Survey of the methane-rich aquifers, Siljan Crater, Mora, Sweden

Preliminary report

Valérie Beaumont, Eric Deville, Virgile Rouchon
IFP Energies Nouvelles, France

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A – Study overview

Our current investigations were limited to the analyses of gases sampled on 3 wells (Vattumyren 1 and 2, and Folhogskolan), together with geological interpretations of field observations and core logs. This work was complemented with an extensive scientific literature. Geochemical analyses of the gas samples were performed at IFPEN labs, and include the analyses of the major molecular composition of the gas, the isotopic composition of carbon (hydrocarbons and CO_2) and of hydrogen (hydrocarbons and H_2) together with the abundance and isotopic compositions of the noble gases. Our investigations are to this date still in progress as we have planned to analyze more samples of gas already sampled, together with core samples. In the few forthcoming months, we will investigate more deeply the gas and rock geochemistry in order to better define our current understanding of the Mora aquifer gas, and to better plan the future work to be done.

B – Geological Framework

The Siljan ring area (Fig. 1) corresponds to an ancient impact crater of a meteorite that fell 360 Ma ago (Devonian-Carboniferous boundary). It is considered to be the largest impact crater known in Europe. The meteorite fell on a Precambrian basement that includes granites and metamorphic rocks of Proterozoic age and a sedimentary cover of Ordovician and Silurian age. No sediments which post-date the impact are known in this area. The Ordovician and Silurian deposits are preserved in a roughly circular gutter of about 30 km in diameter. These Ordovician and Silurian sediments include carbonates, organic-rich shales (notably in the Silurian) and sandstones (Fig. 2).
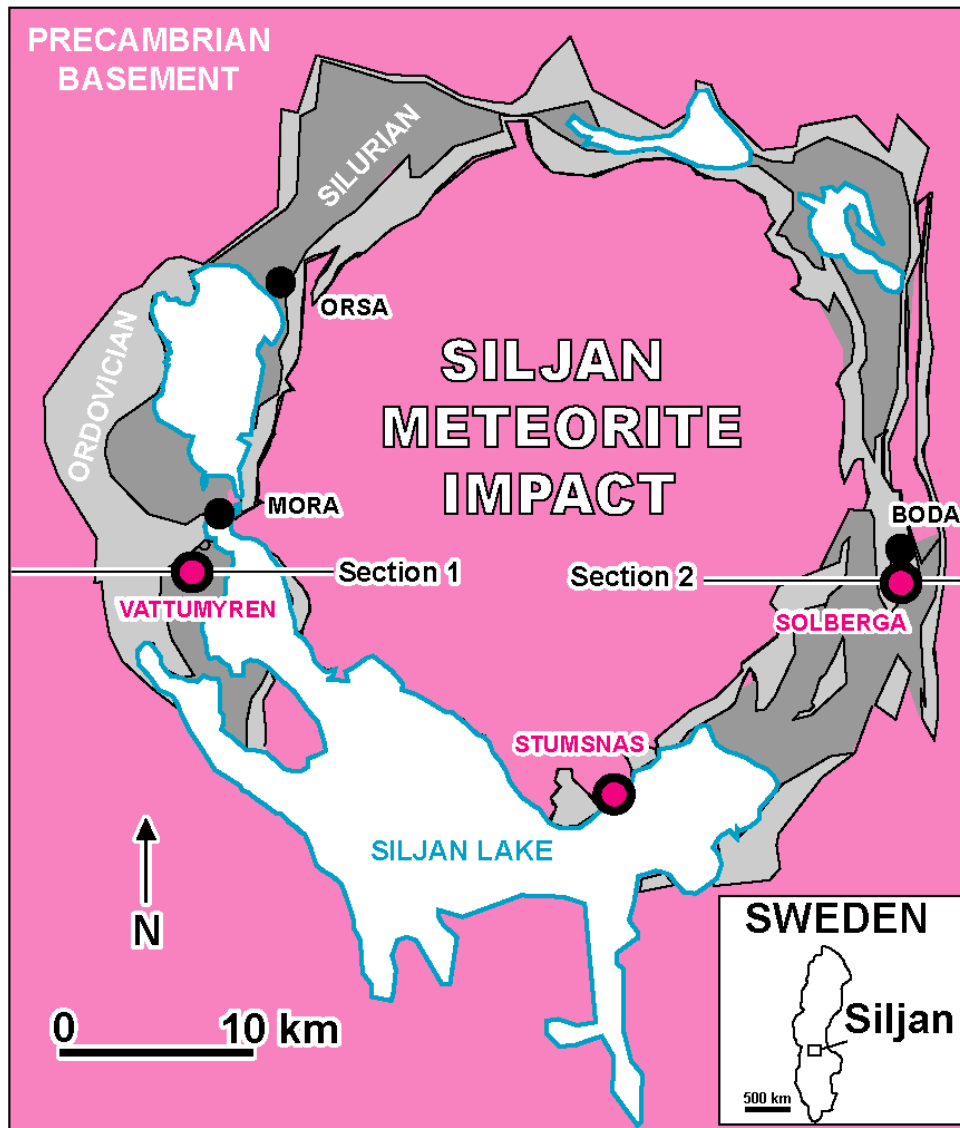
Figure 1 – Structural sketch-map of the Siljan ring area

The organic-rich shales have Total Organic Content (TOC) which are locally up to 10% with S2 up to 51.5 mg/g, and as such can regarded as excellent rocks. The maturity of these shales varies from immature to the oil window (Tmax between 425 and 442°C) (Vlierboom et al., 1986). Oil seepages are known in this area, notably in the area of the Solberga well. Geochemistry studies of these oil shows suggest that the oil was produced on the verge of the oil generation.
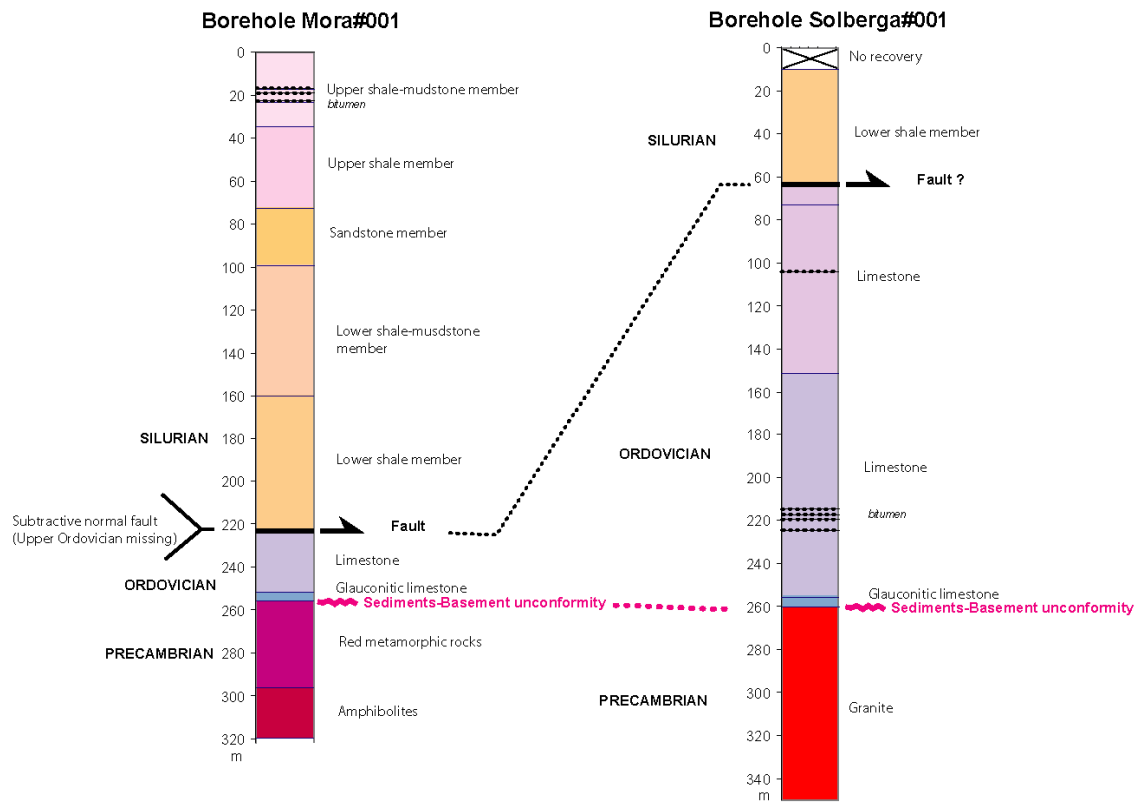
Figure 2 – Simplified stratigraphic logs of the Mora-1 and Solberga-1 Wells

From a structural point of view, in all cases, the CH$_4$-bearing aquifers have been found in the areas located in the ring of Ordovician-Silurian sedimentary cover, below these sediments, inside fractured basement rocks (Fig. 3 & 4).
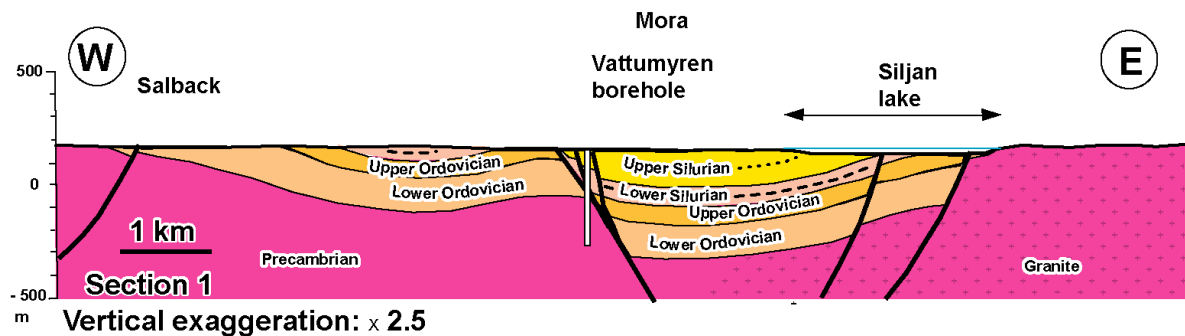

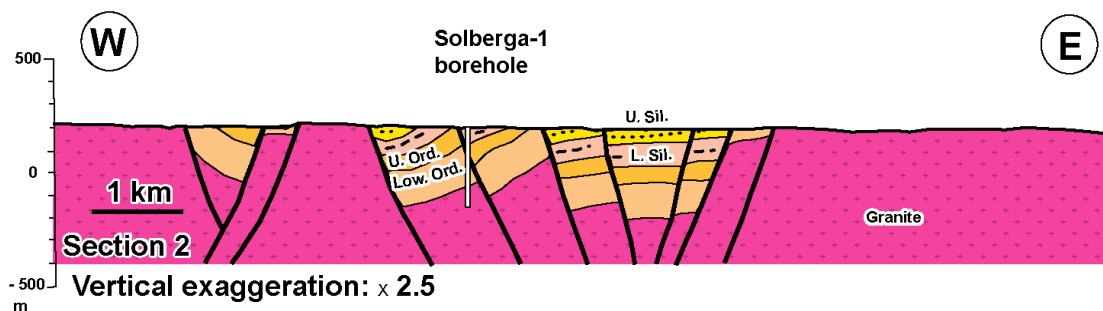*Figure 3 – E-W structural cross-section in the Mora area*

Figure 4 – E-W structural cross-section in the Solberga area

The structure of the Siljan ring where sediments are preserved around the centre of the meteorite impact is controlled by normal faults an tilted faults which is a very classical feature around impact craters (Fig. 5). This interpretation is adequately confirmed by the drilling results (Fig. 2), where we observed normal faults along which parts of the sedimentary pile are missing. Note that Mora#1 and Solberga#1 wells have been drilled on top of tilted blocks (basement highs below Ordovivian deposits) which is a very favourable context to allow a retention of the gas (Fig. 3 & 4).
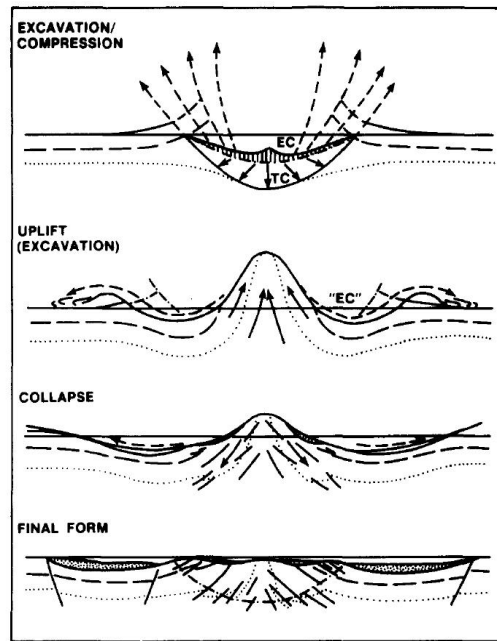

Figure 5 *– Meteorite impact mechanism (from Vlierboom et al., 1986).*

C - Geochemical results

1-Chemical composition

Chemical compositions were determined by Gas Chromatography (GC, data presented in Table 1).

Methane (CH_4) is the predominant gas in the 3 samples from the June 2012 sampling campaign. N_2 is the second more abundant compound (Figure 6). Ethane (C_2H_6) is the only hydrocarbon heavier than methane that was detected. Relatively low methane/ethane ratios (C1/C2) are observed. CO_2, He, H_2 are present from the percent level to the ppm level.
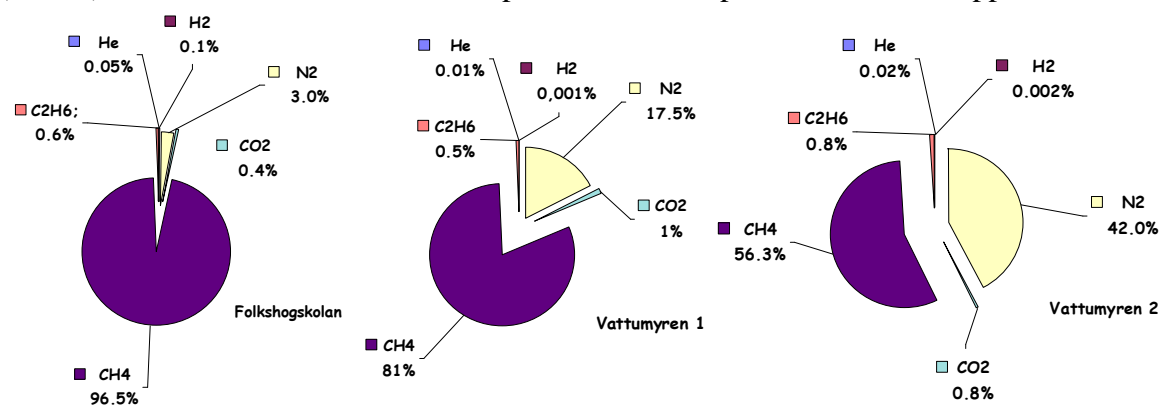

Figure 6. *Distribution of the main gas compounds in the gas samples analyzed*
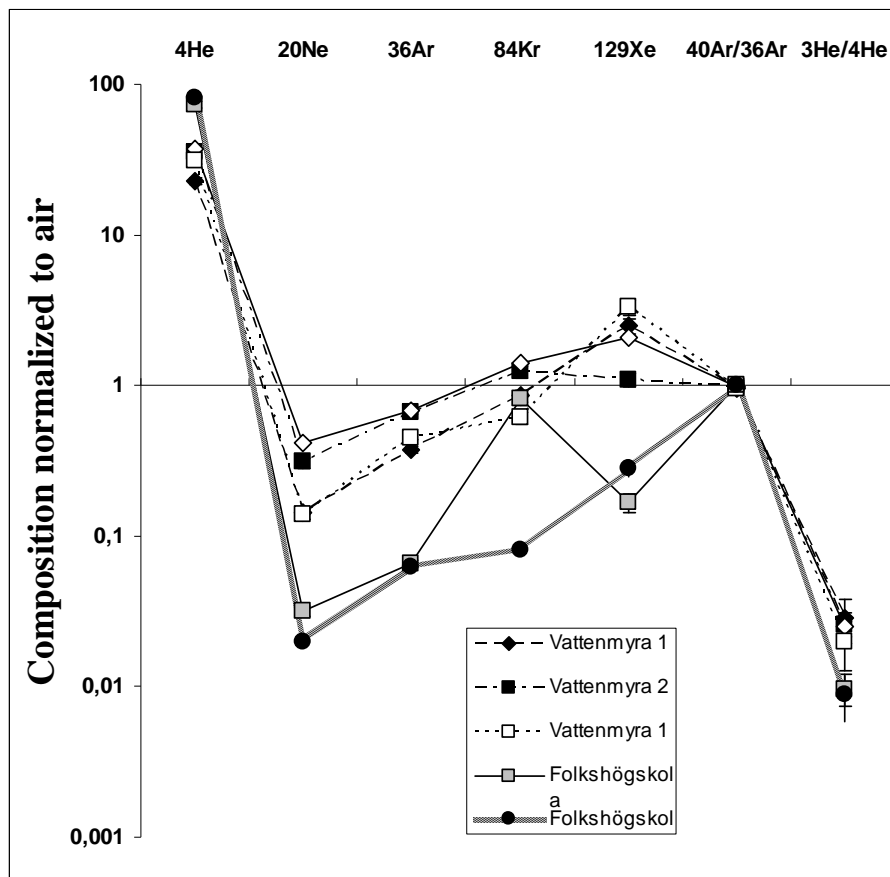
2-Isotopic compositions

The isotopic compositions of carbon and hydrogen were measured when gas concentrations were high enough to obtain significant values. The isotopic composition of methane carbon averages -60 ‰$_{PDB}$, with ethane values between -32 to -42 ‰$_{PDB}$. The carbon isotopic composition of CO_2 ranges between -25 to -38 ‰$_{PDB}$.

The isotopic composition of hydrogen in methane and ethane varies from -290 to -310 ‰$_{SMOW}$, and -120 to 130 ‰$_{SMOW}$, respectively.

The isotopic composition of molecular hydrogen was measured only on the Fokhogskolan samples and averages -207 ‰$_{SMOW}$.

3-Noble gases

Noble gas compositions all show an excess of He relative to air by a factor 20 to 80, with a typical radiogenic isotopic ratio down to $^3He/^4He = 1.2e^{-8}$ (Figure 7). Primordial noble gases (^{20}Ne, ^{36}Ar, ^{84}Ke, ^{129}Xe) display a straight decrease from Xe to Ne for all samples with an identical slope Figure 7), indicative of an atmospheric origin through aquifer recharge. These primordial noble gases are depleted with respect to the air value proportionally to the sample enrichment in He. The $^{40}Ar/^{36}Ar$ ratio is similar to the air value.

Figure 7. *Mass spectrometer elemental and isotopic composition of the noble gases for the Mora area gas normalized to the air value.*

| N°tube	Vattumyren 1	Vattumyren 1	Vattumyren 2	Vattumyren 2	Folkshögsk olan	Folkshögsk olan
Composition	mol%	mol%	mol%	mol%	mol%	mol%
He	0,01	n.m	n.m	0,02	0,05	n.m
H_2	0,00	n.m	n.m	0,00	0,11	n.m
N_2	17,55	n.m	n.m	42,42	3,03	n.m
CO_2	1,09	n.m	n.m	0,78	0,42	n.m
C1	81,34	n.m	n.m	56,78	96,39	n.m
C2	0,54	n.m	n.m	0,84	0,57	n.m
C isotopes	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)
$\delta^{13}C\ CH_4$	-59,209	-59,18	-59,4	-59,75	-60,71	-60,49
$\delta^{13}CO_2$	-32,1	-33,1	-24,9	-26,9	-37,9	-32,9
$\delta^{13}C2$		-31,6	-33,4	-37,6	-41,3	-38,3
H isotopes	δD (‰)	δD (‰)	δD (‰)	δD (‰)	δD (‰)	δD (‰)
$\delta D\ CH_4$	-299,442	-307,37	-303,286	-305,92	-289,046	-288,684
$\delta D\ C2$	-119,85	-128,60			-118,46	-128,10
$\delta D\ H_2$					-205,7	-210,8
Noble gases	ppm	ppm	ppm	ppm	ppm	ppm
^{4}He	120	162	187	194	388	429
^{20}Ne	2,3	2,3	5,0	6,7	0,5	0,3
^{36}Ar	11,6	14,1	20,8	21,0	2,0	2,0
^{84}Kr	5,5E-01	4,0E-01	8,0E-01	9,2E-01	5,3E-01	5,3E-02
^{129}Xe	7,4E-02	1,0E-01	3,3E-02	6,2E-02	5,0E-03	8,4E-03
$^{40}Ar/^{36}Ar$	281,3	283,0	286,4	288,6	294,9	297,8
$^{3}He/^{4}He$	4,0E-08	2,8E-08	3,6E-08	3,5E-08	1,4E-08	1,2E-08
NG uncert.	+/-	+/-	+/-	+/-	+/-	+/-
^{4}He	6	9	10	10	21	23
^{20}Ne	0,18	0,18	0,38	0,51	0,04	0,03
^{36}Ar	0,55	0,66	0,98	0,99	0,10	0,09
^{84}Kr	5,0E-02	3,6E-02	7,3E-02	8,4E-02	4,8E-02	4,9E-03
^{129}Xe	8,0E-03	1,2E-02	3,3E-03	7,2E-03	6,9E-04	1,1E-03
$^{40}Ar/^{36}Ar$	0,9	0,7	1,0	1,0	1,1	1,1
$^{3}He/^{4}He$	1,3E-08	1,0E-08	6,7E-09	7,3E-09	3,2E-09	4,2E-09

Table 1. *Gas compositions*

D - Preliminary discussion

1-General considerations

The ratio of $N_2/^{36}Ar$ is equal to that of the atmosphere, demonstrating that the large majority of the N_2 is atmospheric, through water recharge, similarly to the other primordial noble gases (Ne, Kr and Xe). Considering an atmospheric origin for nitrogen, the CH_4/N_2 ratio of the gas pumped out the aquifer is proportional to the aquifer concentration in dissolved methane. We can conclude that the Folkhogskolan well pumps a richer water in methane than at Vattumyren. The difference between the two Vattumyren wells may simply be explained by the two different well completion types (with and without casing), implying different contact ratios between the gas aquifer and the more superficial ones during pumping. The CH_4 and ^{4}He roughly correlates (at least between Vattumyren wells together and Folkhogskolan), indicating an associated source of CH_4 and ^{4}He. The methane to ethane ratio is rather high straddling between the thermogenic and bacterial/inorganic fields. The isotopic composition of methane carbon indicates a similar ambiguous origin. The isotopic

composition of He together with the Ne to He ratios indicate that the Mora well gases are composed of a mixture of pure radiogenic He and air derived noble gases, with no noticeable contribution from the mantle (Figure 8).

The relatively low salinity of the aquifer water together with its shallow depth and its high permeability through a dense fracture network seem to indicate that the gas-rich aquifer is dynamic. This would imply a short residence time of the water. If this hypothesis holds (needs verifications, see details in the perspectives section), it would argue for a dynamic recharge of gas into the aquifer, indicating that the gas is actively, or has very recently been fluxing into the aquifer.
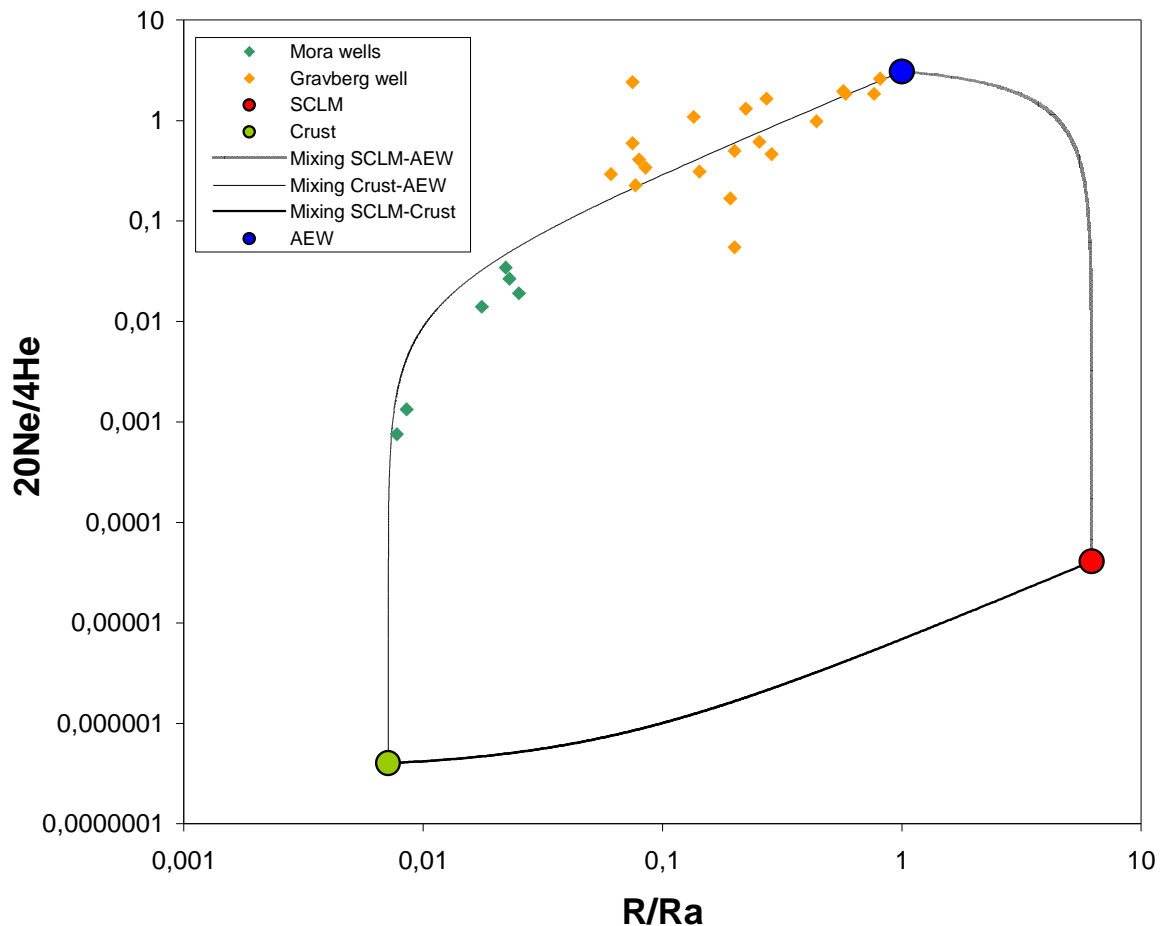
Figure 8: *Mixing diagram for He isotopes and Ne between air equilibrated water (AEW), the sub continental lithospheric mantle (SCLM) and the radiogenic crust. R/Ra stands for the air normalized He isotopic ratio. End member compositions elaborated from Gautheron et al., 2002; Holland and Ballentine, 2006; Gilfillan et al., 2009.*

2-Methane origin: bacterial, thermogenic, or inorganic?

The origin of the natural gas present at any level in the subsurface can usually be tracked using the combination of various stable isotopes and noble gases. In this chapter, we will compare the Mora gases based on our results with what is known of stable isotopes and noble gases from the earth science community worldwide.

In the following diagrams, the data from Mora wells are compared to the data from Gravberg well, when available, and to the data from the Wilson well in North-eastern Kansas, where methane and hydrogen gases are observed in a similar cratonic environment close to

Precambrian basement. The methane in the Wilson well is believed to be have a thermogenic origin that mixed with a bacterial component.

The Bernard Diagram (Figure 9) allows to distinguish between bacterial, thermogenic and inorganic gases using molecular ratio of the lighter hydrocarbons and the isotopic ratio of methane carbon. The Mora well gas samples plot in the mixing trend between bacterial and thermogenic origins, similarly to Wilson well gas. In comparison, the Gravberg samples are to the right of the thermogenic field, in the abiotic domain.

In the CD diagram (Figure 10), the Mora gases plot in the bacterial field to the left border of the methyl fermentation field.

Comparing the isotopic ratio of CO_2 and CH_4 carbon (Figure 11), the values for the Mora gases indicate a mixed origin of the CO_2 and methane from methyl fermentation to CH_4 oxidation. Indeed, the low concentration of CO_2 in gases is probably the result of subsurface oxidation of CH_4 by micro-organisms.

In the light of these results, we can conclude that the process by which methane was generated is bacterial, with a potential minor contribution from a thermogenic gas source (ethane?). However, we can not exclude the possibility that a thermogenic source is at the origin of the gas, but only a diffusive migration would allow a thermogenic source to have such molecular, stable isotope and noble gas compositions.
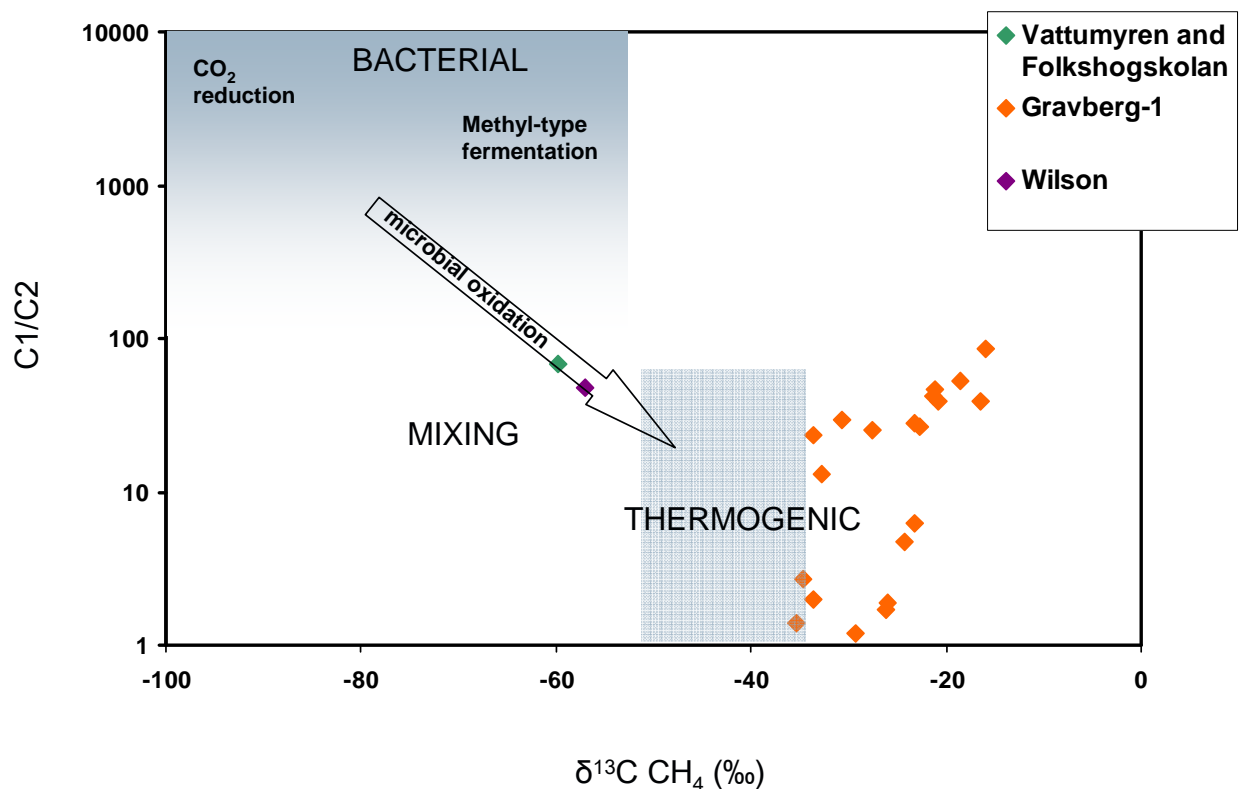

Figure 9: "Bernard diagram" after Whiticar, 1999. Wilson sample from Newell et al., 2007. Gravberg samples from Jeffrey and Kaplan, 1988
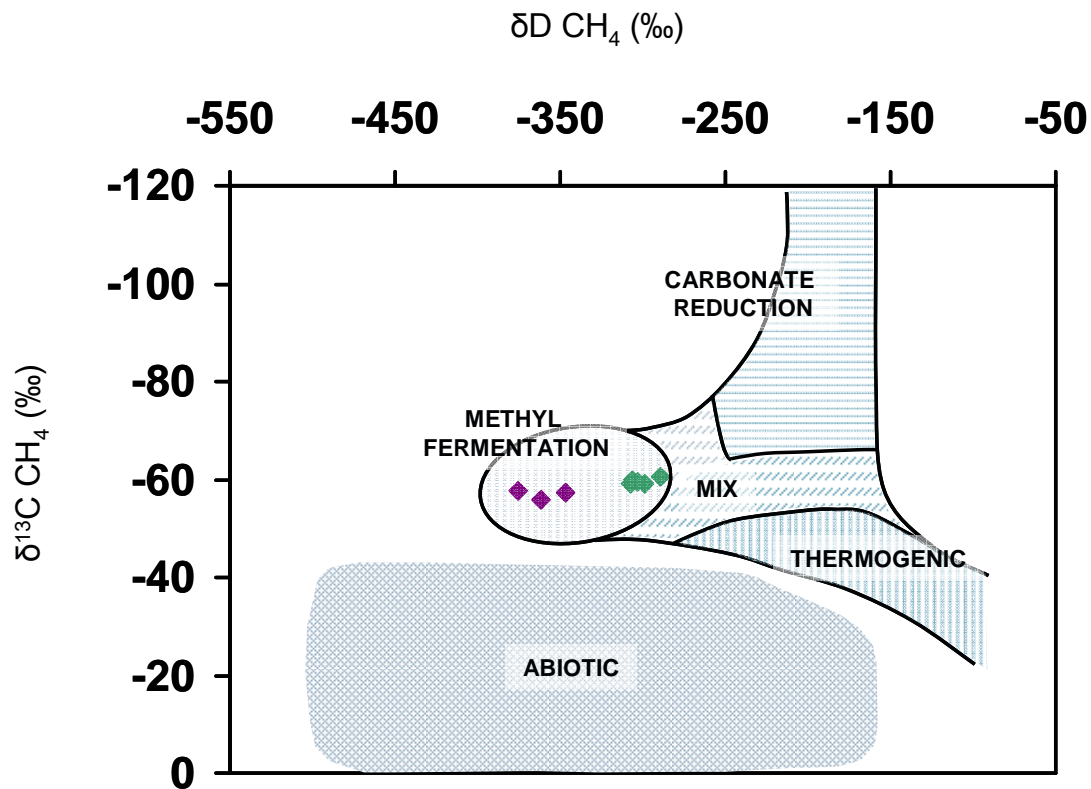
Figure 10: CD-diagram for the Mora and Wilson samples (after Whiticar, 1999). Wilson sample from Newell et al., 2007.
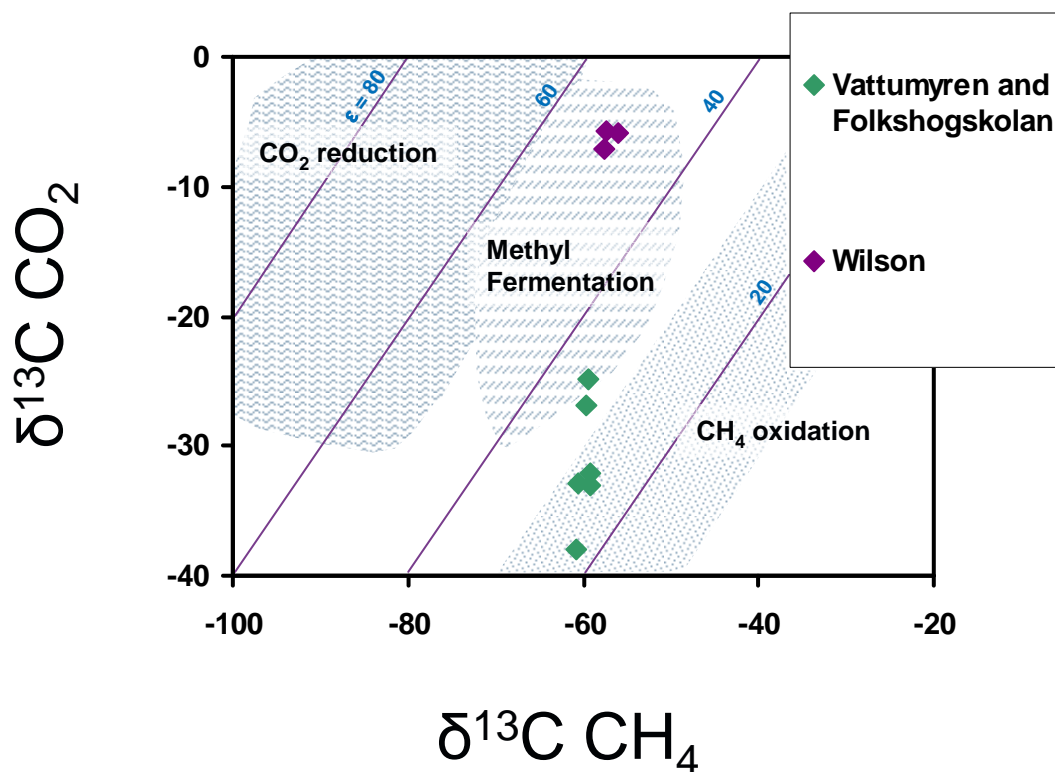

Figure 11: The $\delta^{13}C$ of methane versus the $\delta^{13}C$ of CO_2 for the Mora and Wilson samples (after Whiticar, 1999). Wilson sample from Newell et al., 2007.

The production of methane by bacterial activity may be a consequence of the combination of variable metabolic pathways (Figure 12). Methanogens can be either of the

autotrophic type, using CO_2 as an inorganic carbon source, or heterotrophic such as the acetate based acetoclastic type (Figure 13). Methane can itself be oxidized to CO_2 by methanotrophic bacterias. These different types of bacterial activities are expressed variably in different aquatic environments, a distribution conditioned by the availability of the different nutrients and ultimately the redox conditions of the environment (Figure 12). In the freshwater environment of the Mora gas occurrence aquifers, acetoclastic and autotrophic methanogens may operate. The dominance of either types will be dictated by the availability of both dissolved CO_2 and bio-available organic molecules. In both cases, molecular hydrogen plays a key role either as a primary compound or as a reaction intermediate in the synthesis of methane (Figure 14). The formation of acetate from more complex organic molecules by fermentative acetogenic organisms induces a bacterial H_2 production. Molecular hydrogen may also be produced by inorganic water hydrolysis if the necessary redox conditions (at least) are met.

The carbon sources for autotrophic bacterial methane synthesis may be either the dissolved CO_2 from carbonate rocks or derived from the atmosphere. The carbon source for acetoclastic organisms may be found in organic rich sedimentary rocks covering the gas-rich aquifers (Silurian shale) or in non-localized potential hydrocarbons equivalent to the seepage found in the eastern part of the structure (carbonate rock quarries stained with oil).

The source of hydrogen for autrophic methanogens could therefore be found as the by-product of acetogenic organisms developed on either of both suggested organic carbon sources. An alternative hydrogen source could be derived from fluid-rock interactions at depth inducing the hydrolysis of water. This hypothesis seems reasonable, since the presence of mafic rocks (Diorite) at depth was demonstrated, and that iron oxide mineralizations occur massively in the fracture network of the Siljan granite (Donofrio et al., 1984). Both evidences are consistent with the presence of a reduced Fe(II) source at depth, and its possible oxidation to Fe(III), which could be associated with the production of abiotic H_2.
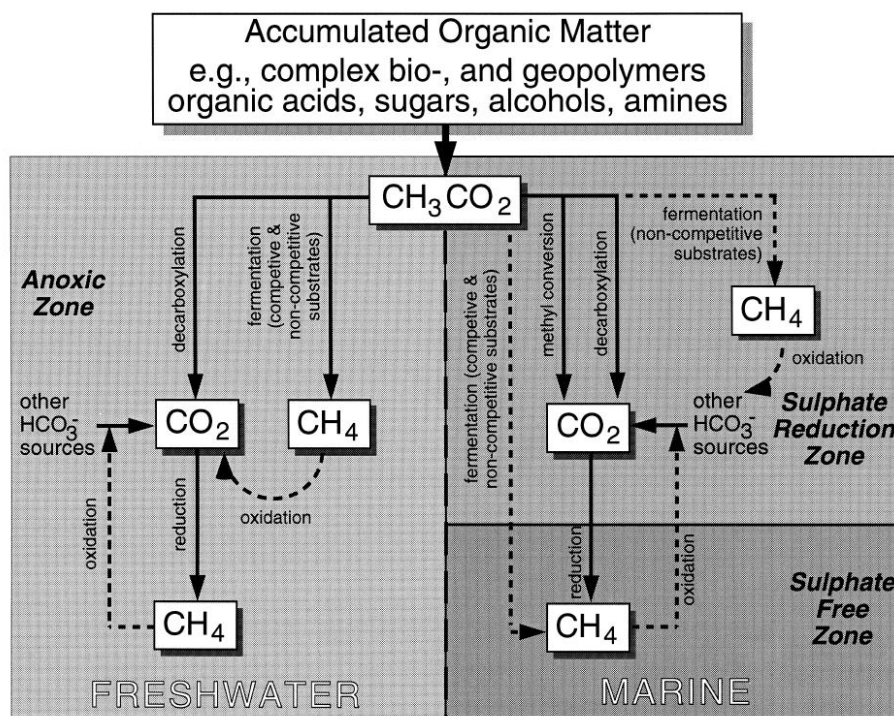

Figure 12: The methanogenic pathway in marine and terrestrial environments (Whiticar, 1999)
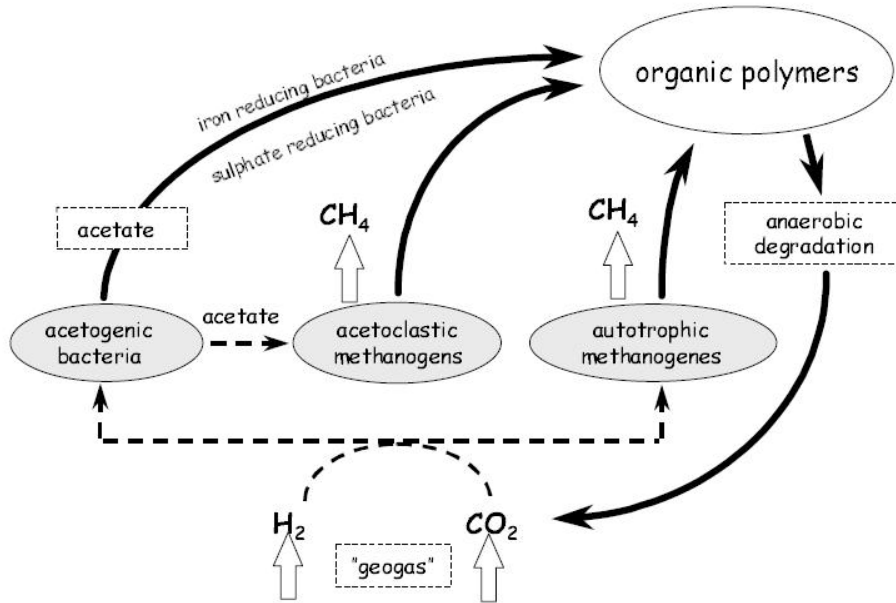
Figure 13: The deep hydrogen driven intra-terrestrial biosphere hypothesis, illustrated by its carbon cycle (Pedersen, 1999)
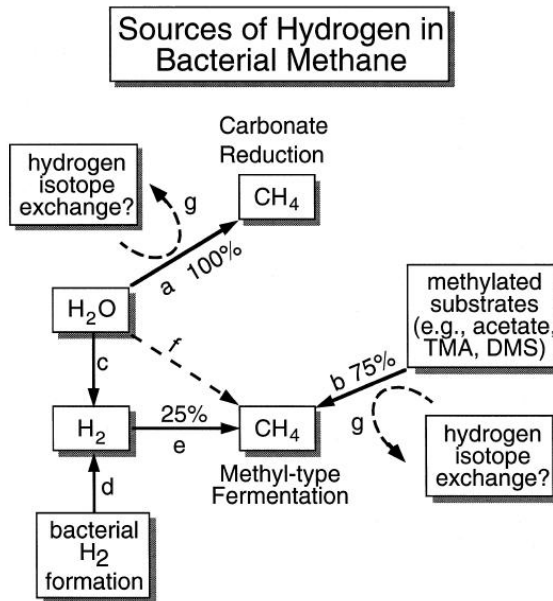

Fig. 9. Sources of hydrogen incorporated into methane through the carbonate reduction and methyl-type fermentation methanogenic pathways. The letters refer to pathways: (a) is the direct utilization of water–hydrogen during carbonate reduction, with an associated isotope effect (ε_H) of 160; (b) is the direct transfer of methyl–hydrogen from the organic matter (δD_{org} ca. $-80‰$); (c) is the dissociation of water to hydrogen gas either inorganically or via biological processes; (d) is the direct synthesis of hydrogen gas by bacterial activity, e.g., acetoclasts; (e) is the incorporation of hydrogen gas as the final hydrogen into the methane molecule (the magnitude of the isotope effect is poorly constrained); (f) is a potential direct utilization of water by methanogens during fermentation.

Figure 14: The different sources of hydrogen for methanogenic pathways (Whiticar, 1999).

E - Preliminary conclusions

Current results give indications for a dynamic recharge of methane in the aquifer in relatively recent timescale, although the temporal and spatial aspects of this recharge need to be better assessed (extent of methane stock zone, rates of recharge, location of stock zone, nature of the recharge migration process) for further estimation of economical interest.

Further investigations imply to test different possible scenarii for the origin of the methane. Two scenarii are listed below, considering known occurences of natural gases elsewhere in the world.

*1.* **Bacterial gas derived from the sedimentary rock system.**

The carbon isotopic composition of methane (-60‰) and the methane/ethane ratio (<200) are typical for bacterial gas. In this context, bacterial gas may originate from organic compound fermentation and/or from CO_2 reduction. The syntrophic consortium of acetogens and methanogens with both fermentative and oxydative pathways can coexist and promote the formation of bacterial methane without residual CO_2, which is the case for the gas found in the Mora wells (CH_4/CO_2 near 100). The required source of organic compounds for the methanogens to operate may be found localy in the Silurian and Ordovician layers just caping the gas-rich aquifers, and/or as the oil stains in carbonate rocks (although not observed in the Mora area). These sedimentary rocks could potentially provide the sufficient radiogenic contribution to explain the enrichment of the aquifers in ^{4}He, whereas the oil stains would not. The stratigraphic configuration at the Mora wells would require the bacterial gas to be migrated from the shales to the underlying aquifers by diffusion or advection through a fracture network. Upwards migration would not be recorded as the absence of a shallower caprock would not allow to retain the gas flow, which would rapidly dissipate to the atmosphere. This first scenario justifies the absence of gas in aquifers not caped by the sedimentary rocks, and the geochemical signature of the gas, both in stable isotopes and in the noble gases.

With this scenario, we propose the following workflow to progress in the understanding of the gas origin and of its importance as a resource:

1. Assessing the sedimentary rocks gas potential by analyzing the trapped gas after crushing in inert atmosphere (stable isotopes, noble gases)
2. Methane and dissolved CO2 radiocarbon age (^{14}C carbon age of the methane and of the dissolved inorganic carbon)
3. Aquifer age below and outside the sedimenary ring (Tritium age of the aquifer water)

2. **Abiotic methane synthesis supported by inorganic H2 production**

The geochemical data remain compatible with an inorganic origin of methane. This could occur by water hydrolysis producing H_2, and then CO_2 being reduced to CH_4 according to the following reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
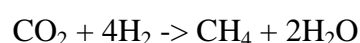
(Here with the electron donor being an Fe(II) bearing mineral phase) This hypothesis is supported by the presence of H_2 in several gas measurements around the Siljan Ring structure, the presence of dolerite dykes in the vicinity of the structure (an Fe(II) bearing rock-type), together with Fe(III)-oxide precipitates in the granite fractures of the area. This abiotic H_2 flux would then require to be oxidized (or metabolized by autotrophs) by a CO_2 source (carbonate reduction) in the subsurface, which could be provided by carbonate rock dissolution, or atmospheric CO_2 circulation in the shallow aquifers (eventually acetoclastic organisms). Considering the observed carbon isotopic composition of methane (-60‰), the carbon isotopic composition of the potential CO_2 sources (between 0 and -5‰) requires a low reaction temperature for the CO_2 to CH_4 conversion (favoring a bacterial rather than inorganic methanogenesis). This would imply a relatively shallow reaction zone. With this hypothesis, little arguments may explain the occurence of methane only below sedimentary units, appart from the sediments acting as efficient caprocks.

With this scenario, we propose the following workflow to progress in the understanding of the gas origin and of its importance as a resource:

1. Quantification of hydrogen fluxes around the Siljan structure (fieldwork)
2. Identification of potential shallow CO_2 sources (bibliographic review)

F – Summary

Exploration results to date indicates the presence of an oil & gas systems in the Siljan's ring, while a dynamic gas accumulation in the Precambrian basement aquifer exists. The gas production is not strictly linked to the thermogenic maturation of subsurface sediments such as in most conventional petroleum systems.

From the analysis of the drilling cores made in the Western area (southwest of Mora), it was concluded that the shale sedimentary layers could constitute the cap rock and the Precambrian basement constitutes the reservoir. The shale sedimentary layers according to conventional view can act as a cap rock for existing reservoirs, a source of organic carbon for oil production and biogenic production of gases.

The extent of the methane reserves is process-controlled and the understanding of the methane origin is a key point. Nevertheless, appropriate thermodynamic and noble gas study can be used to evaluate these reserves based on different solubility properties of noble gases in major gas phases. Such a study will be initiated on new samples from October field campaign. We strongly suggest to continue the investigations on the basis of the present document, and following our future work recommendations.