for past redox conditions (Paper I)

Calcite containing fillings were grouped according to calcite morphology, mineral associations and their relative position in the fracture sequence. The calcite fillings were divided into five groups. Calcite precipitates on the fracture surfaces were identified as Group 1 and 2. This calcite type occurred as clear, thin platelets (~10-200 μm) or small euhedral crystals on open fracture surfaces (Group 1), which in some cases contained minor amounts of silicate inclusions (Group 2). Group 3 calcite fillings occurred in closed veins, or were covered by later calcite precipitates or clays. Group 3 calcite fillings commonly contained inclusions of host rock fragments. Group 4 calcite occurred together with inclusions of kaolinite. Group 5 calcite fillings were massive, vein closing calcite fillings and occasionally contained vugs filled with euhedral crystals up to 1 cm in size. Pyrite was a common co-genetic mineral with calcite, although in few cases, pyrite was the latest mineral precipitate on the fracture surface.

Group 1-2 calcite fillings showed a narrow range in $\delta^{18}O$ values, from -11.3 ‰ to -7.3 ‰, and wide variation in $\delta^{13}C$ values, from -30 ‰ to +31 ‰. A notable feature of the isotope geochemistry of Group 1-2 calcite was the increase in the $\delta^{13}C$ values of the calcite at depths of approximately 50 m, which suggested a transition in the geochemistry of the paleogroundwaters at this depth. Comparison with the isotopic data presented in Blyth et al. (2000) and Gehör et al. (2002) indicated that Group 1-2 fillings represent a new type of calcite fillings not discovered in previous studies. The occurrence of both primary and secondary fluid inclusions were observed although fluid inclusions were typically rare in these calcite fillings. The primary fluid inclusions were all liquid inclusions and indicate that Group 1-2 fillings formed at low temperatures.

In contrast to the late-stage calcite fillings, Group 3-5 fillings had a narrower range in $\delta^{13}C$ values, from -15 ‰ to +4 ‰, and larger variation in $\delta^{18}O$ values, from -16.7 ‰ to -6.6 ‰. The $\delta^{13}C$ and $\delta^{18}O$ values of the calcite fillings in Groups 3-5 overlap. Also, the $\delta^{13}C$ and $\delta^{18}O$ values of Group 3-5 fillings for the most part overlapped with the isotopic compositions reported for OL-KR1 calcite fillings, which have been interpreted to have formed at elevated temperatures (Blyth et al., 2000). A notable difference was the clustering of the $\delta^{13}C$ and $\delta^{18}O$ values between -15 ‰ to -8 ‰ and -12 to -8‰, respectively, in Group 3-5 calcite. Calcite fillings having this isotopic composition were nearly absent from the Blyth et al. (2000) data set. In Group 3-5 fillings, microthermometric measurements obtained from fluid inclusion analyses of five samples, indicated higher formations temperatures, with T_h between 50-130 °C.

4.2. In situ sulphur isotope composition of fracture pyrite indicating microbial processes in the bedrock (Paper II)

The sulfur isotope composition of pyrite grains were measure in situ, resulting in a high spatial resolution of the $^{34}S/^{32}S$ data. The SIMS analysis allowed observation of possible changes in the $\delta^{34}S$ values within grains, which helped to better constrain the characteristics of sulfide precipitation events compared to conventional bulk analyses (e.g. McKibben and Riciputi, 1998). The $\delta^{34}S$ values were highly variable, ranging from -50 ‰ to +82 ‰. The highest variation was observed in pyrite associated with Group 1-2 calcite, in which the $\delta^{34}S$ values ranged from -50 ‰ to +78 ‰. The wide range in the $\delta^{34}S$ values was interpreted as a result of microbial SO_4^{2-} reduction, which occurred in an environment that was partly closed to SO_4^{2-}. Two types of trends were observed in the variation of $\delta^{34}S$ values from grain cores to grain rims. In some grains, the $\delta^{34}S$ values increased from core to rim, as is typical in environments where SO_4^{2-} input is restricted (e.g. Eldridge et al., 1993). In some cases, the $\delta^{34}S$ values of the rims of the crystals were lower than those in the cores. This feature was associated with strongly zoned crystals and indicated input of fresh SO_4^{2-} with a less evolved isotope composition into the fracture. Overall, these characteristics indicate that an isotopically heterogeneous SO_4^{2-} pool existed in the fractures and that the SO_4^{2-} reduction process was a complex one.

The sulfur isotopic composition of Group 3 pyrite was also highly variable; the $\delta^{34}S$ values ranged from -40 ‰ to +82 ‰. Due to the similarities in the range of $\delta^{34}S$ values and trends observed in the distribution of $\delta^{34}S$ values in grains, it is likely that precipitation of pyrite associated with Group 3 calcite was also affected by microbial SO_4^{2-} reduction. Fluid inclusion studies, however, indicated higher formation temperatures, with $T_h<100°C$, for this calcite group. Fracture mineral studies have provided evidence for precipitation events coinciding with the Caledonian burial event (Drake et al., 2009; Sandström et al., 2009; Alm et al., 2005), which, based on multiple lines of indirect evidence, is thought to have affected the Fennoscandian Shield widely, (e.g. Larson and Tullborg, 1998; Larson et al., 1999).

In contrast, Group 4 and Group 5 pyrite had narrower range in $\delta^{34}S$ values, -18 ‰ to +34 ‰, with mineral associations and fluid inclusion studies indicating a hydrothermal origin. The range in $\delta^{34}S$ values, is, however, wider than generally expected for hydrothermal sulfide. The wider variation may be partly explained by recycling of sedimentary sulfur, derived from metasedimentary host rocks.

4.3. Detailed analysis of $^{13}C/^{12}C$ ratios for studying the cycling and sources of carbon in fractured bedrock (Paper III)

The aim of Paper (III) was to investigate the sources and cycling of carbon in the bedrock by measuring the $^{13}C/^{12}C$-ratios of fracture fillings *in situ* by SIMS. More specifically, the data was used to constrain the carbon cycling associated with BSR, as indicated by sulfur isotope data from fracture sulfides (Paper II). The $\delta^{13}C$ values were determined for calcite fillings concentrating on Groups 1-2 and Group 3 from which also sulfur isotope data was available. The $\delta^{13}C$ values showed wide variation, ranging from -53.8 ‰ to +31.6 ‰. The largest range in the $\delta^{13}C$ values was associated with the late-stage fillings of Group 1-2. In addition, the variation in the $\delta^{13}C$ values of Groups 1-2 showed clear depth dependent trends, which was not seen in Group 3 fillings. The $\delta^{13}C$ values of Group 3 calcite varied from -22.1 ‰ to +10.2 ‰. These observations indicated that even if the variations in the $\delta^{34}S$ values of Group 1-2 and Group 3 fillings were similar as shown in Paper II, the geochemical environment in which they precipitated were distinct.

The $\delta^{13}C$ values of Group 3 calcite fillings ranged from -22.1 ‰ to +10.2‰, with most of the samples clustering around the $\delta^{13}C$ value of about -15 ‰. The $\delta^{13}C$ values indicate that degradation of organic matter contributed to the DIC pool. Overall, the DIC pool from which this calcite type precipitated was relatively homogenous. High $\delta^{13}C$ values in few fractures suggested local methanogenetic influence.

The $\delta^{13}C$ values of late-stage calcite (Groups 1-2) varied from -53.8‰ to +31.6 ‰ and changed systematically with depth. At depths

<34 m, the $\delta^{13}C$ values varied from -22.5 ‰ to -6.9 ‰. This depth range coincided with the highest range in the $\delta^{34}S$ values of pyrite of the same groups. A distinct change in the $\delta^{13}C$ values occurred at the depth range of about 30-60 m. Highly negative $\delta^{13}C$ values, down to -53.8 ‰, were found at depths of 34-54 m. Very low $\delta^{13}C$ values in carbonate were commonly attributed to methane oxidation due to the low $\delta^{13}C$ values of CH_4 (e.g. Whiticar, 1999). The transition to positive $\delta^{13}C$ values indicaded a change to a methanogenetic environment at depths >54 m. Overall, the data indicate that fracture mineral precipitation of Group 1-2 fillings was closely related to microbial activity in fractures.

5. Discussion

5.1. Identification of late-stage calcite precipitates

The drill core material used in this study had been, for the most part, obtained using a triple core tubing method, which preserves fragile fracture material in the drilled cores better than conventional single tube drilling method (Bath et al., 2000). The fracture surfaces were, therefore, generally well preserved, as demonstrated by the occurrence of undisturbed soft fracture filling material on open fracture surfaces (Paper I). The calcite fillings were grouped according to calcite morphology, mineral paragenesis and position in the fracture filling sequence into five groups (Paper I). The grouping starts from the calcite fillings which were recognized from the surfaces of open fractures. Group 1 consists of small, euhedral calcite crystals or thin platelets of calcite. Group 2 is separated from Group 1 fillings by the occurrence of minor amounts of silicate material, probably clays. Group 1-2 calcite types closely resemble the latest calcite fillings in fractures described by Blyth et al. (2000) and Gehör et al. (2002). Group 3 calcite fillings are greyish in color, occur in closed fractures or in open fractures covered by later calcite (Group 1-2) or clay and contains host rock fragments as inclusions. By appearance, this filling type corresponds to the platy grey calcite of Blyth et al. (2000). Group 4 calcite filling are associated with massive kaolinite inclusions and Group 5 fillings are thick, massive fillings, some of which contain open cavities filled with large, euhedral crystals. Some of the Group 5 calcite fillings appear to be slightly deformed. This filling type contains a subgroup of calcite with low $\delta^{18}O$ values (<-15 ‰) which corresponds with the crystalline type filling of Blyth et al. (2000).

The origin of the calcite fillings can be further tested by examining the stable isotopic composition of the fillings. Circulation of meteoric or marine waters should be reflected in the oxygen and carbon isotope composition of the fillings obtained from water conducting fractures, as seen in several locations (Bottomley, 1987; Bottomley and Veizer, 1992; Tullborg, 1989; Iwatsuki et al., 2002). Plotted in a $\delta^{13}C$ vs. $\delta^{18}O$-diagram, the $\delta^{18}O$ and $\delta^{13}C$ values of calcite fillings (Papers I-III) cluster in an area in the figure which represents calcite in equilibrium with current groundwaters (black box, Fig. 3). The figure shows also data from drill core OL-KR1 (Blyth et al., 2000; Blyth, 2004), which includes material also from closed veins and non-conducting areas in the bedrock (dashed area, Fig. 3). Comparing these data sets indicates that calcite fillings in water conducting zones represent precipitation from, or re-equilibration (i.e. dissolution and reprecipitation) with, circulating meteoric waters in open fractures (Bottomley, 1987; Bottomley and Veizer, 1992; Tullborg, 1989). However, because the isotopic composition of calcite depends on both the temperature and the composition of the groundwater, it is possible that the calcite

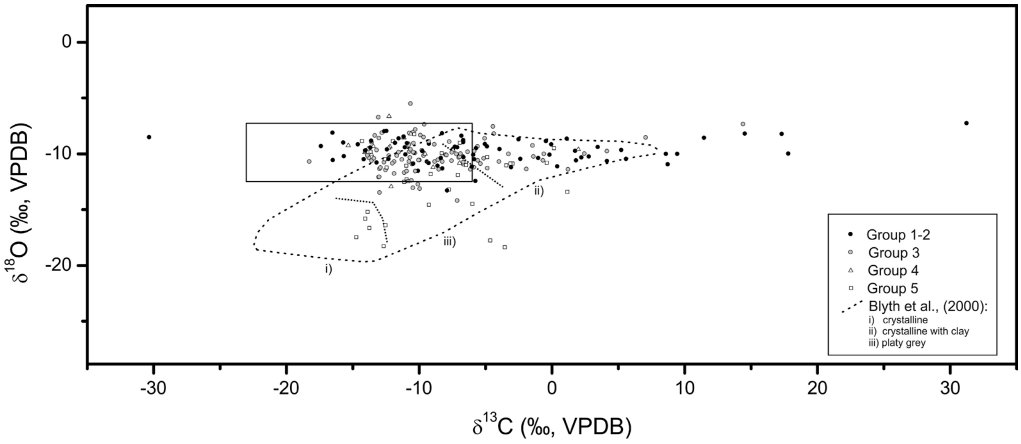


Figure 3. Isotopic composition of fracture filling calcite at Olkiluoto. The boxed area indicates isotopic composition of calcite in equilibrium with present day groundwaters, calculated according to equilibrium fractionation factors of O'Neil et al (1969) for oxygen and Romanek et al. (1992) and Zhang et al., (1995) for carbon, using isotopic composition of groundwaters (Posiva, 2013) and in situ temperatures in the drill holes (Ahokas et al., 2008). Dotted line defines the field of the isotopic composition of calcite from OL-KR1 reported by Blyth et al., 2000.

fillings fall in to the area indicating equilibrium with current groundwaters by chance. In this case, independent information on formation temperatures were obtained from fluid inclusions studies (Papers I-II), which showed that both of the above described scenarios contribute. The results suggest that Group 3-5 fillings formed at elevated temperatures (Papers I-II) and thus are related to the hydrothermal circulation described by Blyth et al., (2000). Due to the higher formation temperatures of Group 3-5 fillings, the fluid which was in equilibrium with these calcite fillings actually tended to have higher $\delta^{18}O$ values compared to current groundwaters (cf. Blyth et al., 2000).

Figure 3 suggest that Group 1-2 calcite fillings precipitated in equilibrium with fluids with similar oxygen isotopic composition as current groundwaters (Paper I), but significantly more variable carbon isotopic composition (Papers I, III). Low formation temperatures of Group 1-2 fillings were confirmed with fluid inclusion data (Paper I). The considerable variation in the $\delta^{13}C$ values of Group 1-2 calcite, from -53.8 ‰ to +31.8 ‰, already suggests differences in the composition of the paleofluids, compared to current groundwaters. The discrepancy between late-stage calcite and current groundwaters was further examined by comparing the oxygen isotopic composition of late-stage calcite with groundwater samples obtained from corresponding drill hole sections (Fig. 4). The results indicate that only a minority of the late-stage calcite fillings actually are in or near equilibrium with the current groundwaters. These observations suggest that the late-stage calcite fillings represent a paleogroundwater environment distinct from the current groundwater conditions.

5.2. Characteristics of massive calcite fillings and comparison to earlier research

Group 3-5 fillings are associated with the hydrothermal circulation described by Blyth et al. (2000) at Olkiluoto (Papers I-III). Comparison with the data presented by Blyth et al. (2000) suggests that Group 5 calcite fillings represent

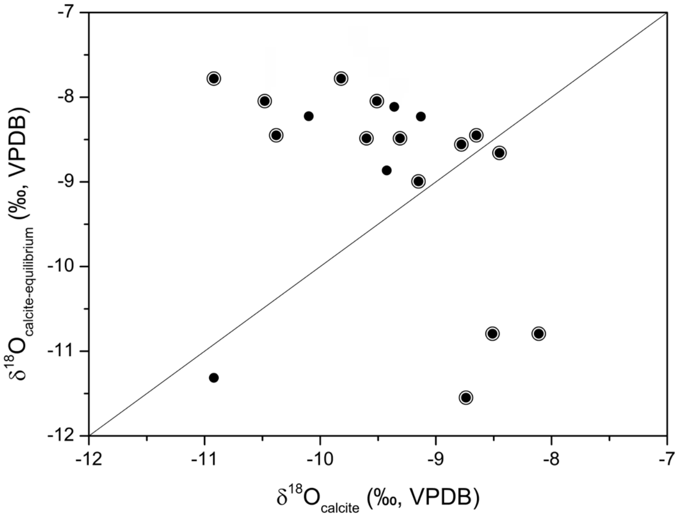


Figure 4. Comparison of the $\delta^{18}O$ values of Group 1-2 (late-stage) calcite to those of modelled, hypothetical calcite in equilibrium with present day groundwaters in the same drill hole section. The equilibrium isotopic composition of calcite was calculated according to the fractionation factors of O'Neil et al. (1969) and in situ temperature in the drill hole from the groundwater data. Fracture filling calcite in equilibrium with the groundwater should fall along the straight line on the diagram. Encircled dots indicate cases where the groundwater sample is determined to represent baseline conditions, i.e. conditions not disturbed by technical activities on the site, and dots indicate cases where the groundwater sample has been categorized as disturbed (Pitkänen et al., 2007).

an earlier episode of hydrothermal circulation, followed by the precipitation of Group 4 fillings (Papers I-II). The corresponding calcite types described by Blyth et al. (2000) are crystalline and crystalline with clay, respectively. The $\delta^{13}C$ and $\delta^{18}O$ values of Group 5 fillings (Fig. 3, Papers I-III) correspond partly with the isotopic composition reported by Blyth et al. (2000) for crystalline calcite type, which had low $\delta^{18}O$ (<-14 ‰) and $\delta^{13}C$ (<-13 ‰) values. The $\delta^{18}O$ values are typically higher for Group 5 fillings (Papers I-II). This discrepancy in the isotopic composition indicates that Group 5 fillings represent a more complex system than that indicated by the data from Blyth et al. (2000) for the crystalline calcite type. Variations in the $\delta^{13}C$ and $\delta^{18}O$ values of hydrothermal calcite may occur due to changes in the physicochemical conditions during precipitation. This process can be examined by analyzing the variations in the isotopic composition across the veins (Zheng, 1990; Zheng and Hoefs, 1993a). Possible variation in the isotopic composition of Group 5 fillings was tested by obtaining a profile of $\delta^{13}C$ and $\delta^{18}O$ values across massive Group 5 veins (Table 2). The results show a tendency of increasing $\delta^{13}C$ and $\delta^{18}O$ values towards the middle of the veins, which indicates that the variations in Group 5 fillings can partly be explained by evolution of a hydrothermal system.

Group 4 fillings are associated with massive kaolinite inclusions and correspond thus with the second hydrothermal cycle described by Blyth et al. (2000) which was characterized by calcite with clay-type fillings. Furthermore, the spread in the $\delta^{13}C$ and $\delta^{18}O$ values of Group 4 calcite and crystalline with clay-type calcite of Blyth et al. (2000) have some similarities (Fig. 3), but the $\delta^{13}C$ values of Group 4 calcite fillings are typically lower. The results obtained by Blyth et al., (2000) indicated that the hydrothermal calcite fillings (crystalline- and crystalline with clay-types) may have taken part in later fluid flow by dissolution and precipitation as the platy

Table 2. Variation of isotopic composition of massive calcite veins (Group 5), analyzed across veins. Point #1 is taken closest to the host rock.

sample	point	Depth (m bsl)	δ^{13}C (‰, VPDB)	δ^{18}O (‰, VPDB)
OL-KR53/175.02-175.10	#1	-143	-13.07	-15.76
	#2		-9.33	-13.53
	#3		-10.57	-13.57
	#4		-10.02	-12.39
	#5		-8.61	-14.38
OL-KR22/108.66-108.74	#1	-84.3	-14.07	-16.48
	#2		-14.74	-18.06
	#3		-13.40	-15.89
	#4		-14.08	-16.62
	#5		-13.36	-14.44
	#6		-10.18	-15.00
OL-KR19/255.58-255.71	#1	-241.6	-13.02	-15.25
	#2		-13.65	-13.79
	#3		-13.77	-11.92
	#4		-13.72	-12.72
	#5		-13.93	-12.12
	#6		-13.74	-14.58

grey calcite-type. The variability in the isotopic compositions of Group 5 and 4 calcite may be a result of dissolution and re-precipitation process affecting some of the fillings. The position of Group 5 and 4 calcite fillings in water conducting fractures in the upper parts of the bedrock have given the infiltrating waters a more readily available target compared to closed veins (Paper I). Therefore, some of the fillings in Group 5 and Group 4 may represent later stage of fluid circulation, and are possibly cogenetic with Group 3 fillings.

Group 5 and 4 fillings are likely related to the rapakivi granite (1570±8 to 1583±3 Ma, Vaasjoki, 1977, 1996) and diabase intrusions (1258±13 to 1264±12 Ma, Suominen, 1991) which caused extensive hydrothermal circulation at Olkiluoto (Aaltonen et al., 2010). One feature of this hydrothermal alteration is extensive illitization and kaolinitization of the bedrock which was both pervasive and fracture controlled (Aaltonen et al., 2010; Posiva, 2013). If the hydrothermal circulation started with the emplacement of rapakivi granite and continued or was rejuvenated by the later diabase intrusions, the fluid evolution was most likely complex and may have included both meteoric and magmatic fluid sources, as indicated by Blyth et al., (2000).

The position of the Group 3 fillings in the fracture mineral sequence, stable isotope composition and fluid inclusion data (Papers I-II) suggest that these fillings corresponds with the platy grey calcite type described by Blyth et al. (2000). In Olkiluoto, intrusions younger than the Mesoproterozoic rapakivi granite and mafic dykes, which could have caused hydrothermal circulation, are absent (e.g. Aaltonen et al., 2010). Blyth et al. (2000) suggested that the high salinity fluids of platy grey calcite (platy grey b) were basinal brines which were possibly derived from the Satakunta sandstone formation located north to east from the island (Fig. 1). However, later studies have found that a Paleozoic thermal event caused circulation of high salinity fluids in several places over the Fennoscandian Shield (Alm, and Sundblad, 2002; Alm et al., 2005; Drake and Tullborg, 2009; Sandström and Tullborg, 2009). The results of Larson et al. (1999) indicate deep burial 350-250 Ma, with loading decreasing eastward from the eroding Caledonides, based on apatite fission track studies. Furthermore, several lines of indirect evidence have been used to indicate deep burial associated with Caledonian foreland basin stage (Larson and Tullborg, 1998; Tullborg et al., 1995). Even though these deposits are currently absent in Finland (Kohonen and Rämö, 2005), the results of Larsson et al. (1999) suggest that the thickness of sedimentary deposits was ca. 1-1.5 km during this period in the Olkiluoto area. It is therefore likely that Group 3 calcite fillings (Paper II) and platy grey b calcite associated fluids (Blyth et al., 2000) which indicate high fluid salinities and moderate formation temperatures are related to the Paleozoic thermal event.

5.3. Evidence for biogenic processes and cycling of sulfur and carbon in bedrock fractures

Analysis of the bulk isotopic composition of Group 1-2 calcite presented in Paper I revealed an anomalously wide variation in the isotopic composition of carbon as well as a depth dependent trend in the distribution of $\delta^{13}C$ values. High $\delta^{13}C$ values in late-stage calcite suggested that transition into methanic conditions occurred at shallow depths of ~50 m (Paper I). Sulfur and carbon cycling were investigated in Papers II and III, respectively, using in situ analysis of the $^{34}S/^{32}S$- and $^{13}C/^{12}C$-ratios of fracture fillings. Because these elemental cycles are often connected in anaerobic environments by microbial activity (e.g. Megonigal et al., 2005), a combination of results from carbon and sulfur isotope systematics sheds light on biogenic processes in the bedrock (Papers II-III).

Sulfur isotope data from fracture pyrite indicated possible biogenic activity associated with Group 3 fillings (Paper II). The $\delta^{34}S$ values of Group 3 pyrite evolved in fractures where sulfate reduction rate exceeded the rate of SO_4^{2-} input and caused progressive enrichment in ^{34}S in sulfide (Paper II), as has been demonstrated from multiple locations (e.g. Drake et al., 2013; Ferrini et al., 2010; McKibben and Riciputi, 1998). In situ analysis of the $\delta^{13}C$ values of associated calcite presented in Paper III, show a range of $\delta^{13}C$ values from -19.7 ‰ to +10.2 ‰ (Paper III, full range $\delta^{13}C$ = -22.1 ‰ to +11.0 ‰) through the studied depth range, with most values in between -10 ‰ and -16 ‰, indicative of degradation of organic matter and possible input form inorganic carbon sources. Blomqvist et al. (1992) identified barite in the fractures, but sulfate bearing minerals have been found to be extremely rare in later studies, therefore suggesting an external SO_4^{2-} source (cf. Pitkänen et al., 2004). Sources for the sulfate and organic matter were most likely derived from fluids intruding into the bedrock fractures from the above lying deposits. A possible source for the sulfate and organic matter may have been early Paleozoic (Cambrian to Silurian) sediments, consisting mainly of shallow marine and marine deposits as well as material derived from the eroding Caledonides, which are thought to have extended over Finland (Larsson et al., 1999; Kohonen and Rämö, 2005). Paleozoic fillings with remnants of organic material which likely originated from the overlying early Paleozoic deposits, occurs at the Forsmark site in western Sweden (Sandström and Tullborg, 2009). Fluid-rock interaction with these deposits could therefore provide organic material for circulating fluids from which Paleozoic fillings precipitated (Drake and Tullborg, 2009; Sandström and Tullborg, 2009).

5.3.1. Late-stage fillings

The sulfur isotope data presented in Paper II combined with the carbon isotope data presented in Paper III reveal that Group 1-2 fillings precipitated in a geochemically variable environment with a complex evolution. The $\delta^{13}C$ values of Group 1-2 calcite fillings indicate that the geochemical environment was stratified with respect to depth, as shown by the bulk analyses (Paper I) and *in situ* carbon isotope data (Paper III). Based on the carbon isotope data (Papers I, III), the bedrock environment could be divided in to three sections: 1) shallow bedrock (0-30 m), 2) intermediate depth (34-54 m) and 3) deep bedrock (> 54 m). The main processes indicated for these depths were 1) degradation of organic matter, 2) degradation of organic matter combined with anaerobic methane oxidation and 3) methanogenesis. Sulfur isotopic evidence, on the other hand, shows that BSR has occurred in fractures down to depths of at least 111 m, and evolved in a complex way as shown by within grain variations of $\delta^{34}S$ values (Paper II). In the following, the paleohydrogeochemical conditions are examined starting from the ground surface.

The shallow bedrock (0-30 m) is characterized by the highest variation in the $\delta^{34}S$ values of pyrite (Paper II), combined with moderate variation in the $\delta^{13}C$ values of calcite (Paper III). These results indicate that sulfate reducing bacteria used mainly organic matter as a substrate. In some parts of the fractures, BSR was able to consume nearly the whole SO_4^{2-} pool, resulting in the enrichment of ^{34}S in the sulfide phase by Rayleigh fractionation (Paper II), a characteristic feature of such environments (e.g. Ferrini et al., 2010; McKibben and Riciputi, 1998). However, a recent study suggests that in the deep bedrock, activity of sulfate reducing bacteria may result in very small scale geochemical stratification in the fracture groundwaters (Drake et al., 2015a). According to Drake et al. (2015a), BSR acting around precipitating pyrite may result in a localized Rayleigh type sulfur isotope evolution in a microenvironment adjacent to the precipitating grain, but the impact on the $\delta^{34}S$ values of the SO_4^{2-} pool as a whole is moderate. Therefore, the highly ^{34}S enriched pyrite occurring in some of the fractures (Paper II) may have evolved without significantly altering the sulfur isotope composition of the infiltrating SO_4^{2-}. In addition, the highly variable $\delta^{34}S$ values and strongly zoned growth structures observed in some of the grains (Paper II) could be the result of interaction of the larger SO_4^{2-} pool in the fracture with the microenvironments around precipitating sulfide grains, rather than reflecting the evolution of the SO_4^{2-} pool as a whole. The study also found that the isotope effect of bacterial sulfate reduction may be as high as 71 ‰ (measured as $\delta^{34}S_{sulfate}$ - $\delta^{34}S_{pyrite}$) in the deep bedrock environment (Drake et al. 2015a). Such a large fractionation effect indicates that the lowest $\delta^{34}S$ values of late-stage pyrite, -50 ‰ (Paper II), could be formed via a single step in BSR without requiring additional oxidative steps (e.g. Canfield and Thamdrup, 1994).

The intermediate depth (34-54 m) was characterized by introduction of ^{13}C depleted carbon into the DIC pool from the oxidation of CH_4 (Paper III). This methanotrophic signature, characterized by $\delta^{13}C$ values as low as -53.8 ‰, is localized and detectable in few samples, whereas most of the calcite has $\delta^{13}C$ values similar to fillings in the shallow bedrock. The calcite with methanotrophic signatures is associated with pyrite (Paper II). These connections suggest that BSR in the fractures used mostly surface derived organic matter and possibly also minor amount of CH_4 as electron donors in sulfate reduction. Anaerobic methane oxidation combined with BSR is known from marine environments, but Drake et al. (2015b) have demonstrated that a similar process is possible also for the deep bedrock environment where BSR may proceed by using methane almost exclusively as an electron donor. At Olkiluoto, it seems that a minor amount of CH_4 may have migrated from deeper parts of the bedrock and was consumed at the intermediate depth, possibly by BSR (Paper III).

The deep bedrock (>54 m) is characterized by a methanogenetic signature in fracture calcite (Papers I, III). In contrast, Paper II indicates the occurrence of BSR at depths of at least 111 m. Methanogenesis is inhibited by the presence of SO_4^{2-} (Winfrey and Zeikus, 1977), which indicates either spatial or temporal separation between the methanogenetic and sulfate reducing systems. It was noted in Paper II that calcite with methanogenetic signature, i.e. positive $\delta^{13}C$ values (cf. Irwin et al., 1977), is not cogenetic with pyrite. Comparing the mineral system with current groundwaters (e.g. Pitkänen et al., 2004) suggests that the methanic environment has been replaced by the infiltration of SO_4^{2-}-rich waters, which occurred at the latest during the Littorina sea stage (Paper I). Evidence for this shift was found in one sample, where calcite with a methanogenetic signature is overgrown by pyrite with $\delta^{34}S$ values indicative of BSR, showing that conditions in the fracture progressed from methanogenetic to sulfate reducing (Paper III).

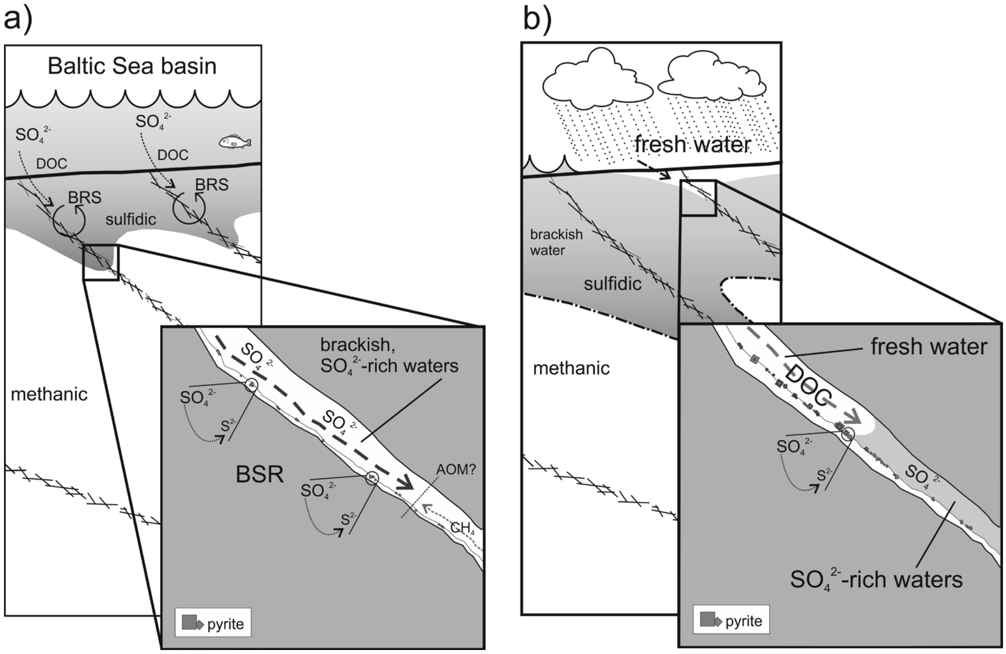


Figure 5. Schematic illustration of the paleohydrogeological evolution at Olkiluoto modified after the model presented in Paper II. a) Infiltration of SO_4^{2-}-containing waters causes BSR in the bedrock fractures. Sulfate in the fractures is consumed by microbial activity, possibly causing small scale chemical stratification in the fractures (cf. Drake et al., 2015a). At the transition zone between sulfidic and methanic environments, portion of upward migrating CH_4 is anaerobically consumed (AOM, anaerobic oxidation of methane) in BSR. b) The island rises above sea level by isostatic movement causing infiltration of meteoric waters which mix in the bedrock fractures, providing organic compounds for microbial communities, causing dilution and consumption of SO_4^{2-} in the shallow bedrock.

5.4. Paleohydrogeochemical evolution

Based on the results obtained in this work, it seems that the majority of late-stage calcite fillings are not in equilibrium with the current groundwaters, but rather represent some earlier stage of fluid circulation in the bedrock fractures, as discussed above. Some important similarities between the earlier and current groundwater environments can be identified. These include a distinct geochemical stratification with respect to depth and the influence of microbial processes on groundwater chemistry which are observed from the current groundwaters (Pedersen et al., 2012; Pitkänen et al., 2004). Figure 5 shows a schematic representation of the possible evolution of paleogroundwaters, which is a modified version of the model presented in Paper II.

According to carbon isotope data from fracture filling calcite, methanogenetic conditions prevailed at depths >54 m (Papers I, III). In the upper parts of the bedrock, infiltration of SO_4^{2-} containing water led to BSR and precipitation of pyrite and calcite (Fig. 5a). Due to the lack of other viable SO_4^{2-} sources (e.g. Pitkänen et al., 2004), introduction of SO_4^{2-} into the fractures most likely occurred when the area has been covered by marine waters (Paper II). The Olkiluoto area has been submerged under marine waters at least during the Littorina Sea stage of the Baltic Sea (Björk, 2008) and during the Eemian interglacial (Miettinen et al., 2002), and possibly also during earlier glaciation-deglaciation cycles in the Pleistocene. The complex sulfur isotope evolution which is observable in late-stage pyrite (Paper II) may thus reflect multiple infiltration events and changes in groundwater flow paths due to glacioisostatic movements (Paper II), as well as formation of very small scale geochemical stratification in fractures (Drake et al., 2015a). The shallow bedrock was eventually flushed by fresh meteoric waters which diluted the Littorina Sea derived groundwaters and BSR consumed the remaining SO_4^{2-} from the upper parts of the bedrock (Fig. 5b).

The brackish and thus denser Littorina Sea water was able to replace the more dilute glacial meltwaters, and progressed until depths of ca. 300 m was reached (Pitkänen et al., 2004). At this depth the Littorina derived brackish SO_4^{2-}-type groundwaters phase into brackish Cl-type, CH_4 containing waters. Microbiological and geochemical data suggest that sulfate reduction at this interface is linked with anaerobic oxidation of methane (Pedersen et al., 2012; Posiva, 2013). Mineralogical evidence suggests that a similar interface was present much closer to the ground surface, at the depth range of 34-54 m (Paper III). Methanic conditions at the depth range of ca. 50-300 m were apparently replaced by infiltrating SO_4^{2-}-rich groundwaters. However, mineralogical evidence for this transition is nearly absent (Paper III). Especially, calcite with methanotrophic signatures is both rare and restricted to the upper parts of the bedrock, and was not found at the depth range of 50-300 m from which CH_4 apparently was consumed at some stage. Drake et al., (2015b) demonstrated that microbial communities can effectively combine anaerobic methane oxidation to sulfate reduction at a sulfate-methane interface progressing in bedrock fractures, with great potential for the precipitation of both calcite and pyrite having isotope compositions characteristic of anaerobic methane oxidation and BSR, respectively. Therefore, it seems unlikely that similar progression of a sulfate-methane front occurred at Olkiluoto. It is possible that some other process flushed out the CH_4 at the 50-300 m depth range prior to the progression of SO_4^{2-}-rich waters in to the bedrock. One possibility for such a process is the infiltration of glacial meltwaters, traces of which are found also in the brackish Cl^--type waters at depths >300 m (Pitkänen et al., 2004).

5.5. Timing of the late precipitation event in Olkiluoto fractures

The timing of the precipitation of late-stage fillings is not well constrained. Isotopic dating of late-stage calcite by using radiocarbon (^{14}C) and ^{230}Th-U-methods have so far not been successful (Paper II). Based on the geological evolution of the site, it can be assumed that temperatures were slowly lowered in the bedrock as a result of the final denudation of the Fennoscandian Shield, which in the Finnish part of the shield occurred in the late Mesozoic and early Cenozoic (Kohonen and Rämö, 2005). This suggests a possible timeframe of several million years. Based on the information gained from the stable isotope studies, i.e. the complex sulfur isotope evolution (Paper II), it seems likely that the late-stage fillings formed during infiltration events associated with deglaciation(s), and therefore precipitated, at least partly, during the Quaternary.

5.5.1. Stagnant saline waters and the occurrence of late-stage fillings

The geochemical stratification and interpretation of the evolution of Olkiluoto groundwaters suggest that the upper ~300 m of the bedrock has been active in groundwater circulation, whereas the deeper bedrock fractures contain presumably very old brine, which have had limited interaction with the groundwaters at shallower depths (Pitkänen et al., 2004). Geochemical stratification in the groundwaters reflects the reduction of flow rates and decrease in the amount of conducting fractures with depth (e.g. Posiva, 2013). Residence times for the deep saline groundwaters have been estimated using $^{36}Cl/Cl$-ratios, which suggest residence times of >1.5 Ma (Gascoyne, 2014). Additionally, He accumulation in groundwaters has been used to estimate residence time in the order of millions of years for saline groundwaters (Delos et al., 2010). It has been speculated that the brine component in groundwaters is associated with the highly saline fluid inclusions in fracture calcite and that this brine component was emplaced in to the fractures during the Paleozoic (e.g. Pitkänen et al., 2004; Posiva, 2013).

The differences in the residence times of groundwaters in the upper dynamic zone of <300 m affected by Holocene infiltrations (Pitkänen et al., 2004) and the deep zone of >300 m suggest that late-stage precipitates in the upper parts of the bedrock may be younger compared to the deep bedrock zone. According to Pitkänen et al., (2004) high Ca-concentrations in the deep groundwaters have, via calcite saturation, stabilized DIC concentrations to low levels. At depths >300m, late-stage calcites of Group 1-2 which occur in water conducting fractures may represent slow accumulation of calcite over a long time period or they may represent last stages of precipitation of Group 3 fillings. At this depth range, the isotopic composition of Group 3 and Group 1-2 calcite fillings tends to converge (Papers I, III), which may indicate, but does not prove, that they represent the same fluid circulation event. In addition, the $\delta^{13}C$ values of DIC also partly overlap with the $\delta^{13}C$ values of Group 1-2 calcite at the depths of >300 m.

5.6. Bulk vs. in situ isotope analyses

The data obtained in this thesis allows for the comparison of bulk isotope analysis (Paper I) to *in situ* analyses (Papers II-III). The carbon and sulfur isotopic compositions in fracture calcite and pyrite observed in the *in situ* analyses show that high variability (>10 ‰) within the space of tens of μm is possible (Papers II-III). Several other studies have shown the importance of microscale variations in sulfide grains, especially related to microbial processes, in interpreting geochemical conditions (e.g. Drake et al., 2013, 2015a; MicKibben and Riciputi, 1998; Virtasalo et al., 2010). The results obtained from this thesis study, and recent paper by Drake et al. (2015b) indicate that *in situ* analysis of calcite fillings may also reveal important geochemical signatures, which could be masked in conventional bulk analyses. This is seen, for example, by comparing the depth dependent trends of bulk analyses (Paper I) to the variability shown by SIMS data (Paper III). Although the general concept can be attained with the bulk analyses, full understanding of the system may require *in situ* analyses, especially in environments where the influence of microbial activity is suspected.

5.7. Recommendations for future research

Restrictions in the available material of Group 1-2 fillings greatly hinder attempts of isotopic dating. So far, the understanding of the late-stage evolution relies on comparisons with current groundwaters and the well-established infiltration history reconstructed for the last deglaciation (Pitkänen et al., 2004) and what is known of the geological history of the site (e.g. Aaltonen et al., 2010). New techniques in ^{14}C dating which have been developed for small sample sizes (Ruff et al., 2010) could potentially be used to date calcite fillings at shallow depths, where groundwater residence times are comparably short and mixing with older groundwaters is limited.

Analysis of clay fillings has indicated the activation of the fracture networks in the Mesoproterozoic and the Paleozoic (Mänttäri et al., 2007). These isotopic dating results cannot be, however, unequivocally connected to calcite precipitation events. Confirmation of the Paleozoic age of Group 3 fillings, which is suspected based on comparison between Swedish and Finnish localities (Paper II), would help to partially constrain the age of the late-stage Group 1-2 fillings. Potential mineral for dating is K-feldspar, which lines some of the fractures containing Group 3 fillings.

A potential tool to further constrain the paleogroundwater composition is the analysis of the trace element concentrations in fracture calcite (Tullborg et al., 2008). For example, rare earth element patterns in calcite fillings can be used to discern fluid-rock interaction, redox conditions and speciation in the paleofluids (e.g. Denniston et al., 1997; Drake and Tullborg, 2009; Sandström and Tullborg, 2009; Vaniman and Chipera, 1996). Due to the limitations in available sample material and impurities like silicate inclusions in calcite, *in situ* analyses, such as laser ablation (e.g. Drake and Tullborg, 2009) or SIMS (e.g. Vaniman ans Chipera, 1996) could be used to provide data on the trace element concentrations in the calcite fillings.

6. Conclusions

In this thesis, the stable isotope composition of fracture filling minerals was used to characterize paleofluid composition and evolution in the bedrock, with emphasis on the low temperature late-stage fillings. High temperature fillings were tentatively linked to the intrusions of rapakivi granite and diabase veins in the Mesoproterozoic and to a Paleozoic burial event, which is known to have affected large parts of the Fennoscandian Shield. They show similar characteristics as described in earlier research for hydrothermal circulation at Olkiluoto. Low temperature fillings were formed on open fracture surfaces, following the reactivation of the fractures after hydrothermal circulations. Analysis of the oxygen, carbon and sulfur isotope compositions of the late-stage calcite and pyrite precipitates from bulk material and *in situ* analysis of carbon and sulfur isotopes allowed identification of biogenic processes in the bedrock and reconstruction of the paleohydrogeochemical environment. The use of *in situ* isotope analyses was especially important in obtaining information on environmental conditions. The main findings can be summarized as follows:

- The late stage fillings are not, for the most part, in equilibrium with the current groundwaters with respect to stable oxygen and carbon isotopes, suggesting that the paleofluid which they represent has been replaced by more recent infiltrations in the bedrock fractures.
- Detailed analysis of the sulfur and carbon isotope variations in the late-stage fillings shows that the late-stage fillings reflect biogenic processes in the bedrock. Isotopic signatures indicating bacterial sulfate reduction and microbial methanogenesis were identified. Furthermore, based on the results obtained from Group 3 fillings, BSR may have been active already in the Paleozoic.
- The results indicate a distinct stratification of the hydrogeochemical conditions with respect to depth, with transitions between geochemically distinct environments occurring in the upper <100 m of the bedrock. Notably, the transition zone between sulfate reducing and methanogenetic environments was identified in shallow bedrock.
- Sulfur isotope variation in fracture pyrite indicates a complex evolution of the sulfate pool in the fractures. Sulfate was mineralized via BSR and the associated sulfur isotope evolution was characterized by restricted sulfate input with occasional open system behavior. BSR signature was observed down to depths of 111 m where it follows the precipitation of calcite with methanogenetic signature.
- The complexity of the paleohydrogeochemical environment is likely related to the infiltration of different water types following deglaciation and glacioisostatic land movements. These infiltration events, which have affected the upper ~300 m of the bedrock, have provided substrates for microbial processes.

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