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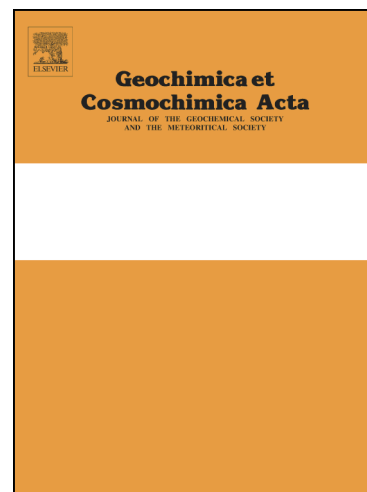
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1 **Abiotic and biotic controls on methane formation down to 2.5 km depth within the**
2 **Precambrian Fennoscandian Shield**

3

4

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32 **Abstract**

33

34 Despite a geological history characterized by high temperature and pressure processes and organic
35 carbon deprived crystalline bedrock, large amounts of hydrocarbons are found in deep groundwaters
36 within Precambrian continental shields. In many sites, methane comprises more than 80% of the
37 dissolved gas phase reaching concentrations of tens of mmol l^{-1} . In this study, we used isotopic
38 methods to study the carbon isotope systematics and sources of crustal methane within the
39 Fennoscandian Shield. The main study sites were the Outokumpu Deep Drill Hole and the Pyhäsalmi
40 mine in Finland, both of which allow groundwater sampling down to 2.5 km depth and have been
41 previously studied for their groundwater chemistry and microbiology. We show that the differences in
42 the amount and isotopic composition of methane are related to the availability of carbon sources as well
43 as processes behind the incorporation of hydrogen and carbon via abiotic and biotic pathways into
44 hydrocarbon molecules. Supported by previously reported occurrences and isotopic data of deep
45 groundwater methane in lithologically different locations in Finland and Sweden, we show that
46 methane formation is controlled by microbial methanogenesis and abiotic reactions, as well as lithology
47 with the metasedimentary environments being the most favourable for methane occurrence. Rather than
48 a thermogenic relic, crustal methane within the Fennoscandian Shield is more likely the result of low
49 temperature formation from ancient organic compounds or their inorganic intermediates such as
50 graphite. Such crustal gases are characterized by the lack of major amounts of C_2+ hydrocarbons and
51 ^{13}C rich methane. Further, microbiological and isotopic geochemical evidence suggest that microbial
52 methane is more common at depths shallower than 1.5 km.

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61 **Keywords:** Methane, ethane, hydrogen, carbon isotopes, calcite, graphite, Fennoscandian Shield,

62 Outokumpu, Pyhäsalmi

63 1. INTRODUCTION

64

65 Methane (CH₄) is a key component in the interface of geological and biological i.e. abiotic and biotic
66 world. Deep saline groundwaters within Precambrian continental shields are among the most peculiar
67 environments where CH₄ has been found, sometimes at vast amounts exceeding 80% of the gas phase
68 (e.g. Sherwood et al., 1988; Ward et al., 2004; Pitkänen and Partamies, 2007; Stotler et al., 2010). The
69 information on processes generating CH₄ and their relative abundance in crystalline bedrock
70 environment is important in evaluating the energetic limitations of microbial life in deep dark biosphere
71 as well as microbe-water-rock interactions. These processes are important in understanding the
72 evolution of life on Earth as well as potential for life on other planets. More practical applications
73 include assessment of groundwater quality, safety of geological disposal of nuclear waste, and deep
74 mining as water-rock interaction and microbial attainment may have an impact on the environment by
75 changing the concentrations or mobility of potentially hazardous or corrosive compounds.

76

77 In deep subsurface environments CH₄ is known to be formed via three main mechanisms: 1)
78 thermogenically by breakdown of organic matter, 2) microbially, and 3) abiotically from reactions of
79 inorganic compounds such as CO₂ and H₂ (Kotelnikova, 2002; Etiope and Sherwood Lollar, 2013;
80 Sephton and Hazen, 2013; Kietäväinen and Purkamo, 2015). Microbial methanogenic processes are
81 commonly divided into autotrophic and heterotrophic pathways which utilize inorganic and organic
82 carbon sources, respectively (Kotelnikova, 2002; Kietäväinen and Purkamo, 2015). The most
83 commonly examined abiotic formation mechanism is the Fischer-Tropsch type (FTT) synthesis, i.e. the
84 catalytic formation of CH₄ from CO and H₂ at high temperature, and its proposed natural analogues
85 (e.g. Anderson, 1984; Horita and Berndt, 1999; Sherwood Lollar et al., 2002; Taran et al., 2007;
86 Jacquemin et al., 2010; Zhang et al., 2013). Other abiotic reactions possibly capable of producing
87 hydrocarbons include thermal decomposition of carbonate minerals, abiotic synthesis from carbon-
88 bearing fluids and sulphide minerals through organosulphur intermediates (e.g. thiols), and clay
89 catalysed synthesis (McCollom, 2013). In deep drill holes, such as the 6.6 km deep Gravberg-1 (Siljan
90 Ring) in Sweden and 9 km deep KTB (Kontinentales Tiefbohrprogramm) in Germany, artificial CH₄
91 formed in reactions promoted by high temperature at the drill bit - rock interface (bit-metamorphism)
92 has also been observed (Jeffrey and Kaplan, 1988; Faber et al., 1999).

93

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

108
109 On one hand this is because the isotopic composition of a product gas, whether abiotic or biotic, is
110 heavily dependent on the isotopic composition of the reactants/substrates (e.g. Schoell, 1983;
111 Kotelnikova, 2002). On the other hand, the isotopic compositions are dependent on such factors as
112 openness of the system, equilibration, time scale, and substrate limitation or excess (Burke, 1993;
113 Whiticar, 1999; Valentine et al., 2004; Kelley et al., 2012; Reeves et al., 2012; Suda et al., 2014).
114 However, these conditions are often poorly known. Therefore it is important to study the relevant
115 chemical components as well as their isotopic compositions in order to get a view of gas generating
116 processes in a given system. In addition, the information on lithology, microbiology and hydrogeology
117 is essential in judging between the different processes.

118
119 We selected two lithologically different sites within the Precambrian crystalline bedrock in Finland
120 within the Fennoscandian Shield for a detailed study of hydrocarbons. In the Outokumpu Deep Drill
121 Hole, characterized by metasediments and ophiolite-derived serpentinites, CH₄ typically comprises
122 over 70 vol-% of the dissolved gas phase with concentrations as high as 32 mmol l⁻¹ (Kietäväinen et al.,
123 2013). Methane producing as well as consuming microorganisms have been found from the drill hole
124 and fracture waters (Itävaara et al., 2011; Purkamo et al., 2015a, 2015b). Residence times of

125 groundwater up to 58 Ma (Kietäväinen et al., 2014) make this one of the oldest known ecosystems on
126 Earth. In addition to dissolved carbon and carbonates, possible sources of carbon in the bedrock include
127 graphite-rich black schist. Serpentinites provide a potential source of H₂ needed in both abiotic CH₄
128 synthesis and microbial methanogenesis (Devirts et al., 1993; McCollom and Bach, 2009; Neubeck et
129 al., 2011; Schrenk et al., 2013), and radiolytic H₂ (Vovk 1987; Lin et al., 2005a, 2005b) may be
130 present. In the Pyhäsalmi mine, ca. 180 km northwest from Outokumpu, the dominant lithologies are
131 felsic to mafic metavolcanic rocks and granite. At Pyhäsalmi, CH₄ is scarcer, with a maximum
132 concentration no higher than 0.55 mmol l⁻¹, but H₂ is abundant (Miettinen et al., 2015). In contrast to
133 Outokumpu, volcanic rocks of Pyhäsalmi lack evident carbon source minerals. Yet, there are
134 indications of CH₄ producing archaea living in the formation fluids of Pyhäsalmi at least down to 2.4
135 km depth (Miettinen et al., 2015).

136

137 In this study we use the isotopic compositions of hydrogen, carbon and oxygen in CH₄, ethane (C₂H₆),
138 propane (C₃H₈), DIC, calcite, graphite, molecular hydrogen (H₂) and water, together with information
139 on gas compositions determined from the Outokumpu Deep Drill Hole and Pyhäsalmi mine fluid
140 samples to determine CH₄ generating processes down to a depth of 2.5 km. To ascertain the
141 representativeness of the samples, different sampling methods are also compared. A regional scale is
142 brought up by comparing the results of this study to previously reported isotopic compositions of CH₄
143 in deep groundwaters in Finland (Heikkinen, 1972; Hyypä, 1981; Sherwood Lollar et al., 1993a,
144 1993b; Haveman et al., 1999, Pitkänen and Partamies, 2007) and Sweden (Jeffrey and Kaplan, 1988).
145 The aim is to reveal possible systematics of CH₄ occurrence and isotopic composition in relation to
146 depth, as well as lithological, physicochemical and microbiological factors in order to gain better
147 understanding on the deep carbon cycle.

148

149 2. STUDY SITES

150

151 The Outokumpu Deep Drill Hole is located in eastern Finland (62°43'02.63"N, 29°03'55.01"E) within
152 the Fennoscandian Shield (Fig. 1). It reaches a maximum depth of 2516 m, which makes it the deepest
153 scientific drill hole in Finland and one of the deepest within the whole Fennoscandian Shield. The 1.9
154 billion year old bedrock at the study site is mainly comprised of amphibolite facies (550 – 675°C at 3 –
155 5 kbar) metasediments, i.e. mica schist and biotite gneiss, which are interlayered with ophiolitic rocks

156 of the Outokumpu assemblage and dissected by slightly younger granitoids (Fig. 1, Claesson et al.,
157 1993; Säntti et al., 2006; Peltonen et al., 2008; Lahtinen et al., 2010; Västi, 2011).

158

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

175

176 Saline water with the concentration of total dissolved solids (TDS) as high as 70 g l^{-1} enters the
177 Outokumpu Deep Drill Hole along fracture zones which are separated from each other by tens to
178 hundreds of meters of impermeable rock (Ahonen et al., 2011; Kietäväinen et al., 2013). A major
179 divide in groundwater composition is seen at around 1300 m depth where the salinity suddenly
180 increases, water and strontium becomes more enriched in the heavier isotopes and the concentration of
181 CH_4 decreases while the proportion of H_2 begins to increase (Kietäväinen et al., 2013). Likewise there
182 is a change in the microbial community structure which seems to closely mirror the change in
183 groundwater chemistry, and lithology (Itävaara et al., 2011; Kietäväinen et al., 2013; Nyysönen et al.,
184 2014; Purkamo et al., 2013, 2015a, 2015b). The Outokumpu Deep Drill Hole groundwater is isolated
185 from the modern meteoric water cycle and both water stable isotopes and noble gases indicate
186 residence times of tens of millions of years (Kietäväinen et al., 2013, 2014). Any contribution of mantle

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

189
190 In addition to an extensive sampling campaign at Outokumpu, samples were also taken from the
191 Pyhäsalmi mine located ca. 180 km northeast from Outokumpu ($63^{\circ}39'\text{N}$, $26^{\circ}03'\text{E}$) along the boundary
192 between the Proterozoic and Archaean parts of the Fennoscandian Shield (Fig. 1). The Pyhäsalmi mine
193 is in a volcanogenic massive sulphide (VMS) type Cu-Zn deposit and among the deepest metal mines
194 in Europe. The deepest hole (R-2247) drilled downwards from the 1430 m depth level of the mine
195 reach the depth of 2400 m below the surface (Fig. 1). Dominant rock types are 1.92 Ga old mafic to
196 felsic volcanites which have metamorphosed at amphibolite facies conditions similar to Outokumpu,
197 with minor occurrence of slightly younger granite (Kousa et al., 1994; Miettinen et al., 2015). Salinity
198 of groundwater increases with depth reaching the TDS concentration of 76 g l^{-1} at 2400 m (Miettinen et
199 al., 2015). Both acidic and basic waters in the shallow and deep parts of the mine, respectively, host
200 liveable microbial communities (Kay et al., 2014; Miettinen et al., 2015).

201

202 **3. MATERIAL AND METHODS**

203

204 Sampling for geochemical analysis, including the stable isotopic composition of water, has been
205 described in Kietäväinen et al. (2013), Purkamo et al. (2013), Rajala et al. (2015) and Miettinen et al.
206 (2015). The overall geochemical characterisation of the Outokumpu Deep Drill Hole and the Pyhäsalmi
207 mine groundwaters has been previously published in Kietäväinen et al. (2013) and Miettinen et al.
208 (2015), respectively. Isotopic compositions of graphite from Outokumpu are provided by Taran et al.
209 (2011). Here we focus on describing the sampling and isotopic analysis of gases and dissolved
210 inorganic carbon (DIC) as well as fracture carbonates.

211

212 **3.1 Fluid sampling**

213

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

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

223

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

236

237 The samples for DIC isotope analyses were taken from the Outokumpu Deep Drill Hole in 2010 and
238 2011. In 2010 DIC isotope samples from pumped fluid from 500 and 2260 m depths were collected
239 into LABCO Exetainer tubes (12 ml), which contained 0.15 ml of 85% phosphoric acid and were
240 flushed and filled with He (purity > 99,996%). During sampling 5 ml of He was removed and 8 ml of
241 sample water immediately injected into each tube. From the tube sampling in October 2011 the samples
242 were collected in evacuated glass bottles (60 ml), specially manufactured to fit the caps from
243 Vacutainer vials. The bottles were prepared by adding 3 ml of 85% phosphoric acid and a magnetic rod
244 and evacuating them on a vacuum line specially designed for extracting DIC from water samples. The
245 sample preparation was done at the Geological Survey of Finland (GTK) in Espoo. Samples for DIC
246 isotope analysis were injected into evacuated glass bottles through a 0.8/0.2 μm supor membrane filter
247 using a plastic syringe. Vials and tubes were stored upturned in dark and cool until analysed.

248

249 3.2 Sample selection and preparation for fracture mineral studies

250

251 In total, 58 rock samples along the Outokumpu deep drill core were selected between 100.90 and
252 2240.70 m depths below the surface. Samples represent both open and sealed fractures and thin veins.
253 Ordinary 30 μm thick polished thin sections were prepared for microscopy and microanalysis studies.
254 Loose fracture fillings were fixed with epoxy resin before cutting. In the case of extremely loose
255 fillings, thin sections were not possible to make and, instead, minerals were mounted on a carbon tape.
256 Calcites for isotopic analysis were carefully selected under a microscope and separated using a steel
257 blade. Where different calcite generations occurred, they were sampled separately. Fractures dissected
258 by the drill holes studied at Pyhäsalmi did not contain carbonate minerals (Miettinen et al., 2015).

259

260 3.3 Analysis

261

262 3.3.1 Dissolved gases

263 The gas composition was analysed by gas chromatography at Ramboll Analytics (Vantaa, Finland) or
264 Isotech Laboratories (Illinois, USA) (Kietäväinen et al., 2013; Miettinen et al., 2015). Within the whole
265 sample set (Table EA 1), relative uncertainties were generally better than 8% for hydrocarbons, 3% for
266 H_2 , 4% for O_2 and N_2 , 6% for CO_2 , and 10% for He and Ar.

267

268 The isotopic compositions of CH_4 , C_2H_6 and from few samples also C_3H_8 from Outokumpu were
269 determined at the Environmental Isotope Laboratory at the University of Waterloo (Ontario, Canada).
270 Samples from the Pyhäsalmi mine were analysed for their isotopic composition at Isotech Laboratories.
271 Following the separation by Trace Ultra Gas Chromatograph (Thermo Finnigan) the different
272 hydrocarbons were converted to CO_2 at 940°C and to H_2 at 1450°C and analysed with a Delta^{plus} XL
273 isotope ratio mass spectrometer (Thermo Finnigan MAT). The isotopic compositions are reported using
274 δ -notation per mill (‰) relative to VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard
275 Mean Ocean Water) standards for C and H, respectively:

276

$$277 \delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000 \quad (1)$$

278

279 where R is either $^{13}\text{C}/^{12}\text{C}$ or $^2\text{H}/^1\text{H}$.

280

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

284

285 3.3.2 Isotopic composition of dissolved inorganic carbon

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

298

299 3.3.3 Characterisation of fracture minerals

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

304

305 3.3.4 Stable isotopes of calcite

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

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

313

314 3.4 Computational methods

315

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

319

$$320 \quad SI = \log \frac{Q}{K} \quad (2)$$

321

322 where Q is the ion activity product and K is the thermodynamic reaction constant (Clark and Fritz,
323 1997). In equilibrium SI equals 0 while positive and negative SI values indicate oversaturation and
324 undersaturation (dissolution), respectively. *In situ* temperatures measured from the Outokumpu Deep
325 Drill Hole (Kukkonen et al., 2011) and on site at the Pyhäsalmi mine (Miettinen et al., 2015) were used
326 in all calculations. The hydrostatic pressure increase of about 100 bar km^{-1} was not taken into account
327 as 1 bar pressure is used by the PHREEQC by default. Increased pressure will increase the solubility of
328 calcite especially at low temperatures (Duan and Li, 2008) and may lead to slight overestimation of the
329 saturation indices presented here. Additionally, high ionic strength of saline waters causes uncertainty
330 in defining thermodynamic activity product (Q) of dissolved species. The field or on-line
331 measurements of pH and alkalinity were used when available, as the pH was observed to rapidly
332 decrease in contact with air apparently due to the dissolution of atmospheric CO_2 into these low
333 alkaline waters with poor buffering capacity.

334

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

336

$$337 \quad \alpha_{x-y} = \frac{1000 + \delta x}{1000 + \delta y} \quad (3)$$

338

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

341

342 $\ln\alpha_{x-y} = aT^{-2} + bT^{-1} + c$ (4)

343

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

345

346 $\Delta_{x-y} = \delta_x - \delta_y$ (5)

347

348 4. RESULTS

349

350 4.1 Gas composition

351

352 A compilation of gas data, including sampling depths and methods, collected from the Outokumpu
353 Deep Drill Hole and the Pyhäsalmi mine is given in the Electronic Annex (Table EA1). CH₄ and N₂ are
354 by far the most abundant dissolved gases at Outokumpu, while H₂ becomes dominant in the deepest
355 part of the drill hole. At Pyhäsalmi the gas phase is dominated by N₂ and He. The PDS samples from
356 500 and 2480 m depths and the sample PYS-2 from the Pyhäsalmi mine have suffered from severe air
357 contamination (O₂ > 5 vol-%), but some O₂ is present in virtually all samples. The pressurised samples
358 are relatively enriched in H₂ and He and depleted in CH₄ compared to samples obtained by pumping,
359 the tube sampler or from free flowing fluid in the mine. At Outokumpu CH₄/(C₂H₆ + C₃H₈) ratio varies
360 from 71 to 333 (Table EA1), such that a decrease is observed towards the surface. At Pyhäsalmi
361 CH₄/C₂+ ratios are typically < 10, with only one drill hole (R-2250) having a significantly higher ratio
362 of 164 (Table EA1). Ethene, propene and butene were below analytical detection (0.001 vol-%) in all
363 samples.

364

365 4.2 Isotopic composition of gases

366

367 The isotopic compositions of CH₄, C₂H₆, C₃H₈ and H₂ are given in Table 2. Variation in the isotopic
368 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‰
369 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 -
370 30‰ VPDB (Fig. 2). ¹³C depleted and ²H enriched CH₄ is unique for the depth of 1470 m at
371 Outokumpu and ¹³C enriched and ²H depleted CH₄ is only found below 2260 m depth. The minimum
372 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

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

375

376 Similarly to CH₄, the most ¹³C enriched C₂H₆ is found from the 2480 m depth at Outokumpu and deep
377 samples from the Pyhäsalmi mine. A fracture zone at 180 m depth has distinctive δ²H_{C₂H₆} values as
378 heavy as -152‰ VSMOW, while the other samples have δ²H_{C₂H₆} around -250‰ VSMOW (Table 2).
379 Isotopic data of C₃H₈ are only available for carbon from two depths from Outokumpu (500 and 2260
380 m) and only pumped fluids are represented. Nevertheless, the isotopic composition of carbon seems to
381 be systematically lighter from CH₄ to C₃H₈ and C₂H₆, except samples from tube sampling in May 2011
382 which, with no apparent reason, show anomalously ¹³C rich values of C₂H₆ (Table 2). This indicates a
383 δ¹³C vs. carbon number trend is V-shaped (Fig. 3) rather than normal (ascending) or inversed
384 (declining), i.e. neither of the two trends which have often been related to thermogenic and FTT type
385 abiotic hydrocarbons, respectively (e.g., Sherwood Lollar et al., 2002; Etiope and Sherwood Lollar,
386 2013; Zhang et al., 2013). Hydrocarbons at Pyhäsalmi seem to differ from this pattern as they show
387 enrichment of ¹³C in C₂H₆ over CH₄ (Fig. 3).

388

389 Molecular hydrogen is extremely depleted in deuterium with the measured isotope range from -798 to -
390 727‰ VSMOW at Outokumpu and from -736 to -680‰ VSMOW at Pyhäsalmi. While the addition of
391 HgCl₂ into one of the gas samples from Pyhäsalmi (PYS-1B) did not affected the C or H isotopic
392 composition of CH₄, the δ²H value of H₂ was 56‰ higher in the fixed sample compared to the
393 untreated sample taken at the same time (Table 2). This one control with eliminated biological activity
394 is clearly not enough for making generalised conclusions on the possible microbial processes during
395 sample storage. However, there was no difference in the concentration of H₂ between the comparative
396 samples which could indicate microbial production or consumption of H₂ (Table EA1).

397

398 **4.3 Dissolved inorganic carbon**

399

400 The modelled concentrations of DIC are very low (Table 2), with an average of 0.16 mmol l⁻¹ at
401 Outokumpu and only 2 μmol l⁻¹ at Pyhäsalmi. Governed by pH and Ca concentration, the main
402 constituent of DIC is HCO₃⁻ or CaCO_{3(aq)} above and below 1500 m, respectively. The isotopic

403 composition of DIC varies from -18.1 to -0.8‰ VPDB with a general increase in ^{13}C with depth (Table
404 2, Fig. 4).

405

406 **4.4 Fracture mineralogy**

407

408 At Outokumpu saturation indices (SIs) of calcites at the ambient temperature and 1 bar pressure
409 typically vary from 0.5 to 1.5 and only the two PDS samples from 1470 m depth show slightly negative
410 SI values (down to -0.12) which are indicative of possible dissolution of calcite. At Pyhäsalmi,
411 however, SI values for calcites are mostly negative as is also demonstrated by the absence of calcites
412 on the fracture surfaces. Except the few more coarse grained (mm sized) crystals found from around
413 500 m depth (Table 3), calcite occurs as fine, powdery layers, thin films or medium sized crystals on
414 fracture surfaces and veins at Outokumpu, and is typically accompanied by zeolite minerals and
415 chlorite. Pyrite and pyrrhotite are common accessory minerals. Eu- to subhedral, box shaped crystals of
416 calcite were most common but elongated crystals were also found (Table 3). Even though the modelled
417 values show oversaturation of calcite throughout the studied range of compositions and depth at
418 Outokumpu no calcite was found below 1500 m depth. Instead, the most common fracture filling
419 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;
420 $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4(\text{H}_2\text{O})$). Overall, fractures become scarce in the deeper part of the drill hole.

421

422 **4.5 Isotopic composition of calcites**

423

424 The isotope geochemistry of fracture filling and vein calcites from the Outokumpu Deep Drill Hole is
425 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 -
426 19.64 to -3.43‰ VPDB. Calcites associated with the Outokumpu assemblage rocks have a narrow
427 range of carbon compositions from -9 to -5‰ VPDB. The $\delta^{18}\text{O}$ values of these calcites are more
428 variable, although all veins/fractures containing chalcopyrite plot between -16 and -14‰ VPDB.

429

430 **5. DISCUSSION**

431

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

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

440

441 **5.1 Comparison of different fluid sampling methods**

442

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

452

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

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

468

469 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
470 different sampling techniques and further investigate post-genetic and post-sampling processes capable
471 of modifying the composition of the gas. The CH_4/N_2 and N_2/Ar ratios are likely governed by the
472 organic carbon composition and content of the source (e.g. Jenden et al., 1988), and may change due to
473 bubbling (solubility), mixing (e.g. Darrah et al., 2014) and, at very long time scales, also by the
474 accumulation of radiogenic Ar. However, as long as only advection is considered, no isotopic
475 fractionation should occur in these processes. Bubbling for example should change the gas composition
476 only along the y-axis in Fig. 5c and d due to preferential partitioning of the less soluble N_2 in the gas
477 phase, and consequential depletion in the remaining fluid. This means that samples taken during and
478 after a bubble burst will differ in their relative gas composition but, if bubbles originate from sources
479 with different isotope signature, may also express linear change in the isotope composition of CH_4 .
480 Diffusion will also preferentially remove N_2 but may also produce ^{13}C (and ^2H) depletion in the
481 diffusing gas while the residual gas will become isotopically heavy (e.g. Prinzhofer and Huc, 1995;
482 Schloemer and Krooss, 2004), although e.g. Fuex (1980) and Schoell (1983) have argued that diffusion
483 related isotope effects will be negligible and may only pertain non-steady state processes, if any, on
484 hydrocarbons. In any case, the overall isotope trend at Outokumpu which shows inverse correlation of
485 $\delta^2\text{H}_{\text{CH}_4}$ with $\delta^{13}\text{C}_{\text{CH}_4}$, does not support modification of isotope composition of CH_4 through diffusion.

486

487 When accompanied with decrease and increase of the $\delta^{13}\text{C}_{\text{CH}_4}$ value, respectively, the decrease and
488 increase in the CH_4/N_2 ratio can also be due to methanogenesis and oxidation of CH_4 , in which case no
489 change in the N_2/Ar ratio is expected. Oxidation seems to explain the difference between the results
490 obtained by pumping and PDS at 1820 m depth and difference in the isotopic composition of CH_4
491 between the drill holes R-2247 and R-2227 at Pyhäsalmi (Fig 5.c,d). However, the most ^{13}C rich CH_4
492 observed at Outokumpu (2480 m) cannot be explained by oxidation, most notably because of the high
493 $\text{CH}_4/\text{C}_{2+}$ value (Table EA1), and depletion in ^2H (Fig. 2).

494

495 **5.2 Hydrogen in the system $\text{H}_2\text{O}-\text{H}_2-\text{CH}_4$**

496

497 Incorporation of hydrogen into the CH₄ molecule can happen either from H₂O, organic matter or H₂.
498 Due to their lower mass and position in a CH₄ 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 CH₄ 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 H₂ 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 H₂O-H₂-CH₄ 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°C) the fractionation is best established
509 between H₂O and H₂ while higher uncertainties are related to the equilibration of hydrogen between
510 CH₄ and H₂ or H₂O (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, CH₄ seems to have formed at equilibrium controlled reactions *in situ* or to represent gas
513 component which has later equilibrated with H₂ and H₂O. 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, CH₄ is not in isotopic equilibrium with H₂O 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 H₂O-H₂-CH₄ is not well
519 constrained but some experimental data and approximations do exist. Using the equations for optimum
520 99% equilibration of ¹³C between CO₂ and CH₄ from Giggenbach (1982) and rate constants for H₂-H₂O
521 and H₂-CH₄ isotope exchange determined by Lécluse and Robert (1994), Suda et al. (2014) calculated
522 that at 50°C the isotopic equilibrium between H₂ and H₂O can be attained within 100 years while the
523 equilibration between H₂ and CH₄ would take 3000 years. The isotopic equilibration of hydrogen
524 between H₂O and CH₄ 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

527 around 1 Ma should be sufficient to equilibrate the hydrogen isotopic compositions in the system H₂O-
528 H₂ to reflect *in situ* temperatures; the time span of which is still clearly less than the estimated
529 residence times of groundwaters at Outokumpu between 4 and 58 Ma (Kietäväinen et al., 2014).

530 However, in the presence of H₂ utilizing microorganisms, the equilibration of hydrogen isotopes may
531 take place remarkably fast. In particular, sulphate reducers and methanogens, also found at Outokumpu
532 and Pyhäsalmi (Itävaara et al., 2011; Nyyssönen et al., 2014; Purkamo et al., 2013, 2015a, 2015b;
533 Miettinen et al., 2015), have been observed to equilibrate hydrogen isotopes between H₂O and H₂
534 within seconds in their metabolic processes (Romanek et al., 2003; Valentine et al., 2004).

535

536 Compared to CH₄, hydrogen isotopes of C₃H₈ can be even more readily exchanged with water and, at
537 long time scales, the isotopic exchange may be significant also for C₂H₆ (Reeves et al., 2012). Based on
538 the equilibrium fractionation determined by Wang et al. (2009) for H isotope exchange between H₂O
539 and C₂H₆, which is much less temperature dependent than fractionation between H₂O and CH₄, and not
540 as likely to be affected by microbial activity, δ²H values below -990‰ VSMOW would be expected for
541 C₂H₆ in equilibrium with H₂O at Outokumpu. Instead the δ²H<sub>C₂H₆ values are between -277‰ and -
542 153‰ VSMOW (Table 2). This suggest that, when observed, the isotopic equilibration of H in the
543 system H₂O-H₂-CH₄ is likely controlled by other factors than the long residence time, such as microbial
544 activity. Difference between the pressurised and non-pressurised methods may arise from technical
545 reasons, most notably the immediate separation of gas from water, which should prevent post-sampling
546 changes in the PDS samples.</sub>

547

548 Beyond the equilibration processes, hydrogen isotope fractionation between CH₄ and H₂O is also
549 dependent on the relative proportion of H derived from H₂O and other sources, and therefore should
550 differ between CO₂ reduction (H from H₂O) and acetate fermentation (H from organic matter and H₂O)
551 pathways (Fig. 7, Sugimoto and Wada 1995; Whiticar 1999). In the case of CH₄ formation from
552 graphite (e.g. 2C + 2H₂ = CH₄ + CO₂, or C + 2H₂O + 4Fe₃O₄ = 3Fe₂O₃ + CH₄; Burruss and Laughrey,
553 2010), the fractionation would likely be similar to CO₂ reduction as in both cases H₂O provides the
554 only hydrogen source. While most of the variation among the samples from Outokumpu and Pyhäsalmi
555 may be explained by the change in the relative proportion of CO₂ reduction and acetate fermentation,
556 values exceeding the suggested limits do occur.

557

558 Isotopic composition of CH₄ is also subject to change after the formation. Such secondary fractionation
559 typically leads to either enrichment or depletion of both C and H isotopes in the same direction
560 (Schoell, 1988). When accompanied with enrichment in ¹³C (Whiticar, 1999; Etiope et al., 2011), the
561 shift towards the less negative δ²H_{CH₄} values in Fig. 7 could be due to oxidation of CH₄. In Pyhäsalmi
562 the more ²H and ¹³C enriched CH₄ from the shallower and more recently made drill hole R-2227, which
563 contains significantly less CH₄ than the drill hole R-2247, might represent oxidised gas, possibly
564 affected by the drilling. However, at Outokumpu the isotopic composition of CH₄ at 1470 m depth does
565 not indicate such post-formational changes as the depletion of ²H is coupled with enrichment of ¹³C
566 (Fig. 2). Instead, distinct rock types surrounding the 1470 m depth, which include serpentinite and thick
567 layers of black schist, may provide an explanation for the different isotopic composition of CH₄. In the
568 case of deep sourced samples, the larger isotope offset towards the more negative δ²H_{CH₄} values may
569 be caused by the high partial pressure of H₂ (Burke 1993, Sugimoto and Wada 1995). The high α<sub>H₂O-
570 CH₄</sub> of up to 1.56 below 2300 m depth could also be indicative of abiotic CH₄ (Sherwood Lollar et al.,
571 2008), although high α_{H₂O-CH₄} values have also been reported for microbial CH₄ produced by the
572 hydrogenotrophic methanogen *Methanobacterium formicicum* (Balabane et al., 1987).

573

574 **5.3 Carbon in the system CH₄-DIC-calcite-graphite**

575

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

582

583 Previously the heaviest isotopic compositions of CH₄ have been related to gases with more than 5%
584 mantle helium (Etiope and Sherwood Lollar, 2013). However, at Outokumpu the extremely ¹³C-rich
585 CH₄ values found below 2300 m are associated with He which has an entirely radiogenic isotope
586 signature (Kietäväinen et al., 2014) and thus a mantle source for the more soluble CH₄ can be excluded.
587 Hence, the main sources of carbon include dissolved and crystalline carbonate carbon as well as
588 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

620 the enrichment of DIC with ^{13}C can occur due to microbial methanogenesis (Claypool et al. 1985), the
621 observed simultaneous increase in $\delta^{13}\text{C}_{\text{CH}_4}$, as most clearly observed at 500 and 2260 m depths (Fig. 4,
622 does not support such isotopic evolution. Furthermore, the values of $\alpha_{\text{DIC-CH}_4}$ (< 1.025) are not
623 consistent with microbial methanogenesis through the CO_2 reduction pathway (Valentine et al., 2004;
624 Sherwood Lollar et al., 2008). However, where aceticlastic methanogens dominate the $\Delta_{\text{DIC-CH}_4}$ is
625 expected to be lower, because the use of organic compounds would not directly affect the isotopic
626 composition of DIC, or abiotic reaction mechanisms may dominate. Unlike hydrogen isotopes in the
627 system $\text{H}_2\text{O-H}_2\text{-CH}_4$, equilibration of carbon is more unlikely due to sluggish kinetics (Sherwood
628 Lollar et al., 2008), and thus, even though DIC and CH_4 are far from isotopic equilibrium
629 ($1000\ln\alpha_{\text{CHCO}_3\text{-CH}_4} = 76.1\text{‰}$ at 25°C ; Clark and Fritz, 1997 after Bottinga, 1969 and Mook et al.,
630 1974) at Outokumpu, abiotic CH_4 formation from CO_2 is possible in the light of DIC isotopes.

631
632 Graphite rich black schist form another potential carbon source at Outokumpu. Compared to DIC,
633 isotopic fractionation of carbon between graphite and CH_4 is likely to be lower, as the reaction does not
634 take place through a dissolved phase. In Outokumpu, within the depth range where graphitic rocks are
635 abundant, the isotopic composition of CH_4 (Fig. 4) is very close to or only slightly depleted in ^{13}C
636 compared to graphite ($\delta^{13}\text{C} -27.4\text{‰} \dots -18.4\text{‰}$ VPDB; Taran et al., 2011). It has been experimentally
637 shown that fractionation is lower if the starting material is graphite compared to CH_4 formation from
638 for example gaseous components (Zhang et al., 2013). This is because CH_4 formation takes place only
639 at the mineral surface where carbon isotopes are randomly dispersed (Zhang et al., 2013). Thus, notable
640 fractionation of carbon isotopes between graphite and CH_4 is not expected.

641
642 The isotopic composition of CH_4 can also depend on the amount of substrates available. The closeness
643 of the system tends significantly decrease fractionation as in the case of near-complete conversion of
644 substrates into CH_4 the isotopic fractionation could follow the Rayleigh distillation trend eventually
645 leading to minimal fractionation (Bradley et al., 2009; Kelley et al., 2012; Tazaz et al., 2013; Suda et
646 al., 2014). Isotope fractionation may also decrease under unlimited supply of substrates. For example,
647 Valentine et al. (2004) observed that the high partial pressure of H_2 decreased fractionation between
648 CO_2 and CH_4 . They suggest that this could be due to limited reversibility of methanogenesis at excess
649 H_2 . High partial pressure of H_2 may also inhibit some methanogenic species (Thauer et al., 2008), thus
650 changing the reaction pathway or even limiting it to abiotic. A combination of limited carbon supply

651 with excess H₂ could explain the high $\delta^{13}\text{C}_{\text{CH}_4}$ values especially below 2300 m depth at Outokumpu
652 and at Pyhäsalmi.

653

654 **5.4 Carbon in the system CH₄-C₂H₆-C₃H₈**

655

656 Even though some subsurface microorganisms may be capable of producing longer chained
657 hydrocarbons (e.g. Taylor et al., 2000; Hinrichs et al., 2006), the vast majority of microbially generated
658 hydrocarbon gas is CH₄, and the high CH₄/C₂₊ ratio (>1000) is commonly used to separate microbial
659 from thermogenic CH₄, even though lower ratios may also be observed due to preferential consumption
660 (oxidation) or escape (diffusive or advective migration) of CH₄ (Bernard et al., 1976; Printzhofer and
661 Huc, 1995; Whiticar, 1999). Figure 9 shows the classification of CH₄ into microbial and thermogenic
662 based on the CH₄/C₂₊ ratio in combination with the isotopic composition of CH₄, i.e. the classical
663 Bernard diagram for the samples from the Fennoscandian Shield (Table EA2). In addition, potential
664 limits are suggested for abiotic CH₄ in Fig. 9 which are based on data from the Zambales ophiolite (ZO)
665 and mid-ocean ridges (MOR) (Horita and Berndt, 1999 and references therein), and artificial CH₄ from
666 bit-metamorphism (Faber et al., 1999). If, instead, previous data from the Precambrian Shields with
667 $\delta^{13}\text{C}_{\text{CH}_4}$ values down to -50‰ VPDB are considered abiotic (cf. Fig. 2 and Sherwood Lollar et al.
668 1993b), the abiotic field would essentially include the whole thermogenic field.

669

670 The CH₄/C₂₊ ratio is not capable of distinguishing abiotic hydrocarbons from microbial and
671 thermogenic very well because the former can have both high and low ratios (Faber et al., 1999; Horita
672 and Berndt, 1999; Tassi et al., 2012). For example, hydrocarbons produced by clay catalysed reactions
673 differ from those of FTT synthesis, as they contain more aromatic compounds, instead of the
674 dominance of linear alkanes typical for FTT, while the organosulphur pathway lacks alkane and alkene
675 products (McCullom, 2013). Longer chained alkanes are also more probably produced in gaseous than
676 aqueous systems (Lewan and Roy, 2011). When associated with extremely ²H-poor and ¹³C-rich CH₄,
677 high concentrations of both H₂ and unsaturated hydrocarbons, the high CH₄/C₂₊ ratio may indicate
678 artificial CH₄ formed (from organic compounds often added in the drilling fluid) by bit-metamorphism
679 (Faber et al., 1999). In this light, different formation processes can explain the different CH₄/C₂₊ ratios
680 of similarly ¹³C enriched CH₄ at Outokumpu and Pyhäsalmi.

681

682 A further indication of different formation mechanisms comes from the comparison of $\delta^{13}\text{C}$
683 compositions of the alkanes (Fig. 3). The typical V-shaped pattern at Outokumpu is similar to that
684 reported by Sherwood Lollar et al. (2008) from the Kidd Creek mine and four other sites in
685 Precambrian shields in Canada and South Africa which they explained by abiotic polymerisation of
686 hydrocarbons. In their model, the first step ($\text{CH}_4 \rightarrow \text{C}_2\text{H}_6$) is associated with isotope depletion but the
687 fractionation then diminishes due to rapid polymerisation and is thereafter only controlled by isotope
688 mass balance which leads to slight enrichment of ^{13}C from C_2H_6 onwards (Sherwood Lollar et al.,
689 2008). The initial step of hydrocarbon generation by this mechanism could not be experimentally
690 reproduced (McCollom et al., 2010) and the actual mechanism still remains elusive. Low (or
691 decreasing) temperature might be a prerequisite for the preservation of such pattern as the polymerised
692 hydrocarbons cannot split, and may explain why this trend is more common in nature than in
693 experiments which have usually been performed at increasing temperatures (Zhang et al., 2013).
694 Reversal of the carbon isotope trend may also be formed at the latest stages of thermogenic gas
695 formation after the formation of longer chained hydrocarbons has ceased, allowing Rayleigh-type
696 fractionation of carbon isotope composition of C_2H_6 and C_3H_8 to occur (Burruss and Laughrey 2010),
697 Thus it may indicate shift from thermogenic to abiotic processes at environments where refractory
698 organic carbon sources are present.

699
700 At Pyhäsalmi C_2H_6 is depleted in ^{12}C compared to CH_4 (Fig. 3), a trend that has been commonly
701 associated with thermogenic hydrocarbons in which it forms as the result of break-up of organic
702 molecules with increasing temperature (e.g. Sherwood Lollar et al., 2002; Zhang et al., 2013). The
703 isotopic compositions are, however, much more ^{13}C enriched than in conventional thermogenic
704 hydrocarbon occurrences and it is also difficult to find a plausible source for such gas in metavolcanic
705 rocks.

707 **5.5 Evidence for microbial methane**

708
709 Methanogenic microorganisms have been found from both Outokumpu and Pyhäsalmi (e.g. Itävaara et
710 al., 2011; Purkamo et al. 2015a, 2015b; Miettinen et al., 2015). Among the other sites within the
711 Fennoscandian Shield, where isotopic data of CH_4 are available (Fig. 1), methanogens have been found
712 also from Olkiluoto (Pedersen et al., 2008; Nyssönen et al., 2012; Bomberg et al., 2014), but not from

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

715

716 Methanotrophs, which oxidize CH₄ for living, also commonly accompany methanogens in deep
717 crystalline rock environments (Nyyssönen et al., 2012; Purkamo et al., 2015a; Bomberg et al., 2015).
718 However, methanogens and methanotrophs typically form only a marginal group of the microbial
719 communities studied (e.g. Miettinen et al., 2015; Purkamo et al. 2015a, 2015b; Simkus et al., 2016). In
720 contrast to previous views which suggest that the deep biosphere is dominated by autotrophs, Purkamo
721 et al. (2015a) hypothesised that the biological deep carbon cycling in Outokumpu is mainly evoked by
722 heterotrophic bacteria. The role of methanogens and methanotrophs in providing carbon for the whole
723 community may however be more important than suggested by their relative proportion (Simkus et al.,
724 2016).

725

726 In the Outokumpu Deep Drill Hole groundwater, methanogenic activity is both more common and
727 more versatile at shallower depths above 1 km compared to the deeper levels (Purkamo et al., 2015a,
728 2015b). Purkamo et al. (2015b) retrieved methanogen communities from the DNA extracted from the
729 fracture fluids of 180, 500, 2260 and 2300 m depths but only the samples from 500 and 967 m
730 contained methanogen RNA. As RNA is used as a proxy for metabolically active species, this may
731 indicate that the active microbial methanogenesis is restricted to the upper 1 km of the drill hole, or the
732 deep dwelling methanogenic species cannot be detected with the methods used. Likewise,
733 methanotrophy is more common at shallower depths not only at Outokumpu where methanotrophic
734 communities have been found at 600, 900 and 1500 m depths but not from deeper levels (Purkamo et
735 al. 2015a) but also in other sites within the Fennoscandian Shield (Kietäväinen and Purkamo, 2015).

736

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

744 metabolically diverse at shallower depths (Kietäväinen and Purkamo, 2015). Isotopic compositions of
745 CH₄ among the Fennoscandian Shield sites also show that $\delta^{13}\text{C}_{\text{CH}_4}$ values below -40‰ are exclusively
746 found in the upper 1 km depth while values heavier than -20‰ appear to be more common at depths
747 greater than 1.5 km (Fig. 10). At some extent this can be due to biased data as samples below 1.5 km
748 are from only three sites (Outokumpu Deep Drill Hole, Pyhäsalmi and Gravberg) and from depths
749 which mainly represent volcanic and igneous rocks. However, similar results have been recently
750 obtained in the Witwatersrand basin in South Africa (Simkus et al., 2016).

751

752 **5.6 Evidence for lithological control on the amount and isotopic composition of methane**

753

754 Within the Fennoscandian Shield sites the depth dependence of CH₄/C₂₊ ratio (Fig. 11) is poor. Instead
755 the variation in CH₄/C₂₊ seems to vary from site to site, which may indicate lithological control on the
756 production of hydrocarbons. Previous observations from around the world suggest that in general
757 hydrocarbons in igneous rocks have low CH₄/C₂₊ ratios (<100), such as those at Pyhäsalmi, while
758 higher ratios, similar to those at Outokumpu, have been found in the Zambales ophiolite and sediment
759 covered ridges and even higher values (>1000) in the sediment free mid-ocean ridges (Fig. 9; Horita
760 and Berndt, 1999; Tassi et al., 2012 and references therein). The differences may be related to
761 availability of organic carbon sources or microbial activity, but may also arise from the differences in
762 the abiotic formation mechanism and temperature/or pressure (see also discussion in 5.4).

763

764 Within the occurrences of crustal CH₄ in the Fennoscandian Shield (Fig. 1), the most ¹³C depleted
765 values are from Enonkoski (Sherwood Lollar et al., 1993a), Muhos and Tyrnävä (Heikkinen, 1972)
766 (Fig. 10). The last two sites also drastically differ in their lithology from the other sites. They are
767 located within glacial sediments on top of a 1300 Ma, non-metamorphosed sedimentary rocks (shale).
768 These represent typical microbial CH₄ formed at low temperatures from abundant organic rich matter.
769 Shallow (< 300 m) groundwater within non-metamorphosed sandstone of Pori also contains low
770 amounts of relatively ¹²C-rich CH₄ (Sherwood Lollar et al., 1993a).

771

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

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

781

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

794

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

804

805 **6. CONCLUSIONS**

806

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

823

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1238 **Figure captions**

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1240 Fig. 1. A simplified lithological map of the Fennoscandian Shield in Sweden and Finland showing the
1241 sites investigated for their isotopic composition of CH₄ in this study and Heikkinen (1972), Hyypä
1242 (1981), Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999) and
1243 Pitkänen and Partamies (2007). Detailed lithologies are given for the Pyhäsalmi mine and Outokumpu
1244 Deep Drill Hole sites: MV = mafic volcanite, T = tonalite, FV = felsic volcanite, MS = mica schist, BS
1245 = black schist, O = ophiolitic rocks, GR = granodiorite. Basemap redrawn after Koistinen et al. (2001).

1246

1247 Fig. 2. Genetic classification of the Outokumpu Deep Drill Hole and Pyhäsalmi mine CH₄ based on the
1248 H and C isotopic composition. Fields are according to Etiope et al. (2013), and are based on traditional
1249 classification of microbial and thermogenic gas (e.g. Schoell 1988) and additional data from various
1250 geological environments. The abiotic field is based on data from volcanic-hydrothermal environments
1251 (V), serpentinized systems (S) and previous data from Precambrian shields (P) (Etiope et al. 2013 and
1252 references therein). Within the thermogenic field “O” refers to CH₄ occurring with oil and “D” refers to
1253 dry gas. Isotopic composition of CH₄ in the atmosphere (Mischler et al., 2009) is marked with X. For
1254 Outokumpu the samples are coded according the sampling technique: small circles = pumped, large
1255 circles = PDS and PAVE, and + = tube sampling. Pyhäsalmi samples = diamonds.

1256

1257 Fig. 3. Plot of carbon isotope compositions of methane, ethane and propane versus carbon number.
1258 Most of the samples from Outokumpu show relative depletion of ¹³C in C₂H₆ compared to CH₄ and few
1259 samples where isotopic composition of C₃H₈ was determined further reveal a V-shaped pattern. In
1260 contrast, two samples from Pyhäsalmi (R-2247) display increase in ¹³C with increasing chain length.

1261

1262 Fig. 4. Carbon isotope compositions of different carbon containing phases along the Outokumpu Deep
1263 Drill Hole. Major zones of groundwater flow are shown with white and gray arrows which indicate
1264 flow into the bedrock and into the drill hole, respectively (Ahonen et al., 2011; Kietäväinen et al.,
1265 2013). Isotopic composition of graphite is from Taran et al. (2011).

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1267 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
1268 d) N_2/Ar at Outokumpu and Pyhäsalmi. All ratios have been corrected for air-contamination by
1269 assuming that the concentration of oxygen in indigenous fracture fluids is zero (Kietäväinen et al.
1270 2014). Symbols as in Fig. 2. In a) and b) different water types described by Kietäväinen et al. (2013) on
1271 the basis of water stable isotopes and dissolved solids, are indicated with roman numerals and appear to
1272 correspond with different gas types. Fluctuation in the relative gas compositions during pumping likely
1273 reflects bubble formation (differences in solubility) and/or heterogeneous gas source. In c) and d)
1274 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
1275 ratio), methanogenesis (decrease in $\delta^{13}\text{C}_{\text{CH}_4}$ and increase in CH_4/N_2 ratio), diffusion (decrease in
1276 $\delta^{13}\text{C}_{\text{CH}_4}$, decrease in CH_4/N_2 and increase in the N_2/Ar ratio in the diffused gas), and mixing (linear
1277 change in the case of two component mixing). Although few samples (1820 m pumped, Pyhäsalmi R-
1278 2227) may have been affected by oxidation, most of the variation can be explained by mixing between
1279 gases emanating from different fracture zones.

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1281 Fig. 6. Hydrogen isotope concordance diagrams for the system $\text{CH}_4\text{-H}_2\text{O-H}_2$, based on equations for a)
1282 $\text{CH}_4\text{-H}_2$ 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).
1283 Samples from the Outokumpu Deep Drill Hole (circles) and Pyhäsalmi mine drill hole R-2247
1284 (diamonds) show equilibration temperatures below 50°C and 100°C , respectively.

1285

1286 Fig. 7. Isotopic fractionation of hydrogen between H_2O and CH_4 . Equilibrium fractionation (Horibe and
1287 Craig 1995) is shown as broken lines for three different temperatures relevant for *in situ* conditions at
1288 the Outokumpu Deep Drill Hole and Pyhäsalmi mine. Characteristic fractionation related to microbial
1289 CO_2 reduction (C) and acetate fermentation (A) were calculated according to Whiticar (1999) with a
1290 maximum isotope offset for the acetate fermentation of -370‰ (lines) and Sugimoto and Wada (1995)
1291 (dotted lines). Symbols as in Fig. 2.

1292

1293 Fig. 8. a) Carbon and b) oxygen isotope compositions of calcites along the Outokumpu Deep Drill
1294 Hole. Isotopic equilibrium at ambient temperatures, indicated with a thick line and gray shading, was
1295 calculated according to isotope fractionation equations given by Salomons and Mook (1986) (according
1296 to Clark and Fritz, 1997) for the calcite- HCO_3^- ^{13}C exchange reaction and by O'Neil et al. (1969) for

1297 the ^{18}O exchange between calcite and water. No DIC isotope data is available between 1000 and 1600
1298 m depth. Error bars are smaller than the size of the symbols.

1299

1300 Fig. 9. The $\text{CH}_4/\text{C}_{2+}$ ratio vs. carbon isotope composition of CH_4 for the Fennoscandian Shield
1301 samples. Pressurised samples from the Outokumpu Deep Drill Hole (DDH) are highlighted with thicker
1302 rims. SCR refers to sediment covered ridges (Tassi et al., 2012 and references therein) and within the
1303 thermogenic field “II” and “III” refer to type II (oil-prone/marine-sapropelic) and type III (gas-
1304 prone/terrestrial) kerogen, respectively. The suggested field for abiogenic CH_4 (shaded) includes gases
1305 from the Zambales ophiolite (ZO) and mid-ocean ridges (MOR) (Horita and Berndt, 1999 and
1306 references therein), and artificial CH_4 from bit-metamorphism (Faber et al., 1999). However, CH_4 as
1307 light as -50% VPDB from Precambrian Shields has in previous studies been classified abiogenic (cf. Fig.
1308 2 and Sherwood Lollar et al., 1993b). Mixing may explain the scatter of data points between the
1309 different blocks, and the isotopic compositions are also subject to fractionation due to oxidation and
1310 isolation/substrate limitation. Data from this study, Jeffrey and Kaplan (1988), Sherwood Lollar et al.
1311 (1993a, 1993b), Haveman et al. (1999) and Pitkänen and Partamies (2007). Diagram modified after
1312 Whiticar (1999).

1313 Fig. 10. Carbon isotopic systematics of CH_4 with depth in the Fennoscandian Shield. Data from this
1314 study, Heikkinen (1972), Hyypä (1981), Jeffrey and Kaplan (1988), Sherwood Lollar et al. (1993a,
1315 1993b), Haveman et al. (1999), and Pitkänen and Partamies (2007). Pressurised samples from the
1316 Outokumpu Deep Drill Hole (DDH) are highlighted with thicker rims. Isotopic composition of CH_4 in
1317 air is from Mischler et al. (2009). The $\delta^{13}\text{C}_{\text{CH}_4}$ values below -40% VPDB are exclusively found in the
1318 upper 1 km depth while values heavier than -20% appear to be more common at depths greater than
1319 1.5 km.

1320

1321 Fig. 11. $\text{CH}_4/\text{C}_{2+}$ with depth in the Fennoscandian Shield. Data from this study, Jeffrey and Kaplan
1322 (1988), Sherwood Lollar et al. (1993a, 1993b), Haveman et al. (1999) and Pitkänen and Partamies
1323 (2007). Pressurised samples from the Outokumpu Deep Drill Hole (DDH) are highlighted with thicker
1324 rims. The ratio varies more from site to site than showing shield scale dependence on depth.

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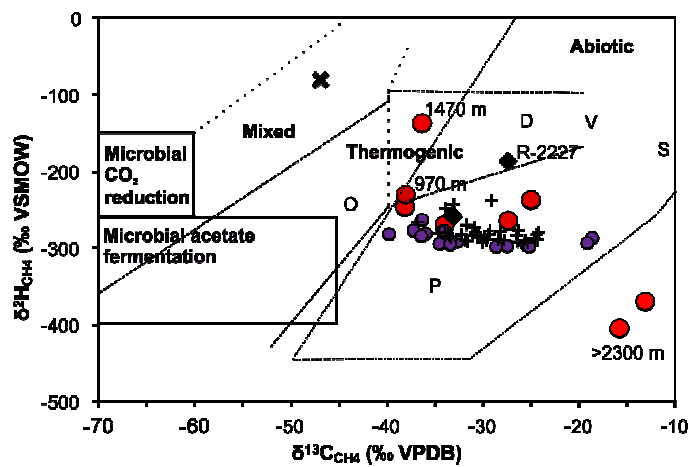
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Fig. 1

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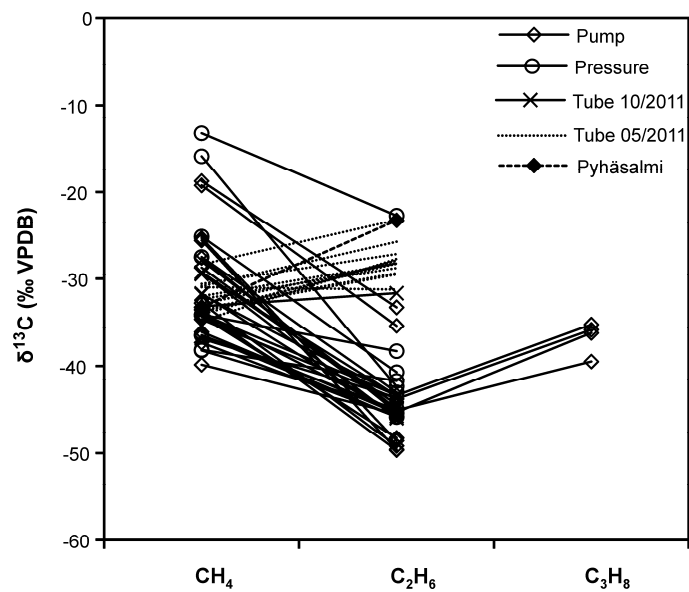
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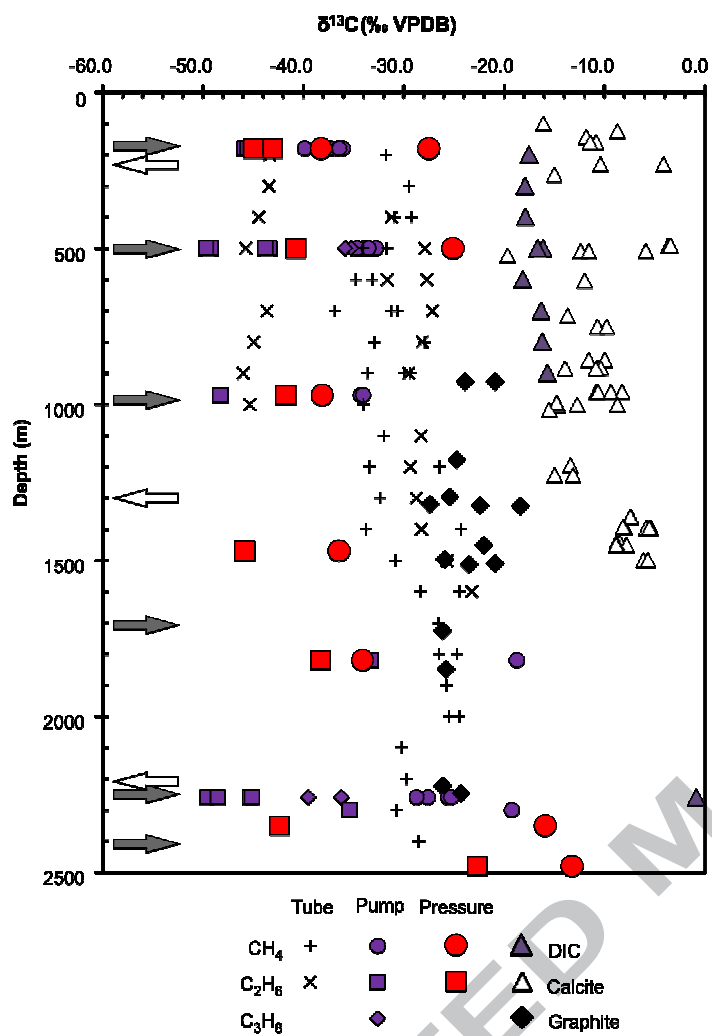
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Fig. 4

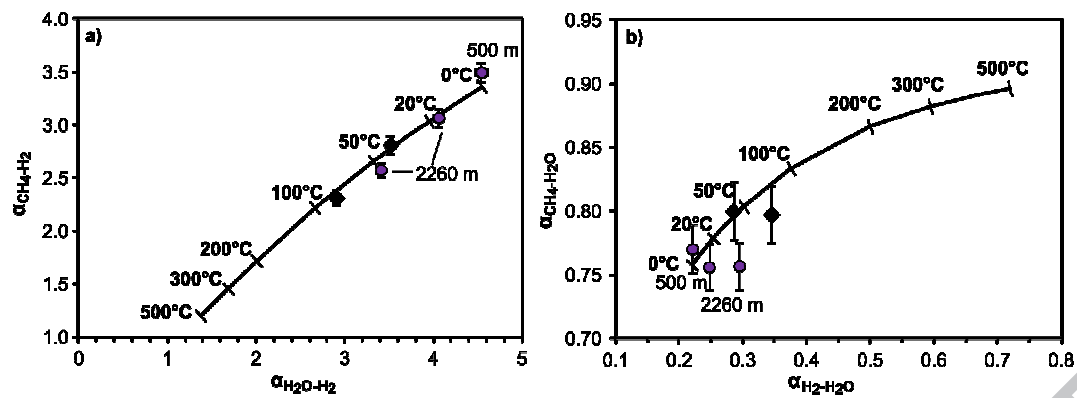
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Fig. 5



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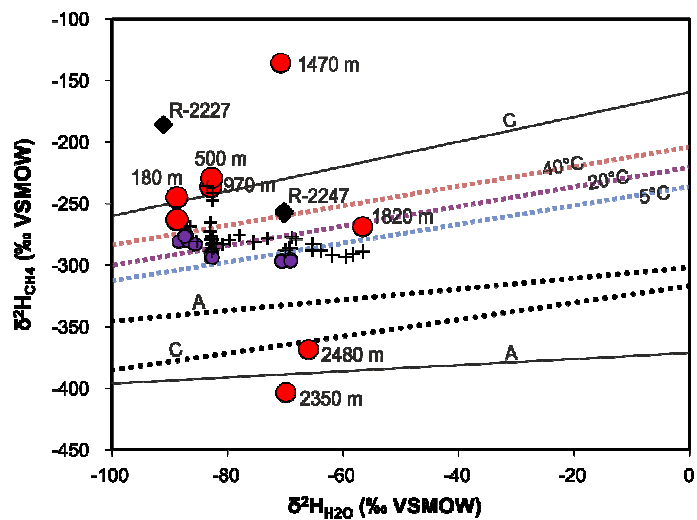
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1371 Fig. 6

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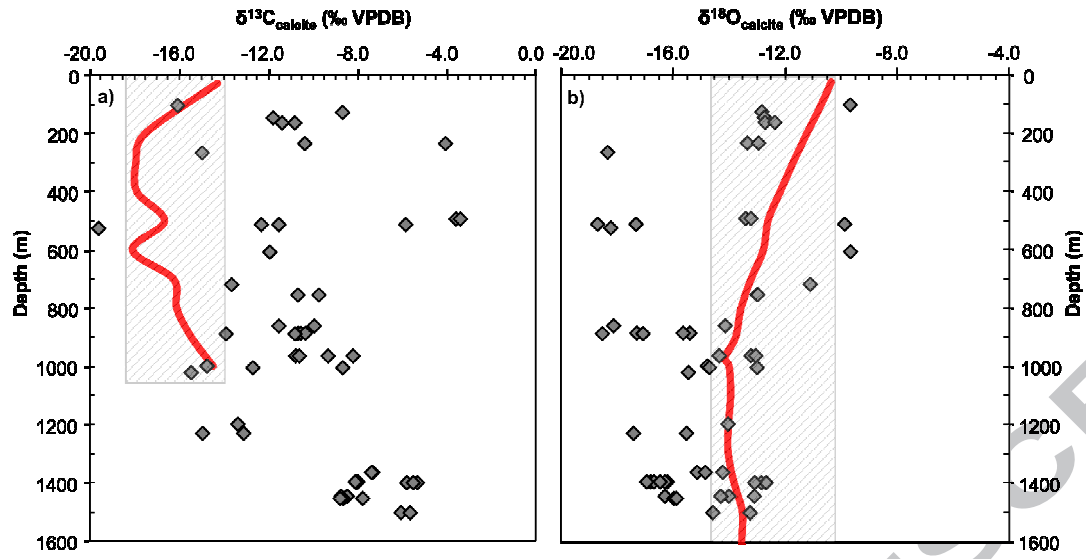
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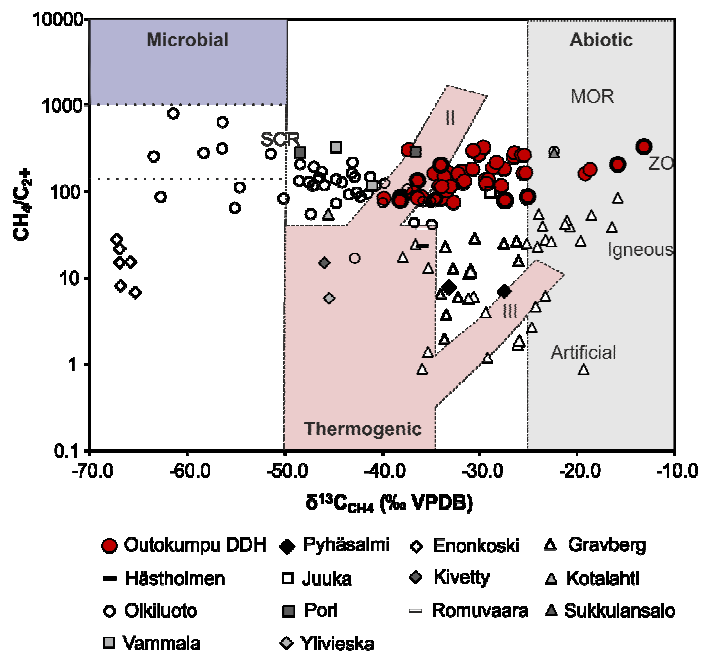
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Fig. 8

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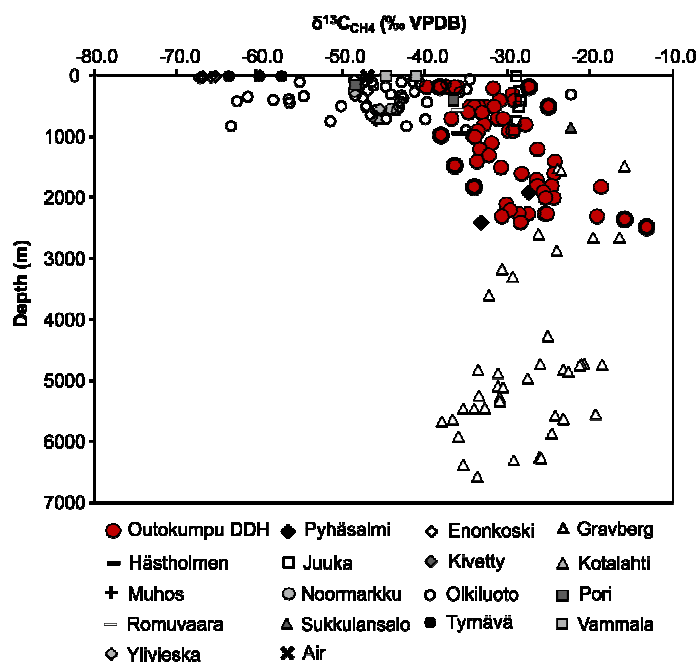
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Fig. 9



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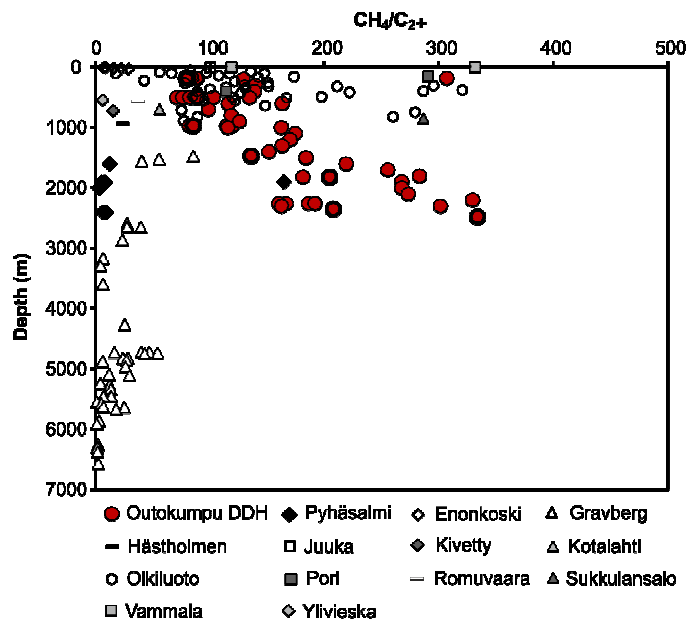
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Table 1.

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

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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	CH ₄	C ₂ H ₆	C ₂ H ₆	C ₃ H ₈	H ₂	H ₂ O ^d	H ₂ O ^d	DIC	DIC ^e
				δ ¹³ C	δ ² H	δ ¹³ C	δ ² H	δ ¹³ C	δ ² H	δ ² H	δ ¹⁸ O	δ ¹³ C	mmol l ⁻¹
				‰ VPDB	‰ VSMOW	‰ VPDB	‰ VSMOW	‰ VPDB	‰ VSMOW	‰ VSMOW	‰ VSMOW	‰ VPDB	
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

1422 ^aData from Nyssönen et al. 2014

1423 ^bData from Toppi 2010

1424 ^cSampling methods: TSI = tube sampling/injection, PI = Pumping/injection, PB = pumping/bucket, PDS = positive displacement
 1425 sampler, PAVE = pressurised sampling device, FFI= from free flowing fluid/injection.

1426 ^dData from Nyssönen et al. 2014, Toppi 2010, Kietäväinen et al. 2013, Miettinen et al. 2015 and this study.

1427 ^eThe concentration of dissolved inorganic carbon was modelled based on geochemical data with PHREEQC software (USGS, 2014)

1428 BAL = below analytical limit

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1431Table 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

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

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* = duplicate sample

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