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Abiotic and biotic controls on methane formation down to 2.5 km depth within the Precambrian Fennoscandian Shield

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Abstract

Despite a geological history characterized by high temperature and pressure processes and organic carbon deprived crystalline bedrock, large amounts of hydrocarbons are found in deep groundwaters within Precambrian continental shields. In many sites, methane comprises more than 80% of the dissolved gas phase reaching concentrations of tens of mmol l⁻¹. In this study, we used isotopic methods to study the carbon isotope systematics and sources of crustal methane within the Fennoscandian Shield. The main study sites were the Outokumpu Deep Drill Hole and the Pyhäsalmi mine in Finland, both of which allow groundwater sampling down to 2.5 km depth and have been previously studied for their groundwater chemistry and microbiology. We show that the differences in the amount and isotopic composition of methane are related to the availability of carbon sources as well as processes behind the incorporation of hydrogen and carbon via abiotic and biotic pathways into hydrocarbon molecules. Supported by previously reported occurrences and isotopic data of deep groundwater methane in lithologically different locations in Finland and Sweden, we show that methane formation is controlled by microbial methanogenesis and abiotic reactions, as well as lithology with the metasedimentary environments being the most favourable for methane occurrence. Rather than a thermogenic relic, crustal methane within the Fennoscandian Shield is more likely the result of low temperature formation from ancient organic compounds or their inorganic intermediates such as graphite. Such crustal gases are characterized by the lack of major amounts of C₂+ hydrocarbons and ¹³C rich methane. Further, microbiological and isotopic geochemical evidence suggest that microbial methane is more common at depths shallower than 1.5 km.

Keywords: Methane, ethane, hydrogen, carbon isotopes, calcite, graphite, Fennoscandian Shield, Outokumpu, Pyhäsalmi

1. INTRODUCTION

Methane (CH_4) is a key component in the interface of geological and biological i.e. abiotic and biotic world. Deep saline groundwaters within Precambrian continental shields are among the most peculiar environments where CH_4 has been found, sometimes at vast amounts exceeding 80% of the gas phase (e.g. Sherwood et al., 1988; Ward et al., 2004; Pitkänen and Partamies, 2007; Stotler et al., 2010). The information on processes generating CH_4 and their relative abundance in crystalline bedrock environment is important in evaluating the energetic limitations of microbial life in deep dark biosphere as well as microbe-water-rock interactions. These processes are important in understanding the evolution of life on Earth as well as potential for life on other planets. More practical applications include assessment of groundwater quality, safety of geological disposal of nuclear waste, and deep mining as water-rock interaction and microbial attainment may have an impact on the environment by changing the concentrations or mobility of potentially hazardous or corrosive compounds.

In deep subsurface environments CH_4 is known to be formed via three main mechanisms: 1) thermogenically by breakdown of organic matter, 2) microbially, and 3) abiotically from reactions of inorganic compounds such as CO_2 and H_2 (Kotelnikova, 2002; Etiope and Sherwood Lollar, 2013; Sephton and Hazen, 2013; Kietäväinen and Purkamo, 2015). Microbial methanogenic processes are commonly divided into autotrophic and heterotrophic pathways which utilize inorganic and organic carbon sources, respectively (Kotelnikova, 2002; Kietäväinen and Purkamo, 2015). The most commonly examined abiotic formation mechanism is the Fischer-Tropsch type (FTT) synthesis, i.e. the catalytic formation of CH_4 from CO and H_2 at high temperature, and its proposed natural analogues (e.g. Anderson, 1984; Horita and Berndt, 1999; Sherwood Lollar et al., 2002; Taran et al., 2007; Jacquemin et al., 2010; Zhang et al., 2013). Other abiotic reactions possibly capable of producing hydrocarbons include thermal decomposition of carbonate minerals, abiotic synthesis from carbon-bearing fluids and sulphide minerals through organosulphur intermediates (e.g. thiols), and clay catalysed synthesis (McCollom, 2013). In deep drill holes, such as the 6.6 km deep Gravberg-1 (Siljan Ring) in Sweden and 9 km deep KTB (Kontinentales Tiefbohrprogramm) in Germany, artificial CH_4 formed in reactions promoted by high temperature at the drill bit - rock interface (bit-metamorphism) has also been observed (Jeffrey and Kaplan, 1988; Faber et al., 1999).

Despite the drastic differences in the formation mechanisms, the separation of different sources of CH₄ is not a trivial task. Traditional classification diagrams for CH₄ such as those by Schoell (1980, 1988) and Whiticar (1999) were mainly based on isotope data from sedimentary and surface environments where organic compounds are ubiquitous. However, deep groundwaters in crystalline bedrock differ greatly from these environments because inorganic and refractory carbon sources dominate and even dissolved inorganic carbon (DIC) is often scarce (e.g. Kietäväinen and Purkamo, 2015 and references therein). Based on the increasing amount of data from crystalline bedrock, modifications have been made to these classical diagrams (e.g. Etiope et al., 2013; Etiope and Schoell, 2014) that now also include abiotic CH₄ of different origins. In addition, approaches have been made to use other parameters such as the combination of isotopic and compositional data (Bernard et al., 1976), and the change of isotopic composition with carbon number, i.e. with the chain length of alkanes (e.g. Sherwood Lollar et al., 2008; Burruss and Laughrey, 2010). Still, the basis of these classifications has in many cases been insufficient to reliably separate between different sources of CH₄ but in a very broad sense.

On one hand this is because the isotopic composition of a product gas, whether abiotic or biotic, is heavily dependent on the isotopic composition of the reactants/substrates (e.g. Schoell, 1983; Kotelnikova, 2002). On the other hand, the isotopic compositions are dependent on such factors as openness of the system, equilibration, time scale, and substrate limitation or excess (Burke, 1993; Whiticar, 1999; Valentine et al., 2004; Kelley et al., 2012; Reeves et al., 2012; Suda et al., 2014). However, these conditions are often poorly known. Therefore it is important to study the relevant chemical components as well as their isotopic compositions in order to get a view of gas generating processes in a given system. In addition, the information on lithology, microbiology and hydrogeology is essential in judging between the different processes.

We selected two lithologically different sites within the Precambrian crystalline bedrock in Finland within the Fennoscandian Shield for a detailed study of hydrocarbons. In the Outokumpu Deep Drill Hole, characterized by metasediments and ophiolite-derived serpentinites, CH₄ typically comprises over 70 vol-% of the dissolved gas phase with concentrations as high as 32 mmol l⁻¹ (Kietäväinen et al., 2013). Methane producing as well as consuming microorganisms have been found from the drill hole and fracture waters (Itävaara et al., 2011; Purkamo et al., 2015a, 2015b). Residence times of

groundwater up to 58 Ma (Kietäväinen et al., 2014) make this one of the oldest known ecosystems on Earth. In addition to dissolved carbon and carbonates, possible sources of carbon in the bedrock include graphite-rich black schist. Serpentinites provide a potential source of H_2 needed in both abiotic CH_4 synthesis and microbial methanogenesis (Devirts et al., 1993; McCollom and Bach, 2009; Neubeck et al., 2011; Schrenk et al., 2013), and radiolytic H_2 (Vovk 1987; Lin et al., 2005a, 2005b) may be present. In the Pyhäsalmi mine, ca. 180 km northwest from Outokumpu, the dominant lithologies are felsic to mafic metavolcanic rocks and granite. At Pyhäsalmi, CH_4 is scarcer, with a maximum concentration no higher than 0.55 mmol l^{-1} , but H_2 is abundant (Miettinen et al., 2015). In contrast to Outokumpu, volcanic rocks of Pyhäsalmi lack evident carbon source minerals. Yet, there are indications of CH_4 producing archaea living in the formation fluids of Pyhäsalmi at least down to 2.4 km depth (Miettinen et al., 2015).

In this study we use the isotopic compositions of hydrogen, carbon and oxygen in CH_4 , ethane (C_2H_6), propane (C_3H_8), DIC, calcite, graphite, molecular hydrogen (H_2) and water, together with information on gas compositions determined from the Outokumpu Deep Drill Hole and Pyhäsalmi mine fluid samples to determine CH_4 generating processes down to a depth of 2.5 km. To ascertain the representativeness of the samples, different sampling methods are also compared. A regional scale is brought up by comparing the results of this study to previously reported isotopic compositions of CH_4 in deep groundwaters in Finland (Heikkinen, 1972; Hyypä, 1981; Sherwood Lollar et al., 1993a, 1993b; Haveman et al., 1999, Pitkänen and Partamies, 2007) and Sweden (Jeffrey and Kaplan, 1988). The aim is to reveal possible systematics of CH_4 occurrence and isotopic composition in relation to depth, as well as lithological, physicochemical and microbiological factors in order to gain better understanding on the deep carbon cycle.

2. STUDY SITES

The Outokumpu Deep Drill Hole is located in eastern Finland ($62^{\circ}43'02.63''N$, $29^{\circ}03'55.01''E$) within the Fennoscandian Shield (Fig. 1). It reaches a maximum depth of 2516 m, which makes it the deepest scientific drill hole in Finland and one of the deepest within the whole Fennoscandian Shield. The 1.9 billion year old bedrock at the study site is mainly comprised of amphibolite facies ($550 - 675^{\circ}C$ at 3 – 5 kbar) metasediments, i.e. mica schist and biotite gneiss, which are interlayered with ophiolitic rocks

of the Outokumpu assemblage and dissected by slightly younger granitoids (Fig. 1, Claesson et al., 1993; Sääntti et al., 2006; Peltonen et al., 2008; Lahtinen et al., 2010; Västi, 2011).

Graphite is common as disseminated grains and black schist layers in mica schist. Occurrence of organic carbon (kerogen and traces of bitumoids) in the black schist has also been reported (Taran et al., 2011). The thickest black schist layers are found in relation with the Outokumpu assemblage between 1300 – 1600 m depth in the drill hole section and were suggested to be deposited under anoxic conditions at the margin of the Karelian Craton which was steadily sinking due to a collision with the Svecofennian (1.93 - 1.91 Ga) arc complex (Kontinen et al., 2006; Loukola-Ruskeeniemi, 1999). In addition to black schist, the Outokumpu assemblage rocks present in the Outokumpu deep drill core consist of ophiolite-derived serpentinites, calc-silicate rocks (skarn) and quartz rocks (Västi, 2011). For a long time the calc-silicate and quartz rocks at Outokumpu were interpreted as sedimentary in origin (e.g. Park, 1988; Karhu, 1993). However, their trace element composition, most notably high contents of chromium and nickel, resemble those of the serpentinites, pointing out their origin by metasomatic alteration of mantle material (Peltonen et al., 2008). Dolomitic carbonate rocks of the Outokumpu assemblage have $\delta^{13}\text{C}$ values between +0‰ and -3‰ VPDB (Karhu, 1993; Kontinen et al., 2006). The highest values are interpreted to represent seawater-derived inorganic carbon, probably introduced in the form of carbonate clasts embodied in turbidites or directly from circulating seawater (Kontinen et al., 2006).

Saline water with the concentration of total dissolved solids (TDS) as high as 70 g l⁻¹ enters the Outokumpu Deep Drill Hole along fracture zones which are separated from each other by tens to hundreds of meters of impermeable rock (Ahonen et al., 2011; Kietäväinen et al., 2013). A major divide in groundwater composition is seen at around 1300 m depth where the salinity suddenly increases, water and strontium becomes more enriched in the heavier isotopes and the concentration of CH₄ decreases while the proportion of H₂ begins to increase (Kietäväinen et al., 2013). Likewise there is a change in the microbial community structure which seems to closely mirror the change in groundwater chemistry, and lithology (Itävaara et al., 2011; Kietäväinen et al., 2013; Nyysönen et al., 2014; Purkamo et al., 2013, 2015a, 2015b). The Outokumpu Deep Drill Hole groundwater is isolated from the modern meteoric water cycle and both water stable isotopes and noble gases indicate residence times of tens of millions of years (Kietäväinen et al., 2013, 2014). Any contribution of mantle

degassing in the Outokumpu fluids can be excluded based on the crustal $^3\text{He}/^4\text{He}$ ratios of $1-2 \cdot 10^{-8}$ (Kietäväinen et al., 2014).

In addition to an extensive sampling campaign at Outokumpu, samples were also taken from the Pyhäsalmi mine located ca. 180 km northeast from Outokumpu ($63^{\circ}39'\text{N}$, $26^{\circ}03'\text{E}$) along the boundary between the Proterozoic and Archaean parts of the Fennoscandian Shield (Fig. 1). The Pyhäsalmi mine is in a volcanogenic massive sulphide (VMS) type Cu-Zn deposit and among the deepest metal mines in Europe. The deepest hole (R-2247) drilled downwards from the 1430 m depth level of the mine reach the depth of 2400 m below the surface (Fig. 1). Dominant rock types are 1.92 Ga old mafic to felsic volcanites which have metamorphosed at amphibolite facies conditions similar to Outokumpu, with minor occurrence of slightly younger granite (Kousa et al., 1994; Miettinen et al., 2015). Salinity of groundwater increases with depth reaching the TDS concentration of 76 g l^{-1} at 2400 m (Miettinen et al., 2015). Both acidic and basic waters in the shallow and deep parts of the mine, respectively, host liveable microbial communities (Kay et al., 2014; Miettinen et al., 2015).

3. MATERIAL AND METHODS

Sampling for geochemical analysis, including the stable isotopic composition of water, has been described in Kietäväinen et al. (2013), Purkamo et al. (2013), Rajala et al. (2015) and Miettinen et al. (2015). The overall geochemical characterisation of the Outokumpu Deep Drill Hole and the Pyhäsalmi mine groundwaters has been previously published in Kietäväinen et al. (2013) and Miettinen et al. (2015), respectively. Isotopic compositions of graphite from Outokumpu are provided by Taran et al. (2011). Here we focus on describing the sampling and isotopic analysis of gases and dissolved inorganic carbon (DIC) as well as fracture carbonates.

3.1 Fluid sampling

Gas samples from the Outokumpu Deep Drill Hole were taken between 2010 and 2012, and cover a depth range from 180 to 2480 m below the surface (bsl). In the Pyhäsalmi mine samples for isotopic analysis of gases were taken in 2014 from two drill holes (R-2247 and R-2227) starting from the mine level of 1430 m bsl and extending down to 2400 m depth. At Outokumpu, five different sampling

methods were used (Table 1): 1) tube sampling with 100 m sections (Nurmi and Kukkonen, 1986), 2) direct pumping, 3) pumping with packers (Ahonen et al., 2011), 4) “PAVE” pressurised sampling device (Haveman et al., 1999; Ahonen et al., 2011), and 5) Leutert positive displacement sampler (PDS; Regenspurg et al., 2010; Kietäväinen et al., 2013, 2014). Samples from the Pyhäsalmi mine were taken from free flowing fluid as described in detail by Miettinen et al. (2015).

From the tube sampler and pumped fluid the samples for gas analyses were taken either by injecting the spontaneously separated gas into head space bottles or diverting the gas into inverted glass bottles (Schott) under sample water (“a bucket method”). In both cases the bottles were flushed with argon and filled with sample water prior to gas collection in order to avoid contamination with air. In these samples some sample water was usually left in the bottles to prevent diffusion through the septa. From the “PAVE” samples (180 m depth) gas was directly released into analysis in the lab, whereas from the PDS, gas was collected into evacuated gas sampling bulbs in a vacuum line and gas separation assisted by heating in an ultrasonic bath in the field (Kietäväinen et al., 2013, 2014). The gas samples were not fixed, except one sample from Pyhäsalmi (PYS-1B) in which a few grains of solid HgCl_2 were added before the evacuation and gas injection. However, microbial activity can be considered minimal for the gas-only (dry) samples which include the PDS samples from Outokumpu and samples taken by the injection method in the Pyhäsalmi mine (method FFI in Table 2 and Table EA 1).

The samples for DIC isotope analyses were taken from the Outokumpu Deep Drill Hole in 2010 and 2011. In 2010 DIC isotope samples from pumped fluid from 500 and 2260 m depths were collected into LABCO Exetainer tubes (12 ml), which contained 0.15 ml of 85% phosphoric acid and were flushed and filled with He (purity > 99.996%). During sampling 5 ml of He was removed and 8 ml of sample water immediately injected into each tube. From the tube sampling in October 2011 the samples were collected in evacuated glass bottles (60 ml), specially manufactured to fit the caps from Vacutainer vials. The bottles were prepared by adding 3 ml of 85% phosphoric acid and a magnetic rod and evacuating them on a vacuum line specially designed for extracting DIC from water samples. The sample preparation was done at the Geological Survey of Finland (GTK) in Espoo. Samples for DIC isotope analysis were injected into evacuated glass bottles through a 0.8/0.2 μm supor membrane filter using a plastic syringe. Vials and tubes were stored upturned in dark and cool until analysed.

3.2 Sample selection and preparation for fracture mineral studies

In total, 58 rock samples along the Outokumpu deep drill core were selected between 100.90 and 2240.70 m depths below the surface. Samples represent both open and sealed fractures and thin veins. Ordinary 30 µm thick polished thin sections were prepared for microscopy and microanalysis studies. Loose fracture fillings were fixed with epoxy resin before cutting. In the case of extremely loose fillings, thin sections were not possible to make and, instead, minerals were mounted on a carbon tape. Calcites for isotopic analysis were carefully selected under a microscope and separated using a steel blade. Where different calcite generations occurred, they were sampled separately. Fractures dissected by the drill holes studied at Pyhäsalmi did not contain carbonate minerals (Miettinen et al., 2015).

3.3 Analysis

3.3.1 Dissolved gases

The gas composition was analysed by gas chromatography at Ramboll Analytics (Vantaa, Finland) or Isotech Laboratories (Illinois, USA) (Kietäväinen et al., 2013; Miettinen et al., 2015). Within the whole sample set (Table EA 1), relative uncertainties were generally better than 8% for hydrocarbons, 3% for H₂, 4% for O₂ and N₂, 6% for CO₂, and 10% for He and Ar.

The isotopic compositions of CH₄, C₂H₆ and from few samples also C₃H₈ from Outokumpu were determined at the Environmental Isotope Laboratory at the University of Waterloo (Ontario, Canada). Samples from the Pyhäsalmi mine were analysed for their isotopic composition at Isotech Laboratories. Following the separation by Trace Ultra Gas Chromatograph (Thermo Finnigan) the different hydrocarbons were converted to CO₂ at 940°C and to H₂ at 1450°C and analysed with a Delta^{plus} XL isotope ratio mass spectrometer (Thermo Finnigan MAT). The isotopic compositions are reported using δ-notation per mill (‰) relative to VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water) standards for C and H, respectively:

$$\delta(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000 \quad (1)$$

where R is either ¹³C/¹²C or ²H/¹H.

Analytical error is estimated to be $\pm 0.5\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 7\text{‰}$ for $\delta^2\text{H}$. The isotopic composition of H_2 gas was analysed from three Outokumpu samples in Hydroisotop GmbH (Schweitenkirchen, Germany) with the analytical uncertainty of $\pm 10\text{‰}$.

3.3.2 Isotopic composition of dissolved inorganic carbon

Isotopic analyses of DIC samples from 2011 were conducted at the Department of Geosciences and Geography at the University of Helsinki as follows. Before isotopic analysis the DIC samples in Vacutainer-fitted vials were heated to 50°C and attached to the vacuum line and CO_2 extracted and collected into Exetainer vials as described by Atekwana and Krishnamurthy (1998). The extraction time was 2×10 minutes. The samples were injected with helium before analysing them on an isotope ratio mass spectrometer (Thermo Finnigan Delta Plus Advantage) using laboratory standards calibrated against an international standard (VPDB). The absolute uncertainty of the DIC isotope analysis with this method was $\leq 0.60\text{‰}$ at 1σ level. DIC samples from the pumped fluid from 500 and 2260 m depths were analysed at the University of Jyväskylä with a Gas-Bench II connected to a Thermo Finnigan XP Advantage, using international measurement standard NBS 19 calcite and an in-house carbon standard, CaCO_3 . In this case the reproducibility of the standard measurements was 0.09‰ at 1σ level ($n=3$). The results are reported using δ -notation (Eq. 1) relative to VPDB standard.

3.3.3 Characterisation of fracture minerals

Fracture mineralogy was studied using both optical and scanning electron microscopy (SEM/ JEOL JSM-5900LV) at the Geological Survey of Finland (GTK) in Espoo. High vacuum, energy dispersive (EDS) mode with voltage of 20 kV and spot size of $50\text{ }\mu\text{m}$ was used during the SEM analysis for carbon coated thin sections. Low vacuum mode was used for uncoated samples on carbon tape.

3.3.4 Stable isotopes of calcite

Approximately $150\text{ }\mu\text{g}$ of calcite sample was weighted into Exetainer vials and reacted with concentrated phosphoric acid for at least 1 h at 70°C . Carbon and oxygen stable isotopes were analysed from the released CO_2 gas by Thermo Finnigan Delta Plus Advantage gas source mass spectrometer at the University of Helsinki, Department of Geosciences and Geography. To test reproducibility of the analysis, an in-house calcite reference was regularly analysed among the samples. The results are

reported using δ -notation (Eq. 1) relative to VPDB standard for both carbon ($R = {}^{13}\text{C}/{}^{12}\text{C}$) and oxygen ($R = {}^{18}\text{O}/{}^{16}\text{O}$). The reproducibility was $\pm 0.07\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.12\text{‰}$ for $\delta^{18}\text{O}$ at 1σ level ($n=20$).

3.4 Computational methods

The speciation and concentrations of dissolved inorganic carbon (DIC) and saturation index (SI) of calcite was calculated using the PHREEQC software, “wateq4f” database (USGS, 2014). A saturation index is determined as follows:

$$SI = \log \frac{Q}{K} \quad (2)$$

where Q is the ion activity product and K is the thermodynamic reaction constant (Clark and Fritz, 1997). In equilibrium SI equals 0 while positive and negative SI values indicate oversaturation and undersaturation (dissolution), respectively. *In situ* temperatures measured from the Outokumpu Deep Drill Hole (Kukkonen et al., 2011) and on site at the Pyhäsalmi mine (Miettinen et al., 2015) were used in all calculations. The hydrostatic pressure increase of about 100 bar km^{-1} was not taken into account as 1 bar pressure is used by the PHREEQC by default. Increased pressure will increase the solubility of calcite especially at low temperatures (Duan and Li, 2008) and may lead to slight overestimation of the saturation indices presented here. Additionally, high ionic strength of saline waters causes uncertainty in defining thermodynamic activity product (Q) of dissolved species. The field or on-line measurements of pH and alkalinity were used when available, as the pH was observed to rapidly decrease in contact with air apparently due to the dissolution of atmospheric CO_2 into these low alkaline waters with poor buffering capacity.

Isotopic fractionation factors (α) between phases x and y were calculated according to Eq. 3:

$$\alpha_{x-y} = \frac{1000 + \delta x}{1000 + \delta y} \quad (3)$$

where δ refers to the determined isotopic compositions in ‰ relative to standard (Eq. 1). The correlation between α and temperature (T , in Kelvin) is:

$$\ln \alpha_{x-y} = aT^{-2} + bT^{-1} + c \quad (4)$$

Isotopic separation (Δ) between phases x and y is simply the difference in their δ -values:

$$\Delta_{x-y} = \delta_x - \delta_y \quad (5)$$

4. RESULTS

4.1 Gas composition

A compilation of gas data, including sampling depths and methods, collected from the Outokumpu Deep Drill Hole and the Pyhäsalmi mine is given in the Electronic Annex (Table EA1). CH₄ and N₂ are by far the most abundant dissolved gases at Outokumpu, while H₂ becomes dominant in the deepest part of the drill hole. At Pyhäsalmi the gas phase is dominated by N₂ and He. The PDS samples from 500 and 2480 m depths and the sample PYS-2 from the Pyhäsalmi mine have suffered from severe air contamination (O₂ > 5 vol-%), but some O₂ is present in virtually all samples. The pressurised samples are relatively enriched in H₂ and He and depleted in CH₄ compared to samples obtained by pumping, the tube sampler or from free flowing fluid in the mine. At Outokumpu CH₄/(C₂H₆ + C₃H₈) ratio varies from 71 to 333 (Table EA1), such that a decrease is observed towards the surface. At Pyhäsalmi CH₄/C₂+ ratios are typically < 10, with only one drill hole (R-2250) having a significantly higher ratio of 164 (Table EA1). Ethene, propene and butene were below analytical detection (0.001 vol-%) in all samples.

4.2 Isotopic composition of gases

The isotopic compositions of CH₄, C₂H₆, C₃H₈ and H₂ are given in Table 2. Variation in the isotopic composition of CH₄ is large from -404 to -136‰ VSMOW for $\delta^2\text{H}_{\text{CH}_4}$ and from -39.9 to -13.2‰ VPDB for $\delta^{13}\text{C}_{\text{CH}_4}$, although most samples have $\delta^2\text{H}_{\text{CH}_4}$ around -280‰ VSMOW and $\delta^{13}\text{C}_{\text{CH}_4}$ around -30‰ VPDB (Fig. 2). ¹³C depleted and ²H enriched CH₄ is unique for the depth of 1470 m at Outokumpu and ¹³C enriched and ²H depleted CH₄ is only found below 2260 m depth. The minimum and maximum values of $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ are generally those from the pressurised samples (PDS and

PAVE). However, the isotopic compositions are not systematically shifted compared to the tube samples.

Similarly to CH_4 , the most ^{13}C enriched C_2H_6 is found from the 2480 m depth at Outokumpu and deep samples from the Pyhäsalmi mine. A fracture zone at 180 m depth has distinctive $\delta^2\text{H}_{\text{C}_2\text{H}_6}$ values as heavy as -152‰ VSMOW, while the other samples have $\delta^2\text{H}_{\text{C}_2\text{H}_6}$ around -250‰ VSMOW (Table 2). Isotopic data of C_3H_8 are only available for carbon from two depths from Outokumpu (500 and 2260 m) and only pumped fluids are represented. Nevertheless, the isotopic composition of carbon seems to be systematically lighter from CH_4 to C_3H_8 and C_2H_6 , except samples from tube sampling in May 2011 which, with no apparent reason, show anomalously ^{13}C rich values of C_2H_6 (Table 2). This indicates a $\delta^{13}\text{C}$ vs. carbon number trend is V-shaped (Fig. 3) rather than normal (ascending) or inversed (declining), i.e. neither of the two trends which have often been related to thermogenic and FTT type abiotic hydrocarbons, respectively (e.g., Sherwood Lollar et al., 2002; Etiope and Sherwood Lollar, 2013; Zhang et al., 2013). Hydrocarbons at Pyhäsalmi seem to differ from this pattern as they show enrichment of ^{13}C in C_2H_6 over CH_4 (Fig. 3).

Molecular hydrogen is extremely depleted in deuterium with the measured isotope range from -798 to -727‰ VSMOW at Outokumpu and from -736 to -680‰ VSMOW at Pyhäsalmi. While the addition of HgCl_2 into one of the gas samples from Pyhäsalmi (PYS-1B) did not affected the C or H isotopic composition of CH_4 , the $\delta^2\text{H}$ value of H_2 was 56‰ higher in the fixed sample compared to the untreated sample taken at the same time (Table 2). This one control with eliminated biological activity is clearly not enough for making generalised conclusions on the possible microbial processes during sample storage. However, there was no difference in the concentration of H_2 between the comparative samples which could indicate microbial production or consumption of H_2 (Table EA1).

4.3 Dissolved inorganic carbon

The modelled concentrations of DIC are very low (Table 2), with an average of 0.16 mmol l^{-1} at Outokumpu and only $2 \text{ } \mu\text{mol l}^{-1}$ at Pyhäsalmi. Governed by pH and Ca concentration, the main constituent of DIC is HCO_3^- or $\text{CaCO}_{3(\text{aq})}$ above and below 1500 m, respectively. The isotopic

composition of DIC varies from -18.1 to -0.8‰ VPDB with a general increase in ^{13}C with depth (Table 2, Fig. 4).

4.4 Fracture mineralogy

At Outokumpu saturation indices (SIs) of calcites at the ambient temperature and 1 bar pressure typically vary from 0.5 to 1.5 and only the two PDS samples from 1470 m depth show slightly negative SI values (down to -0.12) which are indicative of possible dissolution of calcite. At Pyhäsalmi, however, SI values for calcites are mostly negative as is also demonstrated by the absence of calcites on the fracture surfaces. Except the few more coarse grained (mm sized) crystals found from around 500 m depth (Table 3), calcite occurs as fine, powdery layers, thin films or medium sized crystals on fracture surfaces and veins at Outokumpu, and is typically accompanied by zeolite minerals and chlorite. Pyrite and pyrrhotite are common accessory minerals. Eu- to subhedral, box shaped crystals of calcite were most common but elongated crystals were also found (Table 3). Even though the modelled values show oversaturation of calcite throughout the studied range of compositions and depth at Outokumpu no calcite was found below 1500 m depth. Instead, the most common fracture filling minerals below 1500 m are prehnite ($\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$) and Ca-zeolite (laumontite; $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4(\text{H}_2\text{O})$). Overall, fractures become scarce in the deeper part of the drill hole.

4.5 Isotopic composition of calcites

The isotope geochemistry of fracture filling and vein calcites from the Outokumpu Deep Drill Hole is presented in Table 3. The $\delta^{18}\text{O}$ values range from -18.7 to -9.7‰ VPDB and the $\delta^{13}\text{C}$ values from -19.64 to -3.43‰ VPDB. Calcites associated with the Outokumpu assemblage rocks have a narrow range of carbon compositions from -9 to -5‰ VPDB. The $\delta^{18}\text{O}$ values of these calcites are more variable, although all veins/fractures containing chalcopyrite plot between -16 and -14‰ VPDB.

5. DISCUSSION

In order to understand carbon cycling in general, and CH_4 formation processes in particular, we need to know 1) what are the potential sources of hydrogen and carbon needed to build a CH_4 molecule, 2) are

there some physicochemical conditions or microorganisms which could affect CH₄ formation and 3) is CH₄ further consumed, oxidized, polymerized or escaped? In this study we aimed to answer these questions by combining isotope geochemistry of carbon and hydrogen bearing phases with information on lithology and microbiology at Outokumpu and Pyhäsalmi and further extending the study to cover the Fennoscandian Shield based on previously published data. First we start by discussing the different sampling methods and representativeness of the data.

5.1 Comparison of different fluid sampling methods

In a previous study (Kietäväinen et al. 2013) good correlation was observed in the anion and cation contents and composition as well as the isotopic composition of groundwater between the tube sampling and PDS methods at Outokumpu. However, this study has demonstrated that in the case of gases the selection of the sampling method plays a more critical role. Most notably, differences in the isotopic composition of CH₄ were observed between the pressurised (PDS and PAVE) and non-pressurised (tube and pumping) methods. However, the shift in the isotopic compositions was not systematic with respect to sampling method. Therefore the difference cannot be explained by mass dependent isotopic fractionation. For the same reason it is not likely that the changes appeared due to sample storage in different kind of vials.

Based on geochemical and water stable isotope data (Kietäväinen et al. 2013), and supported by the compositional data of gases (Fig. 5), up to five different water types can be discerned at Outokumpu. Therefore, the tube sampling and pumping may give the average composition while the pressurised methods are able to more precisely capture a fluid from a particular depth. In particular, mixing of gases can be promoted by the pressure drop and release of gases during pumping and tube sampling before the fluid reach the surface. Thus, the most likely explanation of the observed differences in the isotopic composition of CH₄ between pressurised and non-pressurised methods is mixing of gases from different fracture systems and different depths either along the drill hole or within the tube. Likewise, the observed relative enrichment of H₂ and He in the pressurised samples can be explained by bubbling as these gases are among the least soluble and thus will be preferentially escaped during degassing. Indeed, during pumping gas compositions fluctuated in a non-linear manner which could be indicative of bubble formation (Table EA1, Fig. 5). Bubbling is also observed at the well head at Outokumpu.

However, the depth at which spontaneous degassing takes place in the drill hole without pumping is likely less than 150 m based on the concentrations and solubility of the main gaseous components (Kietäväinen et al., 2014; Heikkinen 2016).

In Fig. 5 we use the CH_4/N_2 and N_2/Ar ratios and $\delta^{13}\text{C}_{\text{CH}_4}$ values to compare the results obtained by the different sampling techniques and further investigate post-genetic and post-sampling processes capable of modifying the composition of the gas. The CH_4/N_2 and N_2/Ar ratios are likely governed by the organic carbon composition and content of the source (e.g. Jenden et al., 1988), and may change due to bubbling (solubility), mixing (e.g. Darrah et al., 2014) and, at very long time scales, also by the accumulation of radiogenic Ar. However, as long as only advection is considered, no isotopic fractionation should occur in these processes. Bubbling for example should change the gas composition only along the y-axis in Fig. 5c and d due to preferential partitioning of the less soluble N_2 in the gas phase, and consequential depletion in the remaining fluid. This means that samples taken during and after a bubble burst will differ in their relative gas composition but, if bubbles originate from sources with different isotope signature, may also express linear change in the isotope composition of CH_4 . Diffusion will also preferentially remove N_2 but may also produce ^{13}C (and ^2H) depletion in the diffusing gas while the residual gas will become isotopically heavy (e.g. Prinzhofer and Huc, 1995; Schloemer and Krooss, 2004), although e.g. Fuex (1980) and Schoell (1983) have argued that diffusion related isotope effects will be negligible and may only pertain non-steady state processes, if any, on hydrocarbons. In any case, the overall isotope trend at Outokumpu which shows inverse correlation of $\delta^2\text{H}_{\text{CH}_4}$ with $\delta^{13}\text{C}_{\text{CH}_4}$, does not support modification of isotope composition of CH_4 through diffusion.

When accompanied with decrease and increase of the $\delta^{13}\text{C}_{\text{CH}_4}$ value, respectively, the decrease and increase in the CH_4/N_2 ratio can also be due to methanogenesis and oxidation of CH_4 , in which case no change in the N_2/Ar ratio is expected. Oxidation seems to explain the difference between the results obtained by pumping and PDS at 1820 m depth and difference in the isotopic composition of CH_4 between the drill holes R-2247 and R-2227 at Pyhäsalmi (Fig 5.c,d). However, the most ^{13}C rich CH_4 observed at Outokumpu (2480 m) cannot be explained by oxidation, most notably because of the high CH_4/C_2+ value (Table EA1), and depletion in ^2H (Fig. 2).

5.2 Hydrogen in the system $\text{H}_2\text{O}-\text{H}_2-\text{CH}_4$

496

497 Incorporation of hydrogen into the CH_4 molecule can happen either from H_2O , organic matter or H_2 .
498 Due to their lower mass and position in a CH_4 molecule, equilibration of hydrogen isotopes occurs
499 more easily than carbon isotopes (Lyon and Hulston, 1984; Ni et al., 2011; Reeves et al., 2012). This
500 means that hydrogen may be a more sensitive tracer for CH_4 forming processes compared to carbon.
501 However, information carried by hydrogen on its origin may be more easily lost at geological time
502 scales.

503

504 H_2 is a common constituent of the gas phase at both Outokumpu and Pyhäsalmi (Table EA1). In Figure
505 6a-b, the isotopic fractionation of hydrogen in the system H_2O - H_2 - CH_4 is used to examine possible
506 equilibration of the Outokumpu and Pyhäsalmi samples with temperature. Fractionation factors (α)
507 given by Horibe and Craig (1995) for a temperature range 0-370°C were used to calculate the isotopic
508 concordance curves shown (Eq. 4). For low temperatures ($< 200^\circ\text{C}$) the fractionation is best established
509 between H_2O and H_2 while higher uncertainties are related to the equilibration of hydrogen between
510 CH_4 and H_2 or H_2O (Horibe and Craig, 1995). Nevertheless, the results fit well with each other for this
511 limited set of samples and indicate isotopic equilibrium at ambient, or slightly higher, temperatures
512 (Fig. 6). Thus, CH_4 seems to have formed at equilibrium controlled reactions *in situ* or to represent gas
513 component which has later equilibrated with H_2 and H_2O . However, when the whole sample set is
514 considered, it is apparent that, especially in the samples obtained by the pressurised methods at
515 Outokumpu, CH_4 is not in isotopic equilibrium with H_2O at *in situ* temperatures from 5 to 40°C (Fig.
516 7).

517

518 The time span needed for hydrogen isotopes to equilibrate in the system H_2O - H_2 - CH_4 is not well
519 constrained but some experimental data and approximations do exist. Using the equations for optimum
520 99% equilibration of ^{13}C between CO_2 and CH_4 from Giggenbach (1982) and rate constants for H_2 - H_2O
521 and H_2 - CH_4 isotope exchange determined by Lécluse and Robert (1994), Suda et al. (2014) calculated
522 that at 50°C the isotopic equilibrium between H_2 and H_2O can be attained within 100 years while the
523 equilibration between H_2 and CH_4 would take 3000 years. The isotopic equilibration of hydrogen
524 between H_2O and CH_4 is likely to be in the same order or slower (Lyon and Hulston, 1984; Suda et al.,
525 2014), and has been reported for natural gas accumulations in a deep sedimentary basin (Burruss and
526 Laughrey, 2010). Lin et al. (2005b) suggested that in natural bedrock environments, residence time of

around 1 Ma should be sufficient to equilibrate the hydrogen isotopic compositions in the system H_2O - H_2 to reflect *in situ* temperatures; the time span of which is still clearly less than the estimated residence times of groundwaters at Outokumpu between 4 and 58 Ma (Kietäväinen et al., 2014). However, in the presence of H_2 utilizing microorganisms, the equilibration of hydrogen isotopes may take place remarkably fast. In particular, sulphate reducers and methanogens, also found at Outokumpu and Pyhäsalmi (Itävaara et al., 2011; Nyyssönen et al., 2014; Purkamo et al., 2013, 2015a, 2015b; Miettinen et al., 2015), have been observed to equilibrate hydrogen isotopes between H_2O and H_2 within seconds in their metabolic processes (Romanek et al., 2003; Valentine et al., 2004).

Compared to CH_4 , hydrogen isotopes of C_3H_8 can be even more readily exchanged with water and, at long time scales, the isotopic exchange may be significant also for C_2H_6 (Reeves et al., 2012). Based on the equilibrium fractionation determined by Wang et al. (2009) for H isotope exchange between H_2O and C_2H_6 , which is much less temperature dependent than fractionation between H_2O and CH_4 , and not as likely to be affected by microbial activity, $\delta^2\text{H}$ values below -990‰ VSMOW would be expected for C_2H_6 in equilibrium with H_2O at Outokumpu. Instead the $\delta^2\text{H}_{\text{C}_2\text{H}_6}$ values are between -277‰ and -153‰ VSMOW (Table 2). This suggests that, when observed, the isotopic equilibration of H in the system H_2O - H_2 - CH_4 is likely controlled by other factors than the long residence time, such as microbial activity. Difference between the pressurised and non-pressurised methods may arise from technical reasons, most notably the immediate separation of gas from water, which should prevent post-sampling changes in the PDS samples.

Beyond the equilibration processes, hydrogen isotope fractionation between CH_4 and H_2O is also dependent on the relative proportion of H derived from H_2O and other sources, and therefore should differ between CO_2 reduction (H from H_2O) and acetate fermentation (H from organic matter and H_2O) pathways (Fig. 7, Sugimoto and Wada 1995; Whiticar 1999). In the case of CH_4 formation from graphite (e.g. $2\text{C} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$, or $\text{C} + 2\text{H}_2\text{O} + 4\text{Fe}_3\text{O}_4 = 3\text{Fe}_2\text{O}_3 + \text{CH}_4$; Burruss and Laughrey, 2010), the fractionation would likely be similar to CO_2 reduction as in both cases H_2O provides the only hydrogen source. While most of the variation among the samples from Outokumpu and Pyhäsalmi may be explained by the change in the relative proportion of CO_2 reduction and acetate fermentation, values exceeding the suggested limits do occur.

Isotopic composition of CH₄ is also subject to change after the formation. Such secondary fractionation typically leads to either enrichment or depletion of both C and H isotopes in the same direction (Schoell, 1988). When accompanied with enrichment in ¹³C (Whiticar, 1999; Etiope et al., 2011), the shift towards the less negative $\delta^2\text{H}_{\text{CH}_4}$ values in Fig. 7 could be due to oxidation of CH₄. In Pyhäsalmi the more ²H and ¹³C enriched CH₄ from the shallower and more recently made drill hole R-2227, which contains significantly less CH₄ than the drill hole R-2247, might represent oxidised gas, possibly affected by the drilling. However, at Outokumpu the isotopic composition of CH₄ at 1470 m depth does not indicate such post-formational changes as the depletion of ²H is coupled with enrichment of ¹³C (Fig. 2). Instead, distinct rock types surrounding the 1470 m depth, which include serpentinite and thick layers of black schist, may provide an explanation for the different isotopic composition of CH₄. In the case of deep sourced samples, the larger isotope offset towards the more negative $\delta^2\text{H}_{\text{CH}_4}$ values may be caused by the high partial pressure of H₂ (Burke 1993, Sugimoto and Wada 1995). The high $\alpha_{\text{H}_2\text{O}-\text{CH}_4}$ of up to 1.56 below 2300 m depth could also be indicative of abiogenic CH₄ (Sherwood Lollar et al., 2008), although high $\alpha_{\text{H}_2\text{O}-\text{CH}_4}$ values have also been reported for microbial CH₄ produced by the hydrogenotrophic methanogen *Methanobacterium formicicum* (Balabane et al., 1987).

5.3 Carbon in the system CH₄-DIC-calcite-graphite

First of all, the carbon isotopic composition of CH₄ depends on the carbon source. At Outokumpu isotopic data on all phases in the system CH₄-DIC-calcite-graphite, together with additional isotopic and geochemical information such as noble gas isotopes (Kietäväinen et al., 2014) is available which allows us to study the carbon sources and sinks in detail. At Pyhäsalmi, however, the possible carbon sources are more limited and the information on the carbon isotope composition, other than that of hydrocarbons, was not studied and thus will not be discussed here.

Previously the heaviest isotopic compositions of CH₄ have been related to gases with more than 5% mantle helium (Etiope and Sherwood Lollar, 2013). However, at Outokumpu the extremely ¹³C-rich CH₄ values found below 2300 m are associated with He which has an entirely radiogenic isotope signature (Kietäväinen et al., 2014) and thus a mantle source for the more soluble CH₄ can be excluded. Hence, the main sources of carbon include dissolved and crystalline carbonate carbon as well as refractory organic carbon, mainly graphite, within the crust.

589

590 Carbon isotopic compositions from the fracture and vein calcites in this study fall between -3 and -20‰
591 VPDB (Fig. 8a). Even though the modelled positive SI values of calcites suggest calcite precipitation
592 throughout the drill hole section, observations of calcite fillings were limited to the uppermost 1.5 km.
593 The discrepancy is likely related to the increase in the solubility of calcite with pressure which was not
594 taken into account in the model. In addition, the preservation of the latest, and probably the loosest,
595 fracture fillings may be poor because of the rotary drilling technique used. Only few of the more ^{13}C
596 depleted calcites have isotopic composition in equilibrium with the present DIC (Fig. 8a), while the
597 oxygen isotopes of calcites and present groundwater seem to be more interconnected (Fig. 8b). In part
598 the variations are likely due to different calcite generations, some of which can be remarkably old.
599 These include hydrothermal calcites which are characterised by heavy $\delta^{13}\text{C}$ values, typically above -
600 10‰ VPDB, due to preferential fractionation of ^{12}C into vapour phase (steam) during boiling in open
601 system conditions, as well as ^{18}O depleted values (Clark and Fritz, 1997; Wallin and Peterman, 1999;
602 Blyth et al., 2009). In this group belong calcites associated with the Outokumpu assemblage rocks
603 between 1300 and 1500 m depth (Fig. 8).

604

605 Several studies have also shown that carbon isotopic composition of calcites reflect changes emanating
606 from microbial activity (e.g. Pedersen et al. 1997; Blyth et al., 2009; Drake et al., 2015; Sahlstedt et al.,
607 2016). In connection with the modest $\delta^{18}\text{O}_{\text{calcite}}$ values indicative of precipitation from meteoric water
608 at varying degrees of water-rock interaction, the ^{13}C enriched values may originate from microbial
609 methanogenesis because microbes prefer ^{12}C in their metabolic reactions therefore leaving the
610 remaining DIC enriched in ^{13}C (Claypool et al., 1985; Clark and Fritz, 1997; Blyth et al., 2009). In the
611 other end, carbon input from the oxidation of CH_4 is characterised by extremely ^{13}C poor values in
612 calcites, the most ^{13}C depleted values below -15‰ VPDB thus indicating that some CH_4 derived
613 carbon was probably encountered. These occur close to the presently hydraulically active fracture
614 zones at 500 and 1000 m depths as well as in the upper 250 m (Fig. 8).

615

616 While carbon originating from the microbial oxidation of CH_4 seems to be recorded in some of the
617 calcites at active fracture zones, the source of carbon for the build-up of hydrocarbons is less evident.
618 At Outokumpu the isotopic separation (Eq. 5) between DIC and CH_4 , ranges from 11 to 25‰, or
619 between ~8 and 23 ‰ if the $\delta^{13}\text{C}_{\text{CH}_4}$ values of only the PDS samples are considered (Fig. 4). Although

the enrichment of DIC with ^{13}C can occur due to microbial methanogenesis (Claypool et al. 1985), the observed simultaneous increase in $\delta^{13}\text{C}_{\text{CH}_4}$, as most clearly observed at 500 and 2260 m depths (Fig. 4, does not support such isotopic evolution. Furthermore, the values of $\alpha_{\text{CDIC-CH}_4}$ (< 1.025) are not consistent with microbial methanogenesis through the CO_2 reduction pathway (Valentine et al., 2004; Sherwood Lollar et al., 2008). However, where aceticlastic methanogens dominate the $\Delta_{\text{DIC-CH}_4}$ is expected to be lower, because the use of organic compounds would not directly affect the isotopic composition of DIC, or abiotic reaction mechanisms may dominate. Unlike hydrogen isotopes in the system $\text{H}_2\text{O-H}_2\text{-CH}_4$, equilibration of carbon is more unlikely due to sluggish kinetics (Sherwood Lollar et al., 2008), and thus, even though DIC and CH_4 are far from isotopic equilibrium ($1000\ln\alpha_{\text{CHCO}_3\text{-CH}_4} = 76.1\text{‰}$ at 25°C ; Clark and Fritz, 1997 after Bottinga, 1969 and Mook et al., 1974) at Outokumpu, abiotic CH_4 formation from CO_2 is possible in the light of DIC isotopes.

Graphite rich black schist form another potential carbon source at Outokumpu. Compared to DIC, isotopic fractionation of carbon between graphite and CH_4 is likely to be lower, as the reaction does not take place through a dissolved phase. In Outokumpu, within the depth range where graphitic rocks are abundant, the isotopic composition of CH_4 (Fig. 4) is very close to or only slightly depleted in ^{13}C compared to graphite ($\delta^{13}\text{C} -27.4\text{‰} \dots -18.4\text{‰}$ VPDB; Taran et al., 2011). It has been experimentally shown that fractionation is lower if the starting material is graphite compared to CH_4 formation from for example gaseous components (Zhang et al., 2013). This is because CH_4 formation takes place only at the mineral surface where carbon isotopes are randomly dispersed (Zhang et al., 2013). Thus, notable fractionation of carbon isotopes between graphite and CH_4 is not expected.

The isotopic composition of CH_4 can also depend on the amount of substrates available. The closeness of the system tends significantly decrease fractionation as in the case of near-complete conversion of substrates into CH_4 the isotopic fractionation could follow the Rayleigh distillation trend eventually leading to minimal fractionation (Bradley et al., 2009; Kelley et al., 2012; Tazaz et al., 2013; Suda et al., 2014). Isotope fractionation may also decrease under unlimited supply of substrates. For example, Valentine et al. (2004) observed that the high partial pressure of H_2 decreased fractionation between CO_2 and CH_4 . They suggest that this could be due to limited reversibility of methanogenesis at excess H_2 . High partial pressure of H_2 may also inhibit some methanogenic species (Thauer et al., 2008), thus changing the reaction pathway or even limiting it to abiotic. A combination of limited carbon supply

with excess H_2 could explain the high $\delta^{13}C_{CH_4}$ values especially below 2300 m depth at Outokumpu and at Pyhäsalmi.

5.4 Carbon in the system CH_4 - C_2H_6 - C_3H_8

Even though some subsurface microorganisms may be capable of producing longer chained hydrocarbons (e.g. Taylor et al., 2000; Hinrichs et al., 2006), the vast majority of microbially generated hydrocarbon gas is CH_4 , and the high CH_4/C_{2+} ratio (>1000) is commonly used to separate microbial from thermogenic CH_4 , even though lower ratios may also be observed due to preferential consumption (oxidation) or escape (diffusive or advective migration) of CH_4 (Bernard et al., 1976; Printzhofner and Huc, 1995; Whiticar, 1999). Figure 9 shows the classification of CH_4 into microbial and thermogenic based on the CH_4/C_{2+} ratio in combination with the isotopic composition of CH_4 , i.e. the classical Bernard diagram for the samples from the Fennoscandian Shield (Table EA2). In addition, potential limits are suggested for abiotic CH_4 in Fig. 9 which are based on data from the Zambales ophiolite (ZO) and mid-ocean ridges (MOR) (Horita and Berndt, 1999 and references therein), and artificial CH_4 from bit-metamorphism (Faber et al., 1999). If, instead, previous data from the Precambrian Shields with $\delta^{13}C_{CH_4}$ values down to -50‰ VPDB are considered abiotic (cf. Fig. 2 and Sherwood Lollar et al. 1993b), the abiotic field would essentially include the whole thermogenic field.

The CH_4/C_{2+} ratio is not capable of distinguishing abiotic hydrocarbons from microbial and thermogenic very well because the former can have both high and low ratios (Faber et al., 1999; Horita and Berndt, 1999; Tassi et al., 2012). For example, hydrocarbons produced by clay catalysed reactions differ from those of FTT synthesis, as they contain more aromatic compounds, instead of the dominance of linear alkanes typical for FTT, while the organosulphur pathway lacks alkane and alkene products (McCollom, 2013). Longer chained alkanes are also more probably produced in gaseous than aqueous systems (Lewan and Roy, 2011). When associated with extremely 2H -poor and ^{13}C -rich CH_4 , high concentrations of both H_2 and unsaturated hydrocarbons, the high CH_4/C_{2+} ratio may indicate artificial CH_4 formed (from organic compounds often added in the drilling fluid) by bit-metamorphism (Faber et al., 1999). In this light, different formation processes can explain the different CH_4/C_{2+} ratios of similarly ^{13}C enriched CH_4 at Outokumpu and Pyhäsalmi.

A further indication of different formation mechanisms comes from the comparison of $\delta^{13}\text{C}$ compositions of the alkanes (Fig. 3). The typical V-shaped pattern at Outokumpu is similar to that reported by Sherwood Lollar et al. (2008) from the Kidd Creek mine and four other sites in Precambrian shields in Canada and South Africa which they explained by abiotic polymerisation of hydrocarbons. In their model, the first step ($\text{CH}_4 \rightarrow \text{C}_2\text{H}_6$) is associated with isotope depletion but the fractionation then diminishes due to rapid polymerisation and is thereafter only controlled by isotope mass balance which leads to slight enrichment of ^{13}C from C_2H_6 onwards (Sherwood Lollar et al., 2008). The initial step of hydrocarbon generation by this mechanism could not be experimentally reproduced (McCollom et al., 2010) and the actual mechanism still remains elusive. Low (or decreasing) temperature might be a prerequisite for the preservation of such pattern as the polymerised hydrocarbons cannot split, and may explain why this trend is more common in nature than in experiments which have usually been performed at increasing temperatures (Zhang et al., 2013). Reversal of the carbon isotope trend may also be formed at the latest stages of thermogenic gas formation after the formation of longer chained hydrocarbons has ceased, allowing Rayleigh-type fractionation of carbon isotope composition of C_2H_6 and C_3H_8 to occur (Burruss and Laughrey 2010). Thus it may indicate shift from thermogenic to abiotic processes at environments where refractory organic carbon sources are present.

At Pyhäsalmi C_2H_6 is depleted in ^{12}C compared to CH_4 (Fig. 3), a trend that has been commonly associated with thermogenic hydrocarbons in which it forms as the result of break-up of organic molecules with increasing temperature (e.g. Sherwood Lollar et al., 2002; Zhang et al., 2013). The isotopic compositions are, however, much more ^{13}C enriched than in conventional thermogenic hydrocarbon occurrences and it is also difficult to find a plausible source for such gas in metavolcanic rocks.

5.5 Evidence for microbial methane

Methanogenic microorganisms have been found from both Outokumpu and Pyhäsalmi (e.g. Itävaara et al., 2011; Purkamo et al. 2015a, 2015b; Miettinen et al., 2015). Among the other sites within the Fennoscandian Shield, where isotopic data of CH_4 are available (Fig. 1), methanogens have been found also from Olkiluoto (Pedersen et al., 2008; Nyssönen et al., 2012; Bomberg et al., 2014), but not from

Gravberg (Szewzyk et al. 1994), Hästholmen, Kivetty or Romuvaara (Haveman et al., 1999). To our knowledge, the other sites depicted in Fig. 1 have not been studied for their microbiology.

Methanotrophs, which oxidize CH₄ for living, also commonly accompany methanogens in deep crystalline rock environments (Nyyssönen et al., 2012; Purkamo et al., 2015a; Bomberg et al., 2015). However, methanogens and methanotrophs typically form only a marginal group of the microbial communities studied (e.g. Miettinen et al., 2015; Purkamo et al. 2015a, 2015b; Simkus et al., 2016). In contrast to previous views which suggest that the deep biosphere is dominated by autotrophs, Purkamo et al. (2015a) hypothesised that the biological deep carbon cycling in Outokumpu is mainly evoked by heterotrophic bacteria. The role of methanogens and methanotrophs in providing carbon for the whole community may however be more important than suggested by their relative proportion (Simkus et al., 2016).

In the Outokumpu Deep Drill Hole groundwater, methanogenic activity is both more common and more versatile at shallower depths above 1 km compared to the deeper levels (Purkamo et al., 2015a, 2015b). Purkamo et al. (2015b) retrieved methanogen communities from the DNA extracted from the fracture fluids of 180, 500, 2260 and 2300 m depths but only the samples from 500 and 967 m contained methanogen RNA. As RNA is used as a proxy for metabolically active species, this may indicate that the active microbial methanogenesis is restricted to the upper 1 km of the drill hole, or the deep dwelling methanogenic species cannot be detected with the methods used. Likewise, methanotrophy is more common at shallower depths not only at Outokumpu where methanotrophic communities have been found at 600, 900 and 1500 m depths but not from deeper levels (Purkamo et al. 2015a) but also in other sites within the Fennoscandian Shield (Kietäväinen and Purkamo, 2015).

Methanogenic species also vary with depth. At Outokumpu, aceticlastic (heterotrophic) *Methanosarcinales* prevail in the upper part of the drill hole and hydrogenotrophic (autotrophic) *Methanobacteriales* below 1300 m (Nyyssönen et al., 2014; Purkamo et al., 2015a). At Pyhäsalmi *Methanobacteriales* was the most common archaeal order found by DNA and RNA sequencing methods, although in the drill hole R-2247 *Thermoplasmata*, some of which also belong to methanogens, were dominating the archaeal RNA fraction (Miettinen et al., 2015). Indeed a general trend can be detected worldwide within the Precambrian shields that methanogens are more

metabolically diverse at shallower depths (Kietäväinen and Purkamo, 2015). Isotopic compositions of CH_4 among the Fennoscandian Shield sites also show that $\delta^{13}\text{C}_{\text{CH}_4}$ values below -40‰ are exclusively found in the upper 1 km depth while values heavier than -20‰ appear to be more common at depths greater than 1.5 km (Fig. 10). At some extent this can be due to biased data as samples below 1.5 km are from only three sites (Outokumpu Deep Drill Hole, Pyhäsalmi and Gravberg) and from depths which mainly represent volcanic and igneous rocks. However, similar results have been recently obtained in the Witwatersrand basin in South Africa (Simkus et al., 2016).

5.6 Evidence for lithological control on the amount and isotopic composition of methane

Within the Fennoscandian Shield sites the depth dependence of CH_4/C_2+ ratio (Fig. 11) is poor. Instead the variation in CH_4/C_2+ seems to vary from site to site, which may indicate lithological control on the production of hydrocarbons. Previous observations from around the world suggest that in general hydrocarbons in igneous rocks have low CH_4/C_2+ ratios (<100), such as those at Pyhäsalmi, while higher ratios, similar to those at Outokumpu, have been found in the Zambales ophiolite and sediment covered ridges and even higher values (>1000) in the sediment free mid-ocean ridges (Fig. 9; Horita and Berndt, 1999; Tassi et al., 2012 and references therein). The differences may be related to availability of organic carbon sources or microbial activity, but may also arise from the differences in the abiotic formation mechanism and temperature/or pressure (see also discussion in 5.4).

Within the occurrences of crustal CH_4 in the Fennoscandian Shield (Fig. 1), the most ^{13}C depleted values are from Enonkoski (Sherwood Lollar et al., 1993a), Muhos and Tyrnävä (Heikkinen, 1972) (Fig. 10). The last two sites also drastically differ in their lithology from the other sites. They are located within glacial sediments on top of a 1300 Ma, non-metamorphosed sedimentary rocks (shale). These represent typical microbial CH_4 formed at low temperatures from abundant organic rich matter. Shallow (< 300 m) groundwater within non-metamorphosed sandstone of Pori also contains low amounts of relatively ^{12}C -rich CH_4 (Sherwood Lollar et al., 1993a).

The other sites have suffered from high temperature, meaning that preferable escape of lighter isotope has likely taken place leaving the remaining refractory organic remains depleted in ^{12}C (in the case of organic rich metasediments) or ^{12}C rich carbon perhaps never existed (in the case of magmatic rocks).

At Olkiluoto a hydraulically dynamic upper layer of around 200 m thick occurs (e.g. Pitkänen and Partamies, 2007) which could provide microbes with abundant carbon and explain the sporadic discoveries of ^{12}C rich CH_4 . However the ^{12}C -rich CH_4 at Enonkoski, interpreted by Sherwood Lollar et al. (1993a) to represent microbial CH_4 , is more enigmatic and the other sites with confirmed methanogenic activity do not generally show similar isotopic compositions together with C_2+ enriched composition of the gas (Fig. 9).

Deep levels of the Pyhäsalmi mine are an example of magmatic rock environment where most of the CH_4 has likely formed at high temperature, and possible artificial, abiotic synthesis. In addition to CH_4 such synthesis has also produced higher amounts of C_2+ compounds (Fig. 9), but resulted in overall low potential of hydrocarbon generation, and thus low concentrations of hydrocarbons and, opposed to abiotic low temperature hydrocarbons, may be characterised by ^{13}C enrichment with the increasing chain length. In this same group belong Hästholmen (Haveman et al., 1999) and Gravberg (Jeffrey and Kaplan, 1988) sites which are both located in granitic rocks and Romuvaara where the bedrock consists of tonalite gneiss (Haveman et al., 1999). Slightly more ^{12}C -rich CH_4 is found from groundwater within granitic surroundings of Kivetty (Haveman et al., 1999) and serpentinite and gabbro of Ylivieska (Sherwood Lollar et al., 1993a). Except Ylivieska, with the maximum of $8.5 \text{ mmol l}^{-1} \text{ CH}_4$ (Sherwood Lollar et al., 1993a), the concentrations of CH_4 remain well below 1 mmol l^{-1} at these sites (Table EA2).

In contrast to volcanic and granitic rocks, sites within metasedimentary rocks including the Outokumpu Deep Drill Hole, Juuka, Olkiluoto, Vammala, Kotolahti and Sukkulansalo typically contain abundant CH_4 (Fig. 1, Table EA2) and have CH_4/C_2+ ratios generally > 100 . The close relatedness of metasedimentary rocks, graphite rich black schists in particular, and the highest concentrations of CH_4 and high CH_4/C_2+ ratios together with $\delta^{13}\text{C}_{\text{CH}_4}$ usually between -40 and -20 ‰ VPDB strongly support the hypothesis that within the Fennoscandian Shield CH_4 is more commonly produced at low temperatures by microbial methanogenesis and/or abiotic reactions from ancient organic compounds (possibly through inorganic intermediates such as graphite) rather than at high temperature abiotic or thermogenic processes.

6. CONCLUSIONS

Our observations suggest that there is a lithological and microbiological control on the abundance and isotopic composition of CH₄ in deep bedrock environments. Differences are related to the availability of carbon and hydrogen sources as well as processes behind the incorporation of hydrogen and carbon via abiotic and biotic pathways into hydrocarbon molecules. Supported by the whole data set available from the Fennoscandian Shield, which shows that CH₄ is much more abundant in metasedimentary rocks than in magmatic rocks and exceptionally high if graphitic rocks are around, the carbon source for CH₄ formation is suggested to be mainly organic in origin. Rather than being thermogenic relic, crustal CH₄ within the Fennoscandian Shield is more likely produced at low temperatures from ancient organic compounds by microbial methanogenesis or abiotically through inorganic intermediates such as graphite. These crustal gases are characterized by the lack of major amounts of C₂+ hydrocarbons and ¹³C rich CH₄. Microbiological together with isotope geochemical evidence suggest that microbial methanogenesis and thus microbial CH₄ is more common at depths shallower than 1.5 km. Minor amounts of CH₄, especially in magmatic rock settings and greater depths, has likely formed at high temperature abiotic synthesis which has also produced higher proportions of C₂+ compounds, but resulted in overall lower potential of hydrocarbon generation, and thus lower concentrations of hydrocarbons.

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Figure captions

Fig. 1. A simplified lithological map of the Fennoscandian Shield in Sweden and Finland showing the sites investigated for their isotopic composition of CH₄ in this study and Heikkinen (1972), Hyypä (1981), Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999) and Pitkänen and Partamies (2007). Detailed lithologies are given for the Pyhäsalmi mine and Outokumpu Deep Drill Hole sites: MV = mafic volcanite, T = tonalite, FV = felsic volcanite, MS = mica schist, BS = black schist, O = ophiolitic rocks, GR = granodiorite. Basemap redrawn after Koistinen et al. (2001).

Fig. 2. Genetic classification of the Outokumpu Deep Drill Hole and Pyhäsalmi mine CH₄ based on the H and C isotopic composition. Fields are according to Etiope et al. (2013), and are based on traditional classification of microbial and thermogenic gas (e.g. Schoell 1988) and additional data from various geological environments. The abiotic field is based on data from volcanic-hydrothermal environments (V), serpentized systems (S) and previous data from Precambrian shields (P) (Etiope et al. 2013 and references therein). Within the thermogenic field “O” refers to CH₄ occurring with oil and “D” refers to dry gas. Isotopic composition of CH₄ in the atmosphere (Mischler et al., 2009) is marked with X. For Outokumpu the samples are coded according the sampling technique: small circles = pumped, large circles = PDS and PAVE, and + = tube sampling. Pyhäsalmi samples = diamonds.

Fig. 3. Plot of carbon isotope compositions of methane, ethane and propane versus carbon number. Most of the samples from Outokumpu show relative depletion of ¹³C in C₂H₆ compared to CH₄ and few samples where isotopic composition of C₃H₈ was determined further reveal a V-shaped pattern. In contrast, two samples from Pyhäsalmi (R-2247) display increase in ¹³C with increasing chain length.

Fig. 4. Carbon isotope compositions of different carbon containing phases along the Outokumpu Deep Drill Hole. Major zones of groundwater flow are shown with white and gray arrows which indicate flow into the bedrock and into the drill hole, respectively (Ahonen et al., 2011; Kietäväinen et al., 2013). Isotopic composition of graphite is from Taran et al. (2011).

Fig. 5. a) CH_4/N_2 ratio and b) N_2/Ar ratio versus depth at Outokumpu and $\delta^{13}\text{C}_{\text{CH}_4}$ versus c) CH_4/N_2 and d) N_2/Ar at Outokumpu and Pyhäsalmi. All ratios have been corrected for air-contamination by assuming that the concentration of oxygen in indigenous fracture fluids is zero (Kietäväinen et al. 2014). Symbols as in Fig. 2. In a) and b) different water types described by Kietäväinen et al. (2013) on the basis of water stable isotopes and dissolved solids, are indicated with roman numerals and appear to correspond with different gas types. Fluctuation in the relative gas compositions during pumping likely reflects bubble formation (differences in solubility) and/or heterogeneous gas source. In c) and d) changes in the x-y space may occur due to oxidation (increase in $\delta^{13}\text{C}_{\text{CH}_4}$ and decrease in CH_4/N_2 ratio), methanogenesis (decrease in $\delta^{13}\text{C}_{\text{CH}_4}$ and increase in CH_4/N_2 ratio), diffusion (decrease in $\delta^{13}\text{C}_{\text{CH}_4}$, decrease in CH_4/N_2 and increase in the N_2/Ar ratio in the diffused gas), and mixing (linear change in the case of two component mixing). Although few samples (1820 m pumped, Pyhäsalmi R-2227) may have been affected by oxidation, most of the variation can be explained by mixing between gases emanating from different fracture zones.

Fig. 6. Hydrogen isotope concordance diagrams for the system $\text{CH}_4\text{-H}_2\text{O-H}_2$, based on equations for a) $\text{CH}_4\text{-H}_2$ and $\text{H}_2\text{O-H}_2$ and b) $\text{CH}_4\text{-H}_2\text{O}$ and $\text{H}_2\text{-H}_2\text{O}$ isotope equilibrium from Horibe and Craig (1995). Samples from the Outokumpu Deep Drill Hole (circles) and Pyhäsalmi mine drill hole R-2247 (diamonds) show equilibration temperatures below 50°C and 100°C , respectively.

Fig. 7. Isotopic fractionation of hydrogen between H_2O and CH_4 . Equilibrium fractionation (Horibe and Craig 1995) is shown as broken lines for three different temperatures relevant for *in situ* conditions at the Outokumpu Deep Drill Hole and Pyhäsalmi mine. Characteristic fractionation related to microbial CO_2 reduction (C) and acetate fermentation (A) were calculated according to Whiticar (1999) with a maximum isotope offset for the acetate fermentation of -370‰ (lines) and Sugimoto and Wada (1995) (dotted lines). Symbols as in Fig. 2.

Fig. 8. a) Carbon and b) oxygen isotope compositions of calcites along the Outokumpu Deep Drill Hole. Isotopic equilibrium at ambient temperatures, indicated with a thick line and gray shading, was calculated according to isotope fractionation equations given by Salomons and Mook (1986) (according to Clark and Fritz, 1997) for the calcite- HCO_3^- ^{13}C exchange reaction and by O'Neil et al. (1969) for

the ^{18}O exchange between calcite and water. No DIC isotope data is available between 1000 and 1600 m depth. Error bars are smaller than the size of the symbols.

Fig. 9. The $\text{CH}_4/\text{C}_{2+}$ ratio vs. carbon isotope composition of CH_4 for the Fennoscandian Shield samples. Pressurised samples from the Outokumpu Deep Drill Hole (DDH) are highlighted with thicker rims. SCR refers to sediment covered ridges (Tassi et al., 2012 and references therein) and within the thermogenic field “II” and “III” refer to type II (oil-prone/marine-sapropelic) and type III (gas-prone/terrestrial) kerogen, respectively. The suggested field for abiotic CH_4 (shaded) includes gases from the Zambales ophiolite (ZO) and mid-ocean ridges (MOR) (Horita and Berndt, 1999 and references therein), and artificial CH_4 from bit-metamorphism (Faber et al., 1999). However, CH_4 as light as -50‰ VPDB from Precambrian Shields has in previous studies been classified abiotic (cf. Fig. 2 and Sherwood Lollar et al., 1993b). Mixing may explain the scatter of data points between the different blocks, and the isotopic compositions are also subject to fractionation due to oxidation and isolation/substrate limitation. Data from this study, Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999) and Pitkänen and Partamies (2007). Diagram modified after Whiticar (1999).

Fig. 10. Carbon isotopic systematics of CH_4 with depth in the Fennoscandian Shield. Data from this study, Heikkinen (1972), Hyypä (1981), Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999), and Pitkänen and Partamies (2007). Pressurised samples from the Outokumpu Deep Drill Hole (DDH) are highlighted with thicker rims. Isotopic composition of CH_4 in air is from Mischler et al. (2009). The $\delta^{13}\text{C}_{\text{CH}_4}$ values below -40‰ VPDB are exclusively found in the upper 1 km depth while values heavier than -20‰ appear to be more common at depths greater than 1.5 km.

Fig. 11. $\text{CH}_4/\text{C}_{2+}$ with depth in the Fennoscandian Shield. Data from this study, Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999) and Pitkänen and Partamies (2007). Pressurised samples from the Outokumpu Deep Drill Hole (DDH) are highlighted with thicker rims. The ratio varies more from site to site than showing shield scale dependence on depth.

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Table 1.
Fluid sampling campaigns in the Outokumpu Deep Drill Hole in 2010-2012.

Date	Method	Depth (m)	Total water volume retrieved (m ³)
27.5.-20.9. 2010	Pumping, one packer at 1190 m depth	2260	6.9
21.9.-9.11. 2010	Pumping between packers at 478 m and 502 m depths	500	9.8
15.-19.5. 2011	Tube sampling	0-2450	0.154
8.-17.6. & 14.7.- 2.8. 2011	Direct pumping	2300	3.2
3.-18.8. 2011	Direct pumping	1820	1.0
14.-19.8. 2011	Positive displacement sampler (PDS)	500, 970, 1470, 1820, 2350, 2480	0.0048
5.9.-6.10. 2011	Direct pumping	970	3.8
10.-13.10.2011	Tube sampling	0-1050	0.066
5.5.-18.6. 2012	Pumping between packers at 170 m and 190 m depths & PAVE	180	22.5

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Table 2.
Isotopic compositions of methane, ethane, propane, hydrogen, water and dissolved inorganic carbon (DIC) in the Outokumpu Deep Drill Hole and Pyhäsalmi mine, Finland.

Sample	Sampling date	Method ^c	Depth m	CH ₄ δ ¹³ C ‰ VPDB	CH ₄ δ ² H ‰ VSMOW	C ₂ H ₆ δ ¹³ C ‰ VPDB	C ₂ H ₆ δ ² H ‰ VSMOW	C ₃ H ₈ δ ¹³ C ‰ VPDB	H ₂ δ ² H ‰ VSMOW	H ₂ O ^d δ ² H ‰ VSMOW	H ₂ O ^d δ ¹⁸ O ‰ VSMOW	DIC δ ¹³ C ‰ VPDB	DIC ^e mmol l ⁻¹
Outokumpu:													
7 ^a	8/2008	TSI	700	-31.2	-283					-82.0			
9 ^a	8/2008	TSI	900	-29.9	-283					-80.9			
12 ^a	8/2008	TSI	1200	-26.4	-276					-78.0			
14 ^a	8/2008	TSI	1400	-24.3	-279					-68.2			
16 ^a	8/2008	TSI	1600	-24.4	-288					-65.4			
18 ^a	8/2008	TSI	1800	-24.7	-287					-69.3			
20 ^a	8/2008	TSI	2000	-24.5	-281					-75.5			
Oku Pump 970A ^b	08-09-2009	PI	970	-34.3	-277	-48.2	-240	BAL		-87.5		-24.8	
Oku Pump 970B ^b	08-09-2009	PI	970	-34.0	-277	-48.3	-241	BAL		-87.5		-24.1	
OKU2260-G1	20-06-2010	PI	2260	-27.6	-297	-45.3	BAL	-36.2	-727	-70.7	-10.91		
OKU2260-G3	20-06-2010	PI	2260	-28.7	-297	-45.1	BAL	-39.5	-771	-70.7	-10.91		0.21
OKU2260-G7	28-07-2010	PI	2260	-25.6	-295	-49.6	-239			-69.2	-10.95	-0.8	0.26
OKU2260-G10	28-07-2010	PI	2260	-25.3	-297	-48.6	-235			-69.2	-10.95		
OKU500-G3	30-09-2010	PI	500	-34.0	-292	-43.4	BAL	-35.2	BAL	-82.8	-13.06		0.18
OKU500-G4	30-09-2010	PI	500	-32.8	-291	-49.2	-249			-82.8	-13.06		
OKU500-G8	01-10-2010	PB	500	-34.6	-294	-43.8	BAL	-35.8	-798	-82.9	-13.09		0.08
OKU500-G12	13-10-2010	PB	500	-33.5	-294	-49.7	-247			-82.7	-13.07	-16.1	0.09
OK-5	16-05-2011	TSI	400	-31.0	-273	-31.2	-227			-83.1	-12.85		0.11
OK-6	16-05-2011	TSI	500	-34.1	-279	-27.9	-235			-83.0	-12.89		0.12
OK-7	16-05-2011	TSI	600	-34.8	-280	-27.7	-228			-82.7	-12.93		0.20
OK-8	16-05-2011	TSI	700	-30.6	-282	-27.1	-232			-82.6	-12.96		0.13
OK-9	16-05-2011	TSI	800	-32.9	-287	-28.1	-244			-82.5	-12.97		0.12
OK-11	17-05-2011	TSI	900	-33.6	-283	-29.5	-238			-82.8	-12.92		0.15
OK-12	17-05-2011	TSI	1100	-32.0	-290	-28.3	-246			-82.8	-12.93		0.09
OK-13	17-05-2011	TSI	1200	-33.4	-286	-29.3	-263			-82.9	-12.79		0.12

OK-14	2011 17-05-2011	TSI	1300	-32.3	-282	-28.7	-270			-82.3	-12.70		0.12
OK-15	2011 17-05-2011	TSI	1400	-33.7	-280	-28.2	-256			-79.7	-12.15		0.14
OK-16	2011 17-05-2011	TSI	1500	-30.9	-279	-25.7	-203			-73.1	-11.23		0.17
OK-17	2011 17-05-2011	TSI	1600	-28.3	-278	-23.2	-243			-68.9	-10.86		0.09
OK-18	2011 18-05-2011	TSI	1700	-26.6	-282	BAL	-225			-60.5	-10.48		0.20
OK-19	2011 18-05-2011	TSI	1800	-26.5	-291	BAL	-239			-58.4	-10.39		0.16
OK-20	2011 18-05-2011	TSI	1900	-25.7	-289	BAL	-233			-56.6	-10.46		0.19
OK-21	2011 18-05-2011	TSI	2000	-25.5	-293	BAL	-276			-59.6	-10.48		0.17
OK-22	2011 18-05-2011	TSI	2100	-30.2	-292	BAL	-226			-61.9	-10.59		0.11
OK-23	2011 18-05-2011	TSI	2200	-29.7	-288	BAL	-223			-63.9	-10.63		0.17
OK-24	2011 18-05-2011	TSI	2300	-30.7	-283	BAL	-225			-65.3	-10.81		0.14
OK-25	2011 19-05-2011	TSI	2400	-28.5	-289	BAL	-251			-70.0	-11.02		0.19
Sample	Sampling date	Method ^c	Depth m	CH ₄ δ ¹³ C ‰ VPDB	CH ₄ δ ² H ‰ VSMOW	C ₂ H ₆ δ ¹³ C ‰ VPDB	C ₂ H ₆ δ ² H ‰ VSMOW	C ₃ H ₈ δ ¹³ C ‰ VPDB	H ₂ δ ² H ‰ VSMOW	H ₂ O ^d δ ² H ‰ VSMOW	H ₂ O ^d δ ¹⁸ O ‰ VSMOW	DIC δ ¹³ C ‰ VPDB	DIC ^e mmol l ⁻¹
OKU2300-G1	2011 19-07-2011	PB	2300	-19.2	-293	-35.4	-265			-65.4	-10.56		0.18
OKU1820-G1	2011 17-08-2011	PB	1820	-18.7	-286	-33.3	-254			-56.0	-10.47		0.20
OUTO-500 (6)	2011 28-08-2011	PDS	500	-25.1	-237	-40.7	-265			-82.9	-13.11		0.13
OUTO-970 (2)	2011 25-08-2011	PDS	970	-38.1	-230	-41.8	-277			-82.8	-12.94		0.17
OUTO-1470 (8)	2011 29-08-2011	PDS	1470	-36.4	-136	-45.8	-215			-70.8	-10.84		0.15
OUTO-1820 (4)	2011 27-08-2011	PDS	1820	-34.1	-269	-38.3	-268			-56.6	-10.59		0.20
OUTO-2350 (7)	2011 29-08-2011	PDS	2350	-15.9	-404	-42.4	BAL			-69.9	-11.06		0.21
OUTO-2480 (5)	2011 27-08-2011	PDS	2480	-13.2	-369	-22.7	BAL			-66.0	-11.30		0.17
OU-1	2011 11-10-2011	TSI	25							-84.8	-12.00	-14.3	0.26
OU-3A	2011 12-10-2011	TSI	200	-31.8	-269	-43.4	-242			-86.5	-12.38	-17.5	0.20
OU-4A	2011 12-10-2011	TSI	300	-29.5	-281	-43.4	-234			-85.4	-12.69	-17.9	0.15
OU-5A	2011 12-10-2011	TSI	400	-29.2	-237	-44.5	-249			-83.5	-12.95	-17.9	0.17

OU-6A	12-10-2011	TSI	500	-31.7	-291	-45.8	-218	-82.8	-13.05	-16.7	0.17
OU-7A	12-10-2011	TSI	600	-33.1	-242	-31.6	-221	-82.6	-12.98	-18.1	0.19
OU-8A	13-10-2011	TSI	700	-36.9	-266	-43.6	-223	-83.0	-13.11	-16.2	0.18
OU-9A	13-10-2011	TSI	800	-27.9	-289	-44.9	-238	-83.1	-13.06	-16.2	0.17
OU-10A	13-10-2011	TSI	900	-29.4	-277	-46.0	-230	-82.8	-13.01	-15.7	0.18
OU-11A	13-10-2011	TSI	1000	-34.0	-247	-45.4	-234	-82.6	-13.11	-14.7	0.15
OKU180-G1	05-05-2012	PB	180	-37.3	-276	-45.8	-182	-87.2	-12.54		
OKU180-G2	08-05-2012	PB	180	-36.1	-280	-45.4	-163	-87.0	-12.68		
OKU180-G3	14-05-2012	PB	180	-36.5	-284	-45.1	-194	-85.7	-12.79		0.007
OKU180-G6	05-06-2012	PB	180	-36.5	-263	-45.1	-161	-88.6	-12.57		0.21
OKU180-G7	13-06-2012	PB	180	-39.9	-281	-45.5	-170	-88.4	-12.61		
OKU180/25	18-06-2012	PAVE	180	-27.5	-263	-43.1	-157	-88.8	-12.55		
OKU180/27	18-06-2012	PAVE	180	-38.2	-246	-45.0	-153	-88.8	-12.55		
Pyhäsalmi:											
PYS-1B/R2247	11-06-2014	FFI	2400	-33.2	-259	-23.2	BAL	-680	-70.2	-12.27	0.003
PYS-1C/R2247	11-06-2014	FFI	2400	-33.3	-256	-23.2	BAL	-736	-70.2	-12.27	
PYS-2B/R2227	11-06-2014	FFI	1910	-27.5	-186			-91.2	-13.70		0.0005

^a Data from Nyysönen et al. 2014

^b Data from Toppi 2010

^c Sampling methods: TSI = tube sampling/injection, PI = Pumping/injection, PB = pumping/bucket, PDS = positive displacement sampler, PAVE = pressurised sampling device, FFI= from free flowing fluid/injection.

^d Data from Nyysönen et al. 2014, Toppi 2010, Kietäväinen et al. 2013, Miettinen et al. 2015 and this study.

^e The concentration of dissolved inorganic carbon was modelled based on geochemical data with PHREEQC software (USGS, 2014)

BAL = below analytical limit

Table 3.
Carbon and oxygen isotopic compositions of fracture/vein calcites from the Outokumpu Deep Drill Hole.

Sample ID	Depth m	Calcite type and position	Orientation ^a	$\delta^{13}\text{C}$ ‰ VPDB	$\delta^{18}\text{O}$ ‰ VPDB
47	100.90	Platy, open fracture	V	-16.10	-9.7
48	124.80	Massive	?	-8.71	-12.9
50	143.51	Platy, blocky	H	-11.82	-12.8
1	160.80	Blocky, euhedral	V	-10.85	-12.7
2	160.80*	Blocky, euhedral	V	-11.42	-12.4
3	231.80	Platy, flaky, surface 1	V	-10.40	-13.4
4	231.80	Platy, flaky, surface 2	V	-4.10	-13.0
52	263.95	Blocky, open fracture	H	-15.00	-18.4
5	490.70	Thin film	V	-3.63	-13.4
6	490.70*	Thin film	V	-3.43	-13.2
7	510.00	Platy, blocky, coarse	H	-12.35	-18.7
8	510.00*	Platy, blocky, coarse	H	-11.56	-17.3
9	510.00	Flaky, film	V	-5.88	-9.9
54	523.15	Platy, coarse	O	-19.64	-18.2
10	604.85	Powdery	V	-11.97	-9.7
55	716.35	Thin film	V	-13.68	-11.1
56	751.80	Thin film	O	-10.71	-13.0
57	751.80	Massive, upper	O	-9.77	-13.0
58	858.50	Blocky	V	-11.56	-14.2
59	858.50	Massive	V	-9.98	-18.1
11	883.60	Box shaped, subhedral	O	-10.70	-15.4
11B	883.60	Box shaped, euhedral	O	-10.58	-15.7
12	883.60	Platy, blocky, vein	O	-10.38	-17.3
13	885.75	Platy, bent, lower	V	-13.93	-18.5
14	885.75	Massive, upper	V	-10.84	-17.1
15	961.25	Massive, very hard, upper	V	-9.36	-13.2
16	961.25	Massive, very hard, central	V	-10.81	-14.4
17	961.25	Massive, lower	V	-10.65	-13.1
18	961.25	Massive, soft	H	-8.24	-14.4
60	996.20	Massive	O	-14.78	-14.8
19	1001.90	Platy, open fracture	V	-12.73	-14.7
20	1001.90*	Platy	V	-8.70	-13.0
21	1018.60	Powdery	V	-15.49	-15.5
22	1195.70	Powdery	V	-13.40	-14.1
23	1227.20	Box shaped, subhedral	V	-13.14	-15.5
24	1227.20*	Box shaped, subhedral	V	-14.98	-17.4
25	1361.25	Box shaped, vein, central	H	-7.36	-15.2
26	1361.25*	Box shaped, vein, central	H	-7.36	-14.9
27	1361.25	Box shaped, vein, lower	H	-7.41	-14.3
28	1393.67	Needles, upper	O	-8.12	-16.8
29	1393.67	Powdery, lower	O	-8.08	-16.2
30	1393.67	Elongated, upper	O	-8.03	-16.3
31	1393.67	Elongated, upper-central	O	-8.08	-16.7
32	1393.67	Elongated, lower-central	O	-8.02	-16.5
33	1393.67	Elongated, lower-central	O	-8.14	-17.0
34	1396.48	Massive, soft, vein 1, upper	O	-5.83	-12.9
36	1396.48	Massive, vein 2, upper	O	-5.36	-12.7
37	1396.48	Massive, vein 2, lower	O	-5.54	-13.1
38	1442.95	Massive, thin vein	V	-8.78	-13.1
39	1442.95	Box shaped, vein, upper	V	-8.78	-14.0

40	1442.95	Box shaped, blocky, vein, central	V	-8.50	-16.3
41	1442.95	Box shaped, vein, lower	V	-8.50	-14.3
42	1450.75	Massive, vein	V	-7.81	-16.0
43	1450.75	Massive, vein, lower	V	-8.69	-15.9
44	1450.75	Massive, vein, central	V	-8.82	-15.9
45	1499.35	Powdery	V	-6.09	-14.6
46	1499.85	Blocky, vein	H	-5.68	-13.3

^a = V: vertical, H: horizontal, O: oblique

* = duplicate sample