



Working Report 2010-88

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Working Reports contain information on work in progress
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Stable isotope signatures of gases liberated from fluid inclusions in bedrock at Olkiluoto

ABSTRACT

Fluid inclusions in quartzes of the Olkiluoto bedrock contain gaseous N₂, CO₂, H₂, CH₄, and higher hydrocarbons in varying proportions. Stable carbon and hydrogen isotope signatures of the gas phases give valuable information on their origin and the formation conditions. In previous studies (Hämmerli, 2009; Eichinger et al., 2010 a, b), a method to liberate and quantify the gases trapped in fluid inclusions was developed. It allowed determining the carbon isotope signatures of liberated CO₂, CH₄ and higher hydrocarbons (HHC), but no hydrogen isotope data were acquired. The method was advanced and, in this study, also stable hydrogen isotopes of CH₄ and H₂ liberated from fluid inclusions could be analysed. The stable carbon signatures of methane and higher hydrocarbons, as well as the hydrogen isotope signatures of methane indicate a predominant thermogenic provenance for those gases.

Keywords: Olkiluoto, fluid inclusions, gas, isotope signature, composition

Fluidisulkeumista mitattuja kaasujen stabiilien isotooppien koostumuksia Olkiluodon kivissä.

TIIVISTELMÄ

Kvartsirakeiden fluidisulkeumat Olkiluodon kivilajeissa sisältävät vaihtelevissa suhteissa kaasuja, joita ovat mm. N_2 , CO_2 , H_2 , CH_4 ja pidemmät hiilivedyt. Kaasufaasin stabiilien hiili- ja vetyisotooppien leimat muodostavat merkittävän aineiston, josta voidaan tehdä tulkintoja kaasujen alkuperästä ja muodostumisolosuhteista. Hämmerli (2009) ja Eichinger et al. (2010) ovat kehittäneet menetelmän, jolla fluidisulkeumista vapautettujen kaasujen koostumus voidaan kvantitatiivisesti määrittää. Menetelmän avulla pystyttiin mittaamaan myös CO_2 :n, CH_4 :n ja pidempien hiilivetyjen hiiliisotooppileimat, mutta vetyisotooppikoostumuksien määrittäminen CH_4 - ja H_2 -kaasuista ei onnistunut. Menetelmän jatkokehityksen ansiosta on nyt pystytty määrittämään myös vedyn stabiilien isotooppien koostumus fluidisulkeumista. Hiilivetyjen hiilen ja vedyn stabiilien isotooppien koostumukset viittaisivat ensisijaisesti kaasujen termogeeniseen alkuperään.

Avainsanat: Olkiluoto, fluidisulkeuma, kaasu, isotooppileima, koostumus

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1 INTRODUCTION

Fluid inclusions in quartz and feldspar within the bedrock at Olkiluoto contain various gas components. In total, 8 fluid inclusion generations could be distinguished petrographically, each consisting of various proportions of CO₂, N₂, CH₄, H₂ and higher hydrocarbons (HHC), in addition to saline water. Inclusions are present, regardless of depth, in quartz crystals of all lithologies (Hämmerli, 2009; Eichinger et al., 2010 a, b).

All fluid inclusions in the investigated quartz samples are secondary. This means that they were trapped from pore fluids after the host metamorphic quartz had formed and had acquired its metamorphic texture. Determination of the chemical and isotopic signatures of the gases in these inclusions thus provides valuable information on the post-metamorphic history of fluid circulation in inter- and intragranular pore spaces of the bedrock.

In previous fluid inclusion studies (Hämmerli, 2009; Eichinger et al., 2010 b), a method was developed to extract and analyse the gases in the fluid inclusions. By using this method, the carbon isotope signatures of liberated CO₂, CH₄ and higher hydrocarbons (HHC) were determined, but no data on hydrogen isotopes could be collected. Recent advances in methodology now allow the hydrogen isotope ratios of CH₄ and H₂ in fluid inclusions to be determined. The results of these investigations are summarised in this report and will be interpreted and discussed in detail elsewhere.

2 SAMPLES AND METHODS

2.1 Samples

Gases liberated from fluid inclusions in eight core samples from the Olkiluoto investigation site were analysed for their stable isotope signatures. The core samples originate from the two deep, sub-vertical drillholes OL-KR39 (0-430 m b.s.) and OL-KR47 (0-800 m b.s.) and from the sub-horizontal borehole ONK-PH9. The latter was drilled from the ONKALO access tunnel at a depth of 306 m b.s.. The samples used for this fluid inclusion gas study were selected according to depth and availability of core material.

2.2 Methods

Disaggregation of core samples and separation of quartz

To liberate the gases in the fluid inclusions, the drillcore samples were first disaggregated into their component mineral grains using the selective fragmentation device (selFrag™) at the Institute of Geological Sciences, University of Bern. Very short pulsed, high voltage discharges are applied to the sample under water. They produce high pressure waves which propagate along grain boundaries, thereby disaggregating the rock sample. The advantage of the selFrag™ method is that single grains remain intact during separation and much fewer fines are produced compared with grinding methods. The product is thus a sand composed of intact crystals. Hämmerli (2009) carried out Raman and microthermometric analyses on the fluid inclusions on quartz before and after the selFrag™ treatment. The disaggregation showed no impact on the properties of the fluid inclusions.

As quartz contains the highest amount of fluid inclusions in the samples, it is the preferred mineral to be separated for gas analysis. Quartz was therefore separated from the mineral sand by hand-picking under a binocular microscope and put aside for further analysis.

Gas liberation and separation

The hand-picked quartz crystals were crushed in an evacuated piston-cylinder device to liberate the gases trapped in the fluid inclusions. Around 3.5 to 6 g of quartz was placed in the crushing device. Before crushing, the sample chamber was evacuated, flushed twice with He to avoid any air contamination and filled with He to around 300 mbar.

The crushing device is fitted with an induction coil, which drives a piston against the upper end of the cylinder, where it compresses a strong spring. The subsequent expansion of the spring combined with the acceleration caused by the induction coil catapults the piston downwards and crushes the sample. The piston is repeatedly activated for about 20 minutes to ensure fine crushing. During the crushing process the device is heated to 150 °C to avoid gas sorption on the freshly crushed quartz surfaces.

After crushing the device was filled with He to a slight overpressure of 1.3 to 1.5 bar and the gases were allowed to mix for 30 minutes at 150 °C. Subsequently, an aliquot of the gas mixture was taken using a gas-tight syringe (2 x 30 ml) and injected into a glass bottle containing helium for GC-IRMS analyses of the carbon isotopes of CO₂, CH₄ and higher hydrocarbons.

The crushing device was then attached directly to an evacuated gas-separation line. There the individual gas species were sequentially trapped using a series of liquid-nitrogen cold traps and two ovens to oxidise H₂ and CH₄ to CO₂ and H₂O, respectively (Figure 2). In the first cold trap (1) H₂O, CO₂ and the higher hydrocarbons were retained. Methane is retained in a Hayesep Q 100/120 mesh cold trap. The only gas that passes through the traps is H₂. It is oxidised to H₂O in the ovens and collected in a glass test tube in cold trap (4). Elemental Mn reacts with H₂O to form H₂ and MnO. This H₂ was then analysed with the DI-IRMS. Cold trap no. 3 was removed during the H₂ separation. In a second step, cold trap no. 2 was removed to liberate the CH₄ and oxidise it to CO₂ and H₂O in the ovens. The H₂O was captured in cold trap 3 while CO₂ was collected in a fresh test tube and the isotopic composition was measured using the DI-IRMS. The last step included the liberation of the retained H₂O in cold trap 3 and the collection in a third test tube containing elemental Mn. The Mn again reacts with the H₂O to form H₂, which was then analysed by DI-IRMS. Several crushing runs were necessary to yield sufficient H₂O from the various gas species, i.e. CH₄ and H₂.

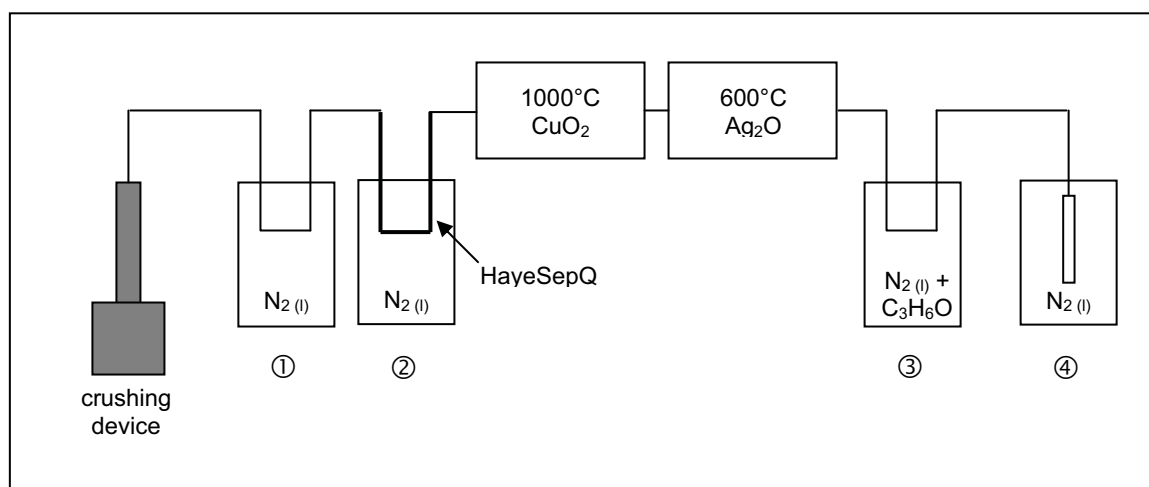


Figure 1. Vacuum line consisting of a series of cold traps and two ovens to separate and oxidise the gases derived from the fluid inclusions.

Analyses of carbon isotope ratios of CO₂, CH₄ and higher hydrocarbons

The carbon isotope signatures of CO₂, CH₄ and higher hydrocarbons were measured by a GC-IRMS equipped with a purge and trap. The line consists of a PTA -3000 purge and trap device (IMT Germany), a GC 3400 gas chromatograph (Varian), a Hayesep Q separation column (VICI) with helium as the carrier phase (2.4 ml/min) and a delta S (Finnigan MAT) isotope ratio mass spectrometer (IRMS). The IsoDat NT software was

used to evaluate the signals. The instrumental error of $\delta^{13}\text{C}$ in CO_2 , CH_4 and higher hydrocarbons is ± 0.3 ‰.

Analyses of hydrogen isotope ratios of CH_4 and H_2

The produced hydrogen from the single gas components (CH_4 , H_2) was analysed by DI-IRMS (DI= Dual Inlet; Delta S, Finnigan MAT). Due to the low amounts of gas, the measured isotope ratios had to be corrected. The correction factor was determined by analysing different volumes of a standard gas and evaluating the linear deterioration of its isotope signatures as the volume of gas is decreased. The analytical uncertainty is ~ 3 ‰.

All analytical work was conducted at Hydroisotop GmbH, Germany

3 RESULTS

Stable carbon isotope signatures ($\delta^{13}\text{C}$) of CO_2 , CH_4 , C_2H_6 , C_3H_8 and partly of *i*- C_4H_{10} and *n*- C_4H_{10} , as well as stable hydrogen isotope signatures ($\delta^2\text{H}$) of CH_4 and H_2 were determined in the present study. The results of the isotope analyses are shown in Figure 2 and Table 1.

The $\delta^{13}\text{C}$ ratios of CH_4 lie between -53.5 and -35.6 ‰ PDB (Table 1, Figure 2a). Most of the samples fall within a fairly tight range between -42 and -34 ‰ PDB, whereas the PH9 sample at 300 m depth has more $\delta^{13}\text{C}$ -depleted values up to -53.5 ‰ PDB.

The $\delta^{13}\text{C}$ signature of ethane (C_2H_6) varies between -53.8 and -37.2 ‰ PDB, and the values for propane (C_3H_8) vary between -50.1 and -30.6 ‰ PDB (Table 1, Figure 2 b, c). In general they show similar trends to methane over depth (Figure 2 b, c). Butane was not detected in every sample. Where it was present in a measurable amount, the obtained $\delta^{13}\text{C}$ signatures of *i*- and *n*- butane were between -50.1 and -31.2 ‰ PDB (Table 1).

In all samples, except for the deepest one (792 m b.s.), the $\delta^{13}\text{C}$ ratios of methane are slightly lower than those of ethane (Figure 3). The higher hydrocarbons show a trend to more enriched $\delta^{13}\text{C}$ -signatures with increasing carbon numbers beyond ethane (Figure 3).

The $\delta^{13}\text{C}$ signatures of CO_2 lie between -18.5 and -12.2 ‰ PDB (Table 1, Figure 2d). The samples taken at 10, 306, 640 and 792 m b.s. have rather similar ratios, but samples from 118 and 592 m b.s. are relatively depleted in ^{13}C (Figure 2d).

The $\delta^2\text{H}$ signatures of CH_4 vary between -210 and -174 ‰ V-SMOW (Table 1, Figure 2e). They are similar in the samples from depths of 10, 592 and 640 m b.s. and slightly depleted in ^2H in the samples from 118 and 792 m b.s. (Figure 2e). The $\delta^2\text{H}$ signatures of methane in core samples at 306 m b.s. (drillhole ONK-PH9) show a much wider spread than in other samples.

The $\delta^2\text{H}$ signatures of H_2 gas lie between -191 and -157 ‰ V-SMOW (Table 1, Figure 2f). The results are similar for all samples, except for the shallowest one which is slightly depleted (Figure 2f).

Table 1. Stable carbon- and hydrogen isotope signatures of various gases trapped in quartz-hosted fluid inclusions in the Olkluoto bedrock. Core samples are taken at different depths from the sub-vertical drillholes OL-KR39 and OL-KR47 and from the horizontal drillhole ONK-PH9.

The cumulated errors are ± 3 ‰ for $\delta^{13}\text{C}$ and ± 5 ‰ for $\delta^2\text{H}$.

Sample	KR39-20	KR39-5	PH9-11	PH9-24	PH9-26	KR47-20	KR47-23	KR47-30
Vertical Depth	10	118	306	306	306	592	640	792
	m	b.s.						
Carbon Isotope Signatures								
$\delta^{13}\text{C-CO}_2$	-14.7	-18.0	-14.2	-14.3	-13.3	-18.5	-12.2	-13.4
$\delta^{13}\text{C-CH}_4$	-41.2	-40.3	-47.7	-53.5	-51.9	-35.6	-36.3	-44.2
$\delta^{13}\text{C-C}_2\text{H}_6$	-43.5	-41.8	-51.5	-53.8	-52.7	-37.2	-39.9	-43.9
$\delta^{13}\text{C-C}_3\text{H}_8$	-30.6	-36.9	-44.0	-50.1	-46.5	-34.1	-35.0	-35.3
$\delta^{13}\text{C-i-C}_4\text{H}_{10}$	-*	-	-	-	-	-	-	-31.2
$\delta^{13}\text{C-n-C}_4\text{H}_{10}$	-	-	-32.8	-43.9	-32.0	-31.2	-	-
Hydrogen Isotope Signatures								
$\delta^2\text{H-CH}_4$	-188	-202	-179	-210	-174	-191	-189	-200
$\delta^2\text{H-H}_2$	-191	-157	-173	-165	-	-178	-164	-177

* - could not determined due to a insufficient amount of gas

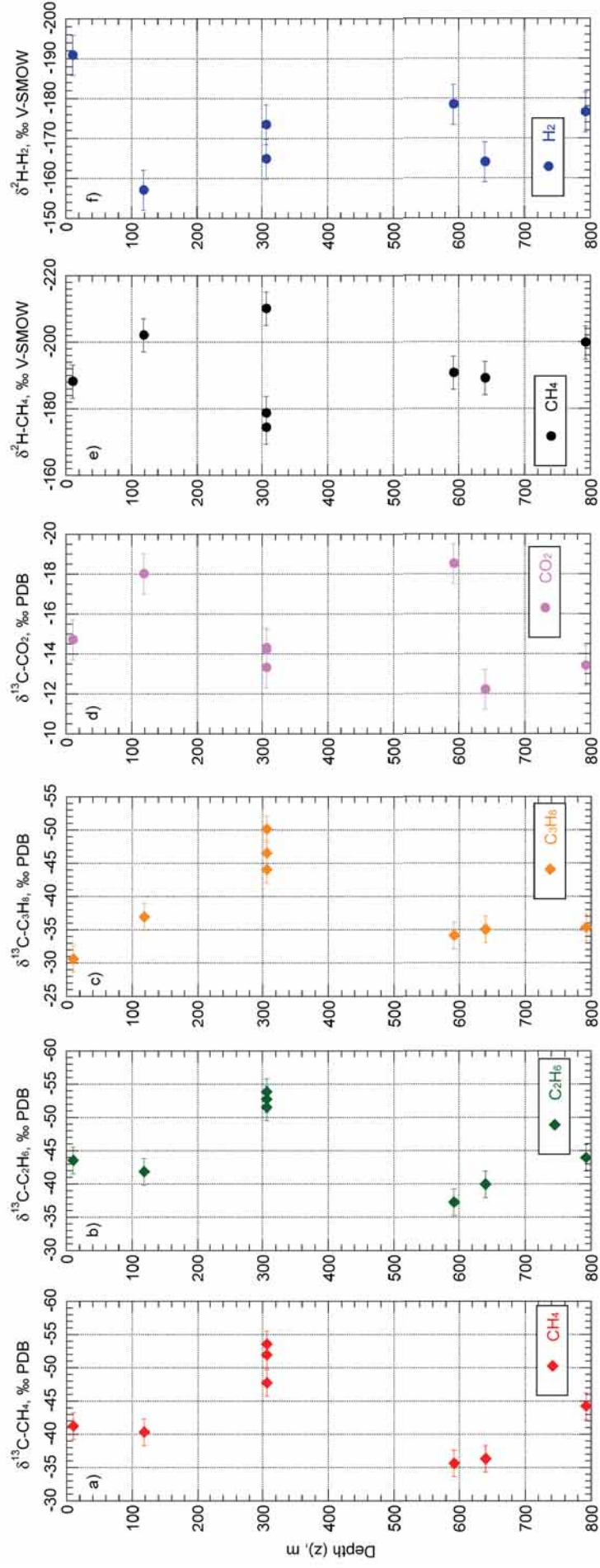


Figure 2. Stable carbon- and hydrogen isotope signatures of gases trapped in quartz-hosted fluid inclusions within the Olkiluoto bedrock versus vertical depth. The rock samples were taken from various depths from the sub-vertical drillholes OL-KR39 and OL-KR47 and from the sub-horizontal drillhole ONK-PH9. The cumulative error is $\pm 3\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 5\text{‰}$ for $\delta^2\text{H}$.

4 DISCUSSION

In interpreting the results it is important to recall that we have used a bulk-sample analytical method. Thus, the analyses reported here reflect the mixed composition of all fluid inclusion generations within a given sample. Presumably there is some variation in isotopic signatures between the generations, but this cannot be easily resolved with our method. As each sample contains variable proportions of the different fluid inclusion generations, at least some of the differences that we have found between samples may be simply due to this unavoidable sampling effect. Hence, it is difficult to identify relationships between isotope ratios and depth.

Nevertheless, the results allow us to draw suggestions on the origin and formation conditions of the gases in the fluid inclusions and hence on the palaeo-fluids themselves if isotopic signatures are primary and no secondary process has changed them before entrapment of the gas phase. Figure 3 shows the $\delta^{13}\text{C}$ isotope ratios of the individual hydrocarbon species within the gas mixtures liberated. Samples from various depths and from three drillholes (OL-KR39, OL-KR47 and ONK-PH9) show similar patterns, first becoming slightly depleted in ^{13}C from C_1 to C_2 and subsequently becoming enriched in ^{13}C with increasing carbon number. According to previous work (James, 1983; Schoell et al., 1988; Sherwood-Lollar et al., 1994), this trend resembles those diagnostic of thermogenic hydrocarbons. The differences in $\delta^{13}\text{C}$ isotope signatures, which are clearly observable in the six samples from drillhole ONK-PH9 taken at the same depth (306 m b.s.), presumably reflect random mixtures of different fluid inclusion generations in the samples, as indicated by the molar ratios of the gases.

The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ data obtained for methane suggest that it originated via thermal breakdown of organic matter, rather than abiogenically (Figure 4). Isotope signatures of methane liberated from inclusions in drillhole ONK-PH9 plot slightly above the field of thermogenic breakdown on the $\delta^{13}\text{C}$ - $\delta^2\text{H}$ diagram, suggesting a possible bacterial influence or an origin from another or changed organic environment.

The provenance and formation conditions of hydrogen and its possible interaction with other gases have not been investigated so far, but are the subject of ongoing studies.

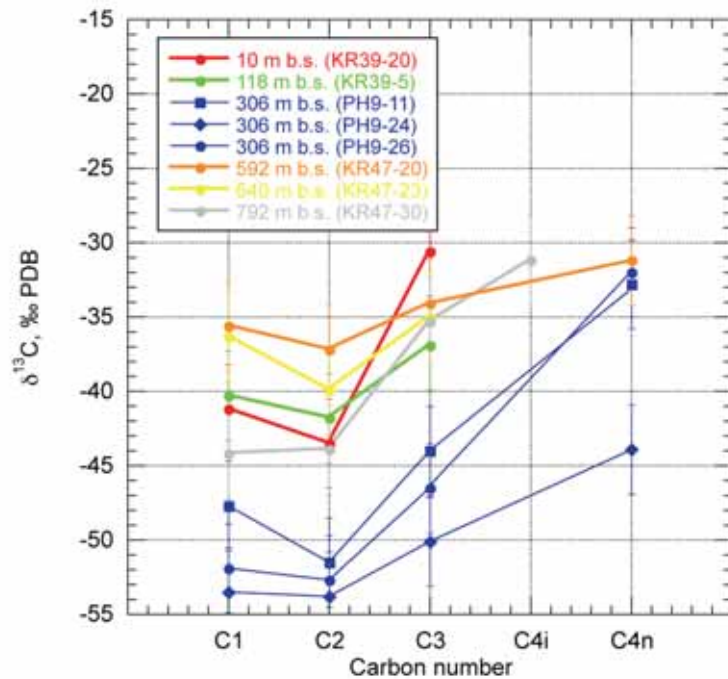


Figure 3. $\delta^{13}\text{C}$ values of saturated hydrocarbons vs. carbon number in gases liberated from fluid inclusions within quartz in core samples from drillhole OL-KR39, OL-KR47 and ONK-PH9; the cumulative errors are ± 3 ‰ PDB.

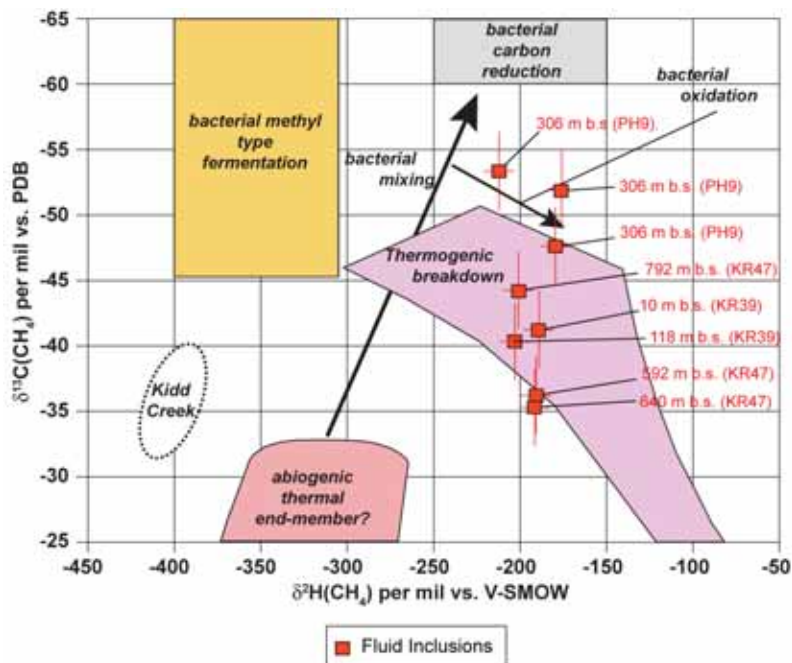


Figure 4. Isotopic signatures of CH_4 in fluid inclusions (red squares) from Olkiluoto bedrock, compared to possible end-member compositions (mod. after Pitkänen and Partamies, 2007); the colored fields indicate the different possible sources of methane.

5 ACKNOWLEDGEMENTS

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