



Biogenic processes in crystalline bedrock fractures indicated by carbon isotope signatures of secondary calcite



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ABSTRACT

Variation in $^{13}\text{C}/^{12}\text{C}$ -isotope ratios of fracture filling calcite was analyzed in situ to investigate carbon sources and cycling in fractured bedrock. The study was conducted by separating sections of fracture fillings, and analyzing the $^{13}\text{C}/^{12}\text{C}$ -ratios with secondary ion mass spectrometry (SIMS). Specifically, the study was aimed at fillings where previously published sulfur isotope data indicated the occurrence of bacterial sulfate reduction. The results showed that the $\delta^{13}\text{C}$ values of calcite were highly variable, ranging from -53.8‰ to $+31.6\text{‰}$ (VPDB). The analysis also showed high variations within single fillings of up to 39‰ . The analyzed calcite fillings were mostly associated with two calcite groups, of which Group 3 represents possible Paleozoic fluid circulation, based on comparison with similar dated coatings within the Baltic Shield and the succeeding Group 1–2 fillings represent late-stage, low temperature mineralization and are possibly late Paleozoic to Quaternary in age. Both generations were associated with pyrite with $\delta^{34}\text{S}$ values indicative of bacterial sulfate reduction. The $\delta^{13}\text{C}$ values of calcite, however, were indicative of geochemical environments which were distinct for these generations. The $\delta^{13}\text{C}$ values of Group 3 calcite varied from -22.1‰ to $+11\text{‰}$, with a distinct peak at -16‰ to -12‰ . Furthermore, there were no observable depth dependent trends in the $\delta^{13}\text{C}$ values of Group 3 calcite. The $\delta^{13}\text{C}$ values of Group 3 calcite were indicative of organic matter degradation and methanogenesis. In contrast to the Group 3 fillings, the $\delta^{13}\text{C}$ values of Group 1–2 calcite were highly variable, ranging from -53.8‰ to $+31.6\text{‰}$ and they showed systematic variation with depth. The near surface environment of $<30\text{ m}$ (bsl) was characterized by $\delta^{13}\text{C}$ values indicative of degradation of surface derived organic matter, with $\delta^{13}\text{C}$ values ranging from -30.3‰ to -5.5‰ . The intermediate depth of $34\text{--}54\text{ m}$ showed evidence of localized methanotrophic activity seen as anomalously ^{13}C depleted calcite, having $\delta^{13}\text{C}$ values as low as -53.8‰ . At depths of $\sim 60\text{--}400\text{ m}$, positive $\delta^{13}\text{C}$ values of up to $+31.6\text{‰}$ in late-stage calcite of Group 1–2 indicated methanogenesis. In comparison, high CH_4 concentrations in present day groundwaters are found at depths of $>300\text{ m}$. One sample at a depth of 111 m showed a transition from methanogenetic conditions (calcite bearing methanogenetic signature) to sulfate reducing (precipitation of pyrite on calcite surface), however, the timing of this transition is so far unclear. The results from this study gives indications of the complex nature of sulfur and carbon cycling in fractured crystalline environments and highlights the usefulness of in situ stable isotope analysis.

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1. Introduction

Subsurface life and associated geochemical processes usually

rely on the circulation of organic and inorganic substrates in groundwater. This is especially true for crystalline bedrock environments, where the bulk of groundwater flow occurs in channels provided by fracture networks. Microbial communities found in these environments are both active and variable (e.g. Bomberg et al., 2015; Hallbeck and Pedersen, 2008; Nyssönen et al., 2012; Pedersen et al., 2008; Pedersen, 2013). A study by Pedersen et al. (1997) found fossil remains of microbial material in fracture fillings and showed that microbial life in crystalline environments

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may have ancient roots. Most of dissolved organic matter introduced into the fractured rock via infiltrating waters will be mineralized by aerobic and anaerobic microbial processes, which, in turn, may lead to fracture mineral precipitation (e.g. Drake et al., 2015a, b; Sahlstedt et al., 2013). In fractured rock, early hydrothermal fillings generally dominate fracture mineralizations (Blyth et al., 2000, 2009; Drake and Tullborg, 2009; Sandström and Tullborg, 2009; Sahlstedt et al., 2010). However, late low temperature fillings commonly occur and mineral phases such as calcite can provide an important record of paleofluid circulation in the bedrock (e.g. Drake et al., 2012, 2015a,b; Iwatsuki et al., 2002; Sahlstedt et al., 2010). Groundwater flow is variable and can be slow or sporadic due to tectonic activity related to, for example, glacioisostatic movements (e.g. Hutri, 2007) which change flow paths in fractured rock. In addition, the composition of the inflowing groundwater may change with time. This is the case in sites located around the Baltic Sea, where multiple distinct infiltrations events characterize groundwater evolution (Laaksoharju et al., 1999; Pitkänen et al., 2004). Even if these types of external forcing factors are absent, microbial activity has the ability to modify their chemical environment by reactions which otherwise would be impossible or very slow. Therefore, understanding the factors that control microbial activity in the subsurface is of primary importance in understanding geochemical evolution in deep bedrock fractures.

The Olkiluoto island on the western coast of Finland (Fig. 1) is an excellent site to study the geochemical evolution of groundwaters in bedrock fractures. Due to the ongoing site characterization and the construction of a deep geological repository intended to host spent nuclear fuel, cored boreholes have been drilled at the site for various studies. This drill core material has been sampled for the purposes of the current study. The geological history of the site during the Pleistocene and Holocene has been complex, and the bedrock fractures have been affected by several, chemically distinct infiltration events. These include, for example, glacial meltwater intrusions during the retreat of continental ice sheets, brackish water from the Baltic basin and fresh meteoric water infiltration after the area was exposed above sea level (e.g. Posiva, 2013). Consequently, the geochemical composition of infiltrating water has likely varied extensively, which has had an impact on the geochemical conditions in the deep bedrock. Information on these infiltration events has been stored in the chemical and isotopic composition of groundwaters (Posiva, 2013; Stotler et al., 2012) and fracture filling minerals (Sahlstedt et al., 2010, 2013).

Sulfur cycling in bedrock fractures is of special interest in localities where SO_4^{2-} -rich waters have been able to infiltrate into the bedrock. At Olkiluoto, SO_4^{2-} containing waters from the Baltic Sea have intruded into the bedrock (Pitkänen et al., 2004; Posiva, 2013) seen today as elevated SO_4^{2-} -concentrations in groundwaters in the depth range of 150–300 m (Posiva, 2013). These SO_4^{2-} -rich waters have been shown to have infiltrated during the Littorina Sea stage of the Baltic Sea (Pitkänen et al., 2004) mainly during its most saline period at around 6000–3000 a (Widerlund and Andersson, 2011). Even earlier Pleistocene events may have introduced SO_4^{2-} into the fractures, including, for example, the marine phase of the Eemian interglacial ca. 130–116 ka ago (Miettinen et al., 2002). Direct evidence for bacterial sulfate reduction (BSR) in bedrock fractures at Olkiluoto has been provided by observations of active microbial sulfate reducers (Haveman et al., 1999; Haveman and Pedersen, 2002; Pedersen et al., 2014), and sulfur isotope signatures of dissolved sulfate (Pitkänen et al., 2004; Posiva, 2013). In addition, recent sulfur isotope studies of fracture bound pyrite indicated that microbial sulfate reduction has been an important process in bedrock fractures repeatedly during the geological history of the site, possibly from the Paleozoic onwards (Sahlstedt et al., 2013).

Some open questions remain about the nature of the sulfate reduction process at Olkiluoto. Relatively high concentrations of SO_4^{2-} of up to 510 mg/L, remain in the deep groundwater at depths of ca. 150–300 m, in a seemingly stable setting (Posiva, 2013). The reason for this stability is thought to be the lack of organic compounds which could be used by microbes as electron donors in SO_4^{2-} reduction (Pitkänen et al., 2004; Posiva, 2013). However, a compositional boundary between SO_4^{2-} and CH_4 containing water masses at a depth of 300 m appears to be an exception. Along this chemical boundary HS^- concentrations are occasionally elevated, indicating that active SO_4^{2-} -reduction (Pitkänen et al., 2004) may occur by microbial mediated anaerobic methane oxidation (Pedersen et al., 2008, 2014; Posiva, 2013). Furthermore, Pedersen (2013) experimentally demonstrated the potential coupling of microbial anaerobic oxidation of methane to sulfate reduction at a depth of 327 m in Olkiluoto. The position of this sulfate reduction zone is well documented in the chemical composition of groundwaters. However, no evidence exists for the past evolution of this interface.

Close to the ground surface, the bedrock fractures were saturated with SO_4^{2-} -rich waters during the Littorina Sea stage of the Baltic Sea. The SO_4^{2-} in the upper 100 m of bedrock has mostly been diluted by subsequent meteoric infiltration and partly been consumed by bacterial sulfate reduction. Fracture bound pyrite in the upper parts of the bedrock, where SO_4^{2-} concentrations are currently low, indicates that past SO_4^{2-} reduction events have occurred (Sahlstedt et al., 2013).

The carbon isotope composition of calcite in the bedrock fractures can be used to examine the substrates involved in sulfate reduction and thus more information can be gained about this important redox process in the bedrock. The aim of this study is to examine carbon cycling in bedrock fractures by analyzing the carbon isotope composition of fracture calcite in situ using secondary ion mass spectrometry (SIMS). The spot analyses reveal a more detailed picture of carbon isotope variability in the calcite fillings and, therefore, provide a more comprehensive picture of the processes involved compared to conventional bulk analyses (cf. Drake et al., 2015b). We especially concentrate on fracture fillings with coexisting calcite and pyrite, where earlier sulfur isotope analyses of pyrite have provided strong evidence for BSR (Sahlstedt et al., 2013).

1.1. Isotopic signature of carbon in dissimilatory sulfate reduction

BSR is a common process in anaerobic, sulfate rich environments, most notably in marine settings (e.g. Knittel and Boetius, 2009; Megoñigal et al., 2005). In BSR, bacteria reduce SO_4^{2-} to S^{2-} , using organic carbon or H_2 as an electron donor. Because BSR is associated with a significant kinetic fractionation effect, analyses of the S-isotopic composition of sulfide may be applied to demonstrate the occurrence of bacterial sulfate reduction. The kinetic fractionation factor associated with BSR varies depending on the environment and micro-organisms involved (Detmers et al., 2001). Pure culture studies have shown that for some strains of bacteria the enrichment factor $\epsilon^{34\text{S}}_{\text{sulfate-sulfide}}$ may be as high as 66‰ (Sim et al., 2011) which is in line with the large, up to ~70‰ fractionations observed in nature (e.g. Drake et al., 2015a; Wortmann et al., 2001). As a result, the bacteria tend to strongly enrich the product sulfide in ^{32}S . If the amount of SO_4^{2-} available for bacteria is limited, the $\delta^{34}\text{S}$ values of the sulfide will become progressively higher as SO_4^{2-} is consumed in the reaction. In bedrock fractures BSR has been demonstrated by a large variation in the $\delta^{34}\text{S}$ values of low temperature pyrite (Drake et al., 2013; Sahlstedt et al., 2013). At Olkiluoto, the $\delta^{34}\text{S}$ values of pyrite in bedrock fractures varied from -50‰ to +82‰ (Sahlstedt et al., 2013) and in Laxemar,

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