



Project acronym and title:

**SECURE – Subsurface Evaluation of Carbon capture  
and storage and Unconventional risks**

**DEVELOPMENT OF A DOWNHOLE SAMPLER AND  
AN INTEGRATED ANALYSIS SYSTEM FOR IN SITU  
DEEP FLUIDS ANALYSIS INCLUDING NOBLE  
GASES**

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## Public introduction

Subsurface Evaluation of CCS and Unconventional Risks (SECURE) is gathering unbiased, impartial scientific evidence for risk mitigation and monitoring for environmental protection to underpin subsurface geoenergy development. The main outputs of SECURE comprise recommendations for best practice for unconventional hydrocarbon production and geological CO<sub>2</sub> storage. The project is funded from June 2018–May 2021.

The project is developing monitoring and mitigation strategies for the full geoenergy project lifecycle; by assessing plausible hazards and monitoring associated environmental risks. This is achieved through a program of experimental research and advanced technology development that includes demonstration at commercial and research facilities to formulate best practice. We will meet stakeholder needs; from the design of monitoring and mitigation strategies relevant to operators and regulators, to developing communication strategies to provide a greater level of understanding of the potential impacts.

The SECURE partnership comprises major research and commercial organisations from countries that host shale gas and CCS industries at different stages of operation (from permitted to closed). We are forming a durable international partnership with non-European groups; providing international access to study sites, creating links between projects and increasing our collective capability through exchange of scientific staff.

## Executive report summary

This report presents the results obtained during two missions for testing the downhole sampler and the integrated analysis system developed by IFPEN and SEMM Logging. This equipment has a very strong innovative character at several levels:

- The manufacture of a specific downhole sampler (patented by IFPEN and its industrial partner SEMM Logging, developed with industrial partner ANTARES) that does not exist on the market: taking into account the requirements of the desired “cleanliness” of the sample until its transfer into the geochemical analysis chain.
- Innovative transfer protocol from the sampler to geochemical analysis.
- Transfer of the geochemical analysis chain conventionally used in the laboratory as close as possible to the sample on the site, in a borehole measurement cabin.
- The tightness of the downhole sampler which allows the identification of noble gas content (in gas and/or dissolved form). Mass balances can also be calculated with these natural inert chemical tracers. In addition, a specific software package has been developed to determine the content of the noble gases of a gas/brine mixture according to physical/thermodynamic parameters such as pressure and temperature. Results are thus representative for different depths; they also take into account dissolution and diffusion rates of the species. The software package should help designing a monitoring strategy.

Two on-site missions have been realized in Switzerland on two different wells: GEO-1 and GEO-2. The first mission on GEO-1 has allowed to highlight an important air contamination (>90%) and that the T555 unit was not adapted to fluid with low GWR. Based on these observations, three main modifications have been made. The results of the second mission show that our process has been improved between the two on-site field tests and became robust. The atmospheric contamination was reduced from more than 90% to 3.5% and an excellent repeatability of the gas composition measurements was reached (< 5%). The results show an increase in the quality of GWR measurements and specifically for low GWR (value < 0,02). The analysis of the geochemical composition of the dissolved gas of this second mission gave major information regarding both the origin of the gas and the hydrogeology of the zone with the detection of a gas arrival or accumulation at 800 m depth.



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# 1 INTRODUCTION

The downhole sampler and the integrated analysis system supply to a need of characterization and monitoring of deep fluids. Gas, noble gases and isotopic compositions are essential parameters for gas storage/formation comprehension and accident prevention. A known disadvantage of conventional industrial sampling equipment is the outgassing of volatiles from its in-depth sampling to compositional and isotopic analysis in laboratory. The establishment of a monitoring system requires sampling and analyses of fluids (water, gas, oil) in the field in situ and therefore specifically designed tools and methodology.

With the development of this package, IFPEN and its industrial partner SEMM Logging provide a new way of understanding of the quantification of major gases and traces on location, whether they are oil, geothermal or storage sites. This contribution will lead to :

- A better quality analysis by maintaining the physical constants present at the time of sampling and quality transfer.
- Time saving on calculating results thanks to reliable geochemical analysis directly on site. With the possibility of adapting the sampling according to the first results on site.
- A significant financial gain for customers who will obtain results within a very short time and be able to make quicker, informed business decisions.
- A partial or total end of the transfer of pressurized cells by conventional means of transport which are becoming increasingly complex for safety reasons.
- A cohabitation of a cutting-edge geochemical analysis activity and a conventional drilling measurement activity by pooling site units.

Our role in work package 4.1.3 was to test on the field and to validate the tool and the integrated analysis system to make in situ measurements of physico-chemical parameters of water, Gas to Water Ratio and gas composition. The tool recovers samples representative of prevailing conditions in a reservoir or aquifer and can therefore be used to monitor the composition of produced or stored gas and can be an early warning system for leak detection.

Over the duration of the project SECURE, IFPEN and its industrial partner completed first tests of the downhole sampler and the integrated analysis system on the field. This part includes:

- (1) Samplings at different depths in the subsurface to establish a baseline of the geochemical species. Along with sample acquisition, physical parameters were measured.
- (2) A fluid transfer and analyses (thermodynamical and geochemical determination) of deep gases (and dissolved gases): Major gases composition (CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, C<sub>1</sub> to C<sub>4</sub>), isotopic signatures of <sup>13</sup>C and <sup>2</sup>H and noble gas composition (Ar, He).

In a first part of this report, we will introduce the technical aspects of the downhole sampler and the integrated analysis system. In a second part we will present the first field tests and proceed with the deep fluids analysis in the conclusion.



## 2 TECHNICAL PRESENTATION

IFPEN and SEMM Logging have collaborated to develop an innovative mobile cabin with a downhole sampler. This collaboration was partly associated to the GECOSAMPA project funded by ADEME (Ricroch et al., 2020).

The use of the downhole sampler and the integrated analysis system is divided into 3 consecutive steps : (1) sampling the deep fluids at reservoir conditions, (2) fluid transfer in the T555 unit with the gas to water ratio (GWR) and gas composition measurement, and (3) the calculation of dissolved gas composition at reservoir conditions (pressure, temperature and salinity) (Figure 1).

The first step is made possible by a specific tool designed by IFPEN and constructed by ANTARES (the subcontractor of SEMM Logging in Germany): the downhole sampler. It will be presented in Section 2.1. The sampled fluid is then risen to the surface and transferred to equipment localised in a cabin for specific measurement (step 2 and 3). This will be presented at a later stage in Section 2.2.

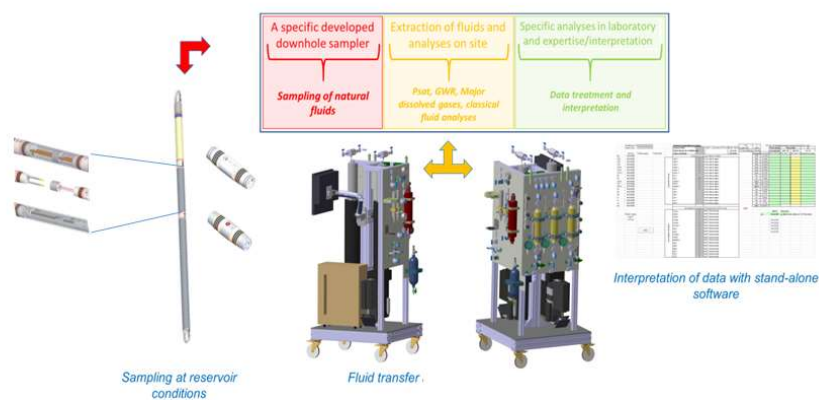


Figure 1: The three parts of the complete deep gas analysis device

### 2.1 THE DOWNHOLE SAMPLER

The downhole sampler was designed to collect any type of fluid (water / oil / gas) with a sufficient volume and without any contamination or leakage to analyse the geochemical composition of the gas/dissolved gas with high sensitivity e.g. possibility to use it for noble gas analysis. It had also to respect the following functional and operational specifications:

- The possibility of integrating the sampler as a module in an existing and already very complete tool set. This point was essential because it directly positioned the sampler as an additional element of a set already validated and recognized as a benchmark in the logging market ;
- The ease of use and maintenance ;
- The ease for transferring the sampled fluid to a transfer cell for gas analysis ;
- The ease of disassembly for cleaning after each use.

Based on these specifications, ANTARES designed the sampler shown in Figure 2. Its technical characteristics are summarized in **Error! Reference source not found.** The sampled fluid is collected then preserved in the sample chamber with the opening/closure of the chamber door that is motorised and controlled in real time from the surface. The temperature and the pressure at the sampling depth are not maintained but it is possible to re-compress the sample at the reservoir pressure when the sampler is at the surface. Indeed, the current design includes a variable volume sample chamber and a pressure compensation which allows us to control the surface pressure.

The sample chamber is leak-tight and enables the fluid integrity from the reservoir sampling point to surface. During the operation, pressure, temperature, depth and the volume of sampling are recorded by telemetric measurement thanks to upper and lower electronics.

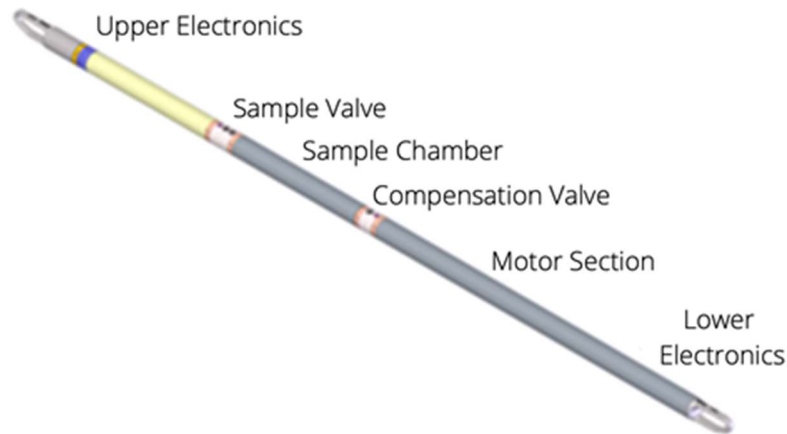


Figure 2: Downhole sampler

Table 1: Technical characteristics of the sampler

Parameters	Values
Pressure max	35 Mpa
Temperature max	125°C
External diameter	63.5 mm (70 mm with stand-off)
Maximum sampling volume (variable)	600 mL
Weight	38 Kg
Material	Stainless steel <sup>1</sup>
Temperature measurement uncertainty	±0,05°C
Pressure measurement uncertainty	± 0,2 MPa
Minimum borehole pressure to operate valves	2 MPa
Length	2.5 m

The sampler was designed to measure in real time the following specific data:

- time
- descent/ascent speed
- depth
- cable tension
- motor voltage
- temperature
- external pressure
- pressure in the sampling chamber
- the collected fluid volume in the chamber

<sup>1</sup> There are limitation in H2S use as the material used to design the sampler are of 3 types : austenitic + martensitic + Titan alloys with high resistance to tensile strength up to 720 MPA. For austenitic stainless steel 316, the limits for use are 60 ° C and 1 bar of H2S (or alternatively 3.5 bar of H2S if the chloride content is less than 50 mg / L). For martensitic, the limit is given at 34 mbar of H2S and a pH which must be greater than 4.5 For titanium, no use limit under the conditions usually encountered in O&G production.





- Gamma Ray (GR)

The sampler was validated as part of the GECOSAMPA project (ADEME funding, Ricroch et al., 2020) both in laboratory and in real conditions.

Three different tests have been carried out to verify the robustness of the downhole sampler in the laboratory of ANTARES in Germany:

- A sealing test was carried out injecting water in the sampler chamber with a piston-pump to increase the pressure up to 350 bar at ambient temperature. After 12 hours of test, no pressure decrease was observed, that validates the tightness of the sampler.
- The second sealing test was performed to verify the sampler's compatibility to conditions close to operational temperature and pressure. They tested the downhole sampler in an autoclave at 95°C and 250 bar. A sampling was done at these conditions. After a return to pressure and temperature surface conditions (25°C, 1bar) a verification is made to see if the pressure inside the sample chamber and the volume of the fluid sampled are conserved. It was verified.
- A specific gas SF6 (sulphur hexafluoride) was inserted into the sampling chamber. SF6 is an historic tracer of gas leaking. After a few minutes/and 12 hours, a SF6 detector was carefully passed around the downhole sampler and no gas leak was detected (ANTARES do not specify the detection limit of the detector).

In addition to the effective tests of the tools, the main objective was also to build a technical feedback on the deployment of all the equipment in particular on the ease of use of the sampler and the time of each step in the field. A validation test aimed to evaluate the equipment in real conditions was undertaken in an aquifer located in Bonnefont, in France with 2 samplings at 500 m and 1500 m depth. The logistics necessary for the implementation of the sampler on site takes about half a day. For the sampling, the expected time descent of the downhole sampler is 22 m/min and the ascent is 30 m/min.

## 2.2 THE CABIN



**Figure 3: "On-site" view of the cabin during GEO-2 campaign**

The 10 feet by 10 feet cabin (approximately 3 m x 3 m) (Figure 3) contains a sampling tool, a transfer cell to extract the gas phase (T555), a micro gas chromatograph ( $\mu$ -GC) to analyse the gas composition and a thermodynamic model (pc installed package) to predict the dissolved gas composition at different conditions.



The cabin is composed of different equipment. The packing list of the equipment is presented below (Table 2), including the order of magnitude of weight:

**Table 2: Equipment packing list**

	Weight (Kg)
μ-GC INFICON custom by Chemlys (7015052)	16
Primary pump DUO 3M Pfeiffer (N°PK 195 152)	30
Primary pump (16750058)	30
Pirani vacuum pressure transducer (sensor and viewer)	2
Specific sampler introduction (376506)	1
2 Pressure reducers Liquids	8
2 Pressure reducers Air Products	8
24 inch screen	1
Portable PC	3
T555 Unit	300
Argon gas bottle B20	30
2 Nitrogen gas bottles B20	60
Helium gas bottle B20	30
10 sampling tubes	5
Mettler analytical balance	10

One of the major advantages of the presented measuring tool in comparison to the existing industrial tools is the capability of keeping, transferring and analysing the sample while minimizing leaks and air contamination. Another main advantage is to deliver fluid composition analysis in a reduced time (0.5/1 day) and to optimize the experimental design of the fluid samplings according to the fluid analysis results. This cabin can be easily displaced by a truck on a site at different locations.

### 2.2.1 DESIGN WORK IN 3D

Design work with a 3D interior design software package has been carried out to optimize the area of the cabin, to secure the equipment and to ease the process of sampling, fluid transferring and gas analysing.

The view of the cabin designed with the CATIA software is presented below (Figure 4). This work was very useful to study the ergonomics of the cabin itself and the specific implementation of all equipment at an early stage of the design. The cabin being small, a 3D analysis review was very important at design stage to optimise the use of space and avoid potential clashes between different pieces of equipment at the design and build stage.

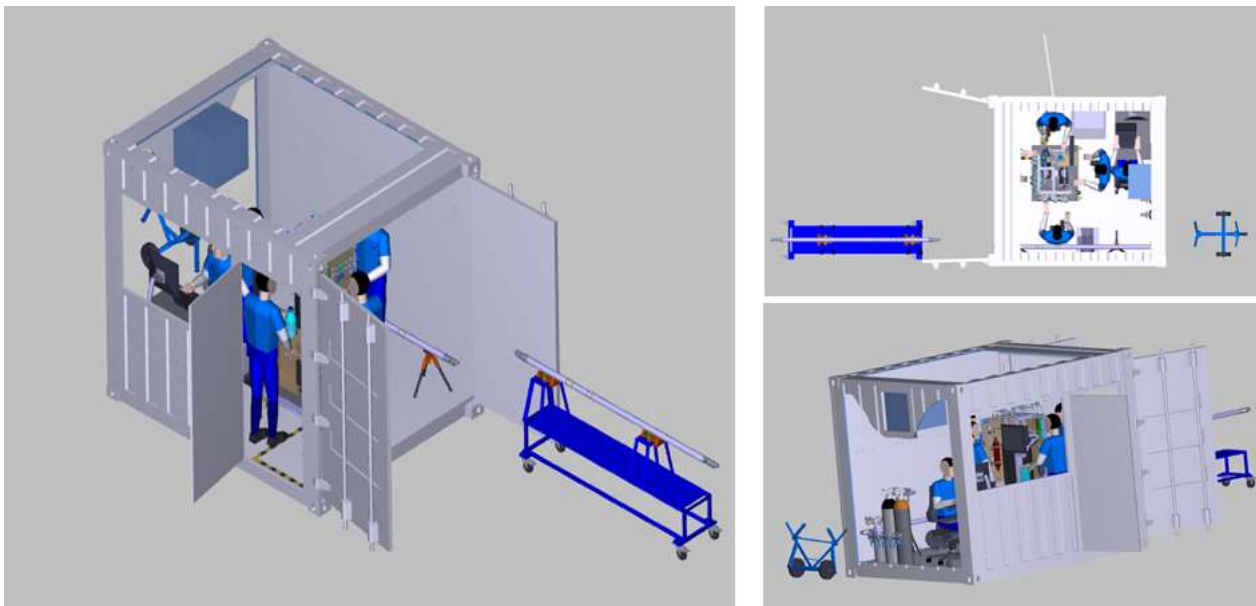


Figure 4: 3D conceptual view of the cabin

### 2.2.2 THE T555 UNIT

The T555 unit (Figure 5) allows the transfer of the fluid phase (1) into a calibrated volume dedicated to the gas-oil (GOR) or gas-water (GWR) ratio measurements, and then (2) into a micro-chromatograph ( $\mu$ -GC) for gas compositions analysis. This installation was also designed to measure the bubble point also called  $P_{sat}$ .

T555 consists of :

- 2 Quizix QX600-10K pumps. These allow to work under pressure for fluid samples (maintaining and increasing pressure). Their performance characteristics are: a maximum pressure of 700 bar, and a fluid rate ranges between 0,001 and 200 mL\*min<sup>-1</sup>.
- 3 transfer cells. They can contain a variable volume up to 300 ml at ambient temperature and resist to a pressure up to 350 bar. They are compatible with the following “in-situ” phases: light hydrocarbons (CO<sub>2</sub>, C1, C2, C3), H<sub>2</sub>S, crude oil, brines.
- a micro gas chromatograph ( $\mu$ -GC) which measures the gas composition of the extracted fluid. It is an INFICON  $\mu$ -GC customized by Chemlys (specific low volume gas introducer). The  $\mu$ GC is composed of three modules with a micro TCD detector : the first one with Argon as gas carrier measures H<sub>2</sub>, He, N<sub>2</sub>, O<sub>2</sub> with a 10m MS5A sieve, the second one with Helium as gas carrier measures O<sub>2</sub>, Ar, N<sub>2</sub> and CH<sub>4</sub> thanks to 20m MS5A sieve, the third one with Helium as gas carrier measures C2 to C4, H<sub>2</sub>S and CO<sub>2</sub> with 12m RT-Q Bond. The gas composition is given in molar fraction (mol%). The molar fraction variation of the gas composition in mol% is 5%. The detection limits are about 1 to 10 ppm depending on the species.

T555 is also composed of a fluid pressure maintenance system (BPR<sup>2</sup>). Valves, fittings, lines, tubes are in HASTELLOY® C-276<sup>3</sup>.

<sup>2</sup> A BPR valve is a device that maintains a defined pressure upstream of itself, at its own inlet. When fluid pressure at the inlet exceeds the setpoint, the valve opens to relieve the excess pressure for safety reasons.

<sup>3</sup> Alloy C-276 has excellent resistance to pitting, stress-corrosion cracking and oxidizing atmospheres up to 1900°F. Alloy C-276 has exceptional resistance to a wide variety of chemical environments. To be more specific, due to its high nickel content, Alloy C276 is immuned to stress corrosion cracking due to chlorides. The alloy's high molybdenum and chromium contents allow it to withstand oxidizing, non-oxidizing and mixed acid environments, while exhibiting exceptional resistance to pitting and crevice corrosion. The addition of tungsten prevents the development of pitting. Finally, C276 is suitable for offshore applications where resistance to hydrogen sulfide (H<sub>2</sub>S) stress corrosion cracking is essential.

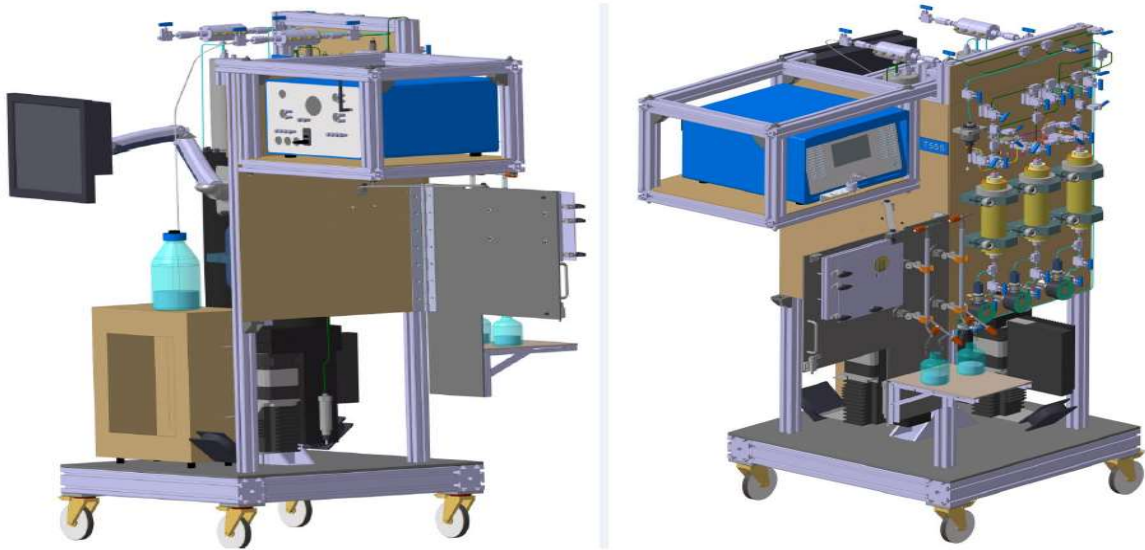


Figure 3: T555 unit with associate chromatograph

**Psat (saturation pressure) measurement**

For a given temperature, Psat is the pressure at which the gas is released from the liquid phase. The sample is therefore no longer monophasic but contains two phases.

After transferring the sampled fluid into a piston cell, the fluid is depleted by flow regulation (rate set at 1-2 cc/h) using the Quizix QX600-10K pump. The Psat is therefore the value corresponding to the break in the pressure slope (Figure 6).

**GWR or GOR measurement (Gas-Water Ratio or Gas-Oil Ratio)**

This is the volume of the gas phase versus the liquid phase (water or oil) at surface conditions.

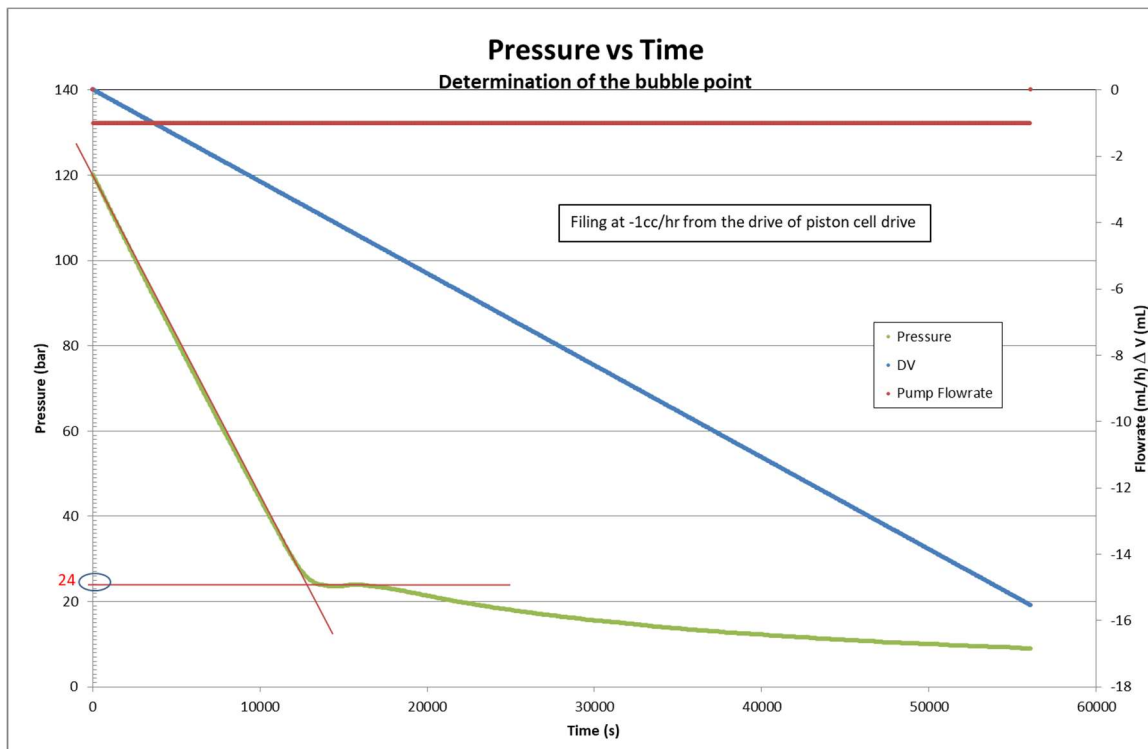


Figure 4: Psat determination – Pressure monitoring example



### 2.2.3 DATA ACQUISITION

The data measured with the T555 unit are used as input data of the thermodynamic model developed by IFPEN and described below in the following sections.

### 2.2.4 THE THERMODYNAMIC MODEL

The thermodynamic model has been developed by IFPEN Thermodynamic Department. It aims to validate the experimental results by comparison with the model results or to estimate the fluid composition at different temperature and pressure conditions from the measured gas composition at surface conditions.

It is used to define phase equilibrium between water, salt and gaseous components such as methane, CO<sub>2</sub>, N<sub>2</sub> and noble gases. The procedure starts by using the Soreide & Whitson et al., 1992 approach. This model is an adaptation of the Peng Robinson equation of state (EoS) whose form is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2+2vb-b^2}$$

Where P is the pressure and of the system, T is its temperature, v is the molar volume. This equation has two parameters: the covolume b and the attractive term a(T). The covolume of a phase is expressed by the following mixing rule:

$$b = \sum_i x_i b_i$$

Where x<sub>i</sub> is the molar fraction of the component and the covolume of each compound is given by:

$$b_i = \frac{0.07780RT_{c,i}}{P_{c,i}}$$

a(T) is the attractive term, two attractive terms have been determined, one for the non-aqueous phase and one for the aqueous phase:

$$a^{na} = \sum_i \sum_j y_i y_j \sqrt{a_i a_j} (1 - k_{ij}^{na})$$

$$a^{aq} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}^{aq})$$

Where x<sub>i</sub> and y<sub>i</sub> are the molar fractions in the aqueous and non-aqueous phase. The attractive term of each component is given by

$$a_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha(T_{r,i})$$

There are also different formulations for the α term, two relatives to the non-aqueous component:

$$\alpha(T_r) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})]^2 \text{ with } \omega < 0.49$$

$$\alpha(T_r) = [1 + (0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3)(1 - \sqrt{T_r})]^2 \text{ with } \omega \geq 0.49$$

and one relatives to the aqueous or brines component (salt water is considered to be a pseudo-compound):

$$\alpha(T_r) = [1 + 0.4530(1 - T_r(1 - 0.0103C_{sw}^{1.1})) + 0.0034(T_r^{-3} - 1)]^2$$

With

C<sub>sw</sub> = the salinity



$T_r$  = the pure water reduced temperature  $T_r = T/T_c$

The ways to express the evolution of the Binary Interaction Parameters (BIPs) as a function of reduced temperature and salinity of the aqueous phase and only function of the temperature for the non-aqueous phase. In their 1992 publication, Soreide and Whitson (1992) gave expressions of the  $k_{\text{water},i}^{\text{aq}}$  and the  $k_{\text{water},i}^{\text{na}}$  for the light hydrocarbons ( $\text{CH}_4$ - $n\text{C}_6\text{H}_{14}$ ),  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{N}_2$ .

In this work we extended these expressions to noble gases (He, Ne, Ar, Kr, Xe). BiP's depend on the values of  $T_c$ ,  $P_c$  and acentric factor of pure components. To do this work we used the values (Table 3) from the DIPPR database.

**Table 3: Parameters, from the DIPPR database, used to set the Binary Interaction Parameters**

	<b>Tc (K)</b>	<b>Pc (Pa)</b>	<b>Acentric factor (-)</b>
H <sub>2</sub> O	647.30	2.212e+007	0.3434
He	5.20	2270005	-0.39003
Ne	44.40	2653000	-0.03960
Ar	150.86	4898000	0.0
Kr	209.35	5502000	0.0
Xe	289.74	5840000	0.0

We have compiled the available experimental water-noble gas and brine-noble gas equilibrium data and regressed the model's binary interaction parameters. The model thus defined is used to represent multi-constituent systems.





### 3 FIELD RESULTS

Following the validation tests operated in ANTARES laboratory (Germany) and on the site in Bonnefont (France) (See Section 1.1) as part of the GECOSAMPA project, two additional field tests have been conducted by IFPEN and SEMM LOGGING within SECURE project to validate the full process of data acquisition by the downhole sampler and the integrated analysis system. Thanks to SIG (Geothermal stakeholder in Switzerland), the equipment has been tested on two geothermal wells in the Geneva Basin GEO-1 and GEO-2 (Figure 7). The first one led to technical changes for improvements in system robustness and system adaptability for low GWR. The second one validated the full process for GWR measurement and gas composition for deep gases with low GWR.

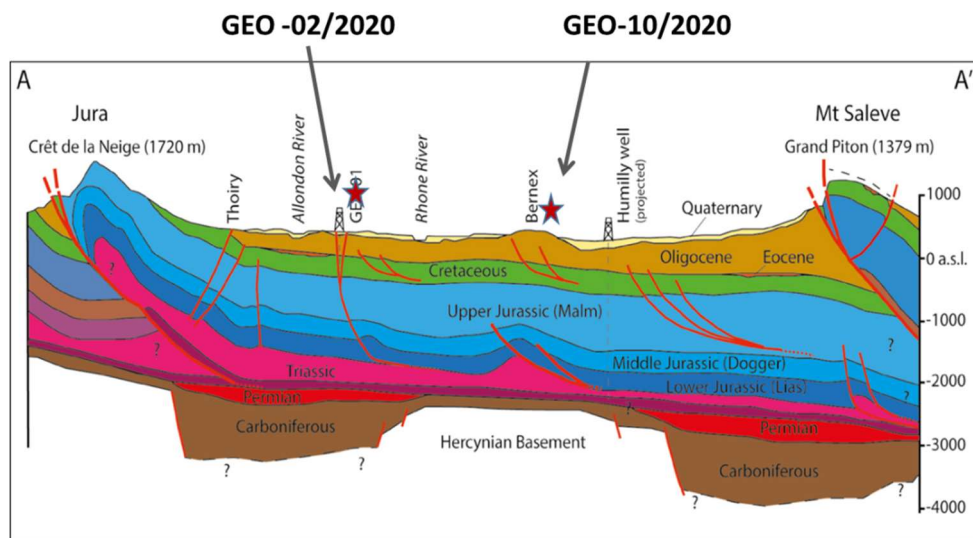


Figure 5: Geological cross-section of the Geneva Basin (McCann et al., 2006)

#### 3.1 SITE TESTS - GEO-1

The GEO-1 well is located in Satigny (Switzerland). It is an artesian well with a water flow rate of 5 l/s. The test has been conducted in 02/2020. Complex logistical support (three trucks) by SEMM Logging was necessary to deploy the entire device on site (Figure 8).



Figure 6: Logistic at Satigny site operating “GEO\_01 well”

Five samples were recovered at 200 and 400 m depth (Table 4). The sampler system worked well with relevant telemetry data and sample recovery. The transfer of the fluid, from the downhole sampler to T555 and from T555 to the  $\mu$ -GC, did not work properly which led to major air contamination. This explains the high values and the atmospheric ratio of  $N_2$  and  $O_2$  compositions observed with  $\mu$ -GC results (Table 5). The gas volumes were insufficient for gas analyses, leading to the requirement for the addition of an inert gas ( $N_2$  or He) and then a loss of sensitivity during our analyses. Several assemblies were tested and the system involving the smallest addition of inert gas was chosen (40% - Table 5). However, despite these issues, the result at different sample depths of gas compositions corrected from atmospheric contamination was in agreement with expected results from SIG.



The measured GWR were lower than 0.3 (Table 6). The GWR measurement method was not appropriate for such low gas volumes leading to inaccurate and non-repeatable measurements.

Also Psat measurements were conducted. The pressure at the sampling depth was not maintained but it is possible to re-compress the sample at the reservoir pressure to make this measure when the sampler is at the surface. Two tests of recompression were carried out but after about 12 hours, the fluids still remained two-phased so the Psat measurements could not be done. Several tests in laboratory have been carried out and have shown that the dissolution of the gas due to recompression could take a minimum of 48 hours (depending on gas type and quantity) that is not possible to envisage on site if we want to do one sampling per day.

**Table 4: GEO-1 Sampling and telemetric data**

	1	2	3	4	5
<b>Date</b>	10/02/20	11/02/20	11/02/20	12/02/20	12/02/20
<b>Hours</b>	11h36	10h59	14h00	10h44	13h56
<b>Depth (m)</b>	400	200	200	400	400
<b>T (°C)</b>	34.5	34.3	34.3	34.4	34.4
<b>P (bars)</b>	41.5 to 42	21.2	21.4	41.5 to 42	41.5 to 42
<b>Sampled Fluid Volume (cm<sup>3</sup>)</b>	570	255	565	200	565

After these first tests, it was internally decided to modify the T555 unit during 6 months (from 02/2020 to the end of 08/2020), in order to improve the robustness of the entire device. Three main modifications have been made:

- The design of a custom glass burette to adapt our system to low GWR (Figure 9).
- The reduction of the dead volume between the burette and the  $\mu$ -GC, to maintain as much gas pressure as possible (Figure 9).
- The improvement of the tightness of the entire system to prevent air contamination.

After a delay due to sanitary confinement measures, this upgrade was finalized in 09/2020 before going to the site in 11/2020 for another full test of the downhole sampler and the integrated analysis system on the GEO-2 well.



**Figure 7: Custom glass burette and optimized dead volumes between burette and  $\mu$ -GC**





**Table 5: Gas compositions measured and inert gas proportion according to assembly setting**

Test	Date	N°	Inert gas	μ-GC composition (%mol) (without inert gas)										Inert gas proportion (%)
				O2	Ar	N2	CH4	C02	C2H6	H2S	C3H8	i-C4H10	n-C4H10	
Geol-pvt1	10/02/2020	1	N2	<b>20,4</b>	2,2	<b>76,7</b>	0,014	0,594	0,001	nd	0,004	nd	0,004	<b>69</b>
Geol burette	10/02/2020	1	N2	<b>20,6</b>	0,9	<b>78,2</b>	0,048	0,193	nd	0,008	nd	nd	nd	<b>0</b>
Geol-pvt2-gazo	11/02/2020	2	N2	<b>20,5</b>	1,9	<b>77,0</b>	0,016	0,580	nd	nd	nd	nd	nd	<b>91</b>
Geol-pvt2-gazoPV	11/02/2020	2	N2	<b>20,6</b>	1,6	<b>77,5</b>	0,003	0,348	nd	nd	nd	nd	nd	<b>85</b>
Geol-pvt3-T40	12/02/2020	3	He	Non analyzed – too low quantity of gas										<b>68</b>
Geol-pvt3-T30-run1	12/02/2020	3	He	<b>20,4</b>	1,0	<b>78,5</b>	0,020	0,105	0,001	0,001	nd	nd	nd	<b>49</b>
Geol-pvt3-T30-run2	12/02/2020	3	He	<b>20,4</b>	1,1	<b>78,3</b>	0,047	0,163	0,003	0,003	0,004	nd	nd	<b>47</b>
Geol-pvt3-T50	12/02/2020	3	He	<b>20,5</b>	1,1	<b>78,4</b>	0,009	0,062	0,001	nd	nd	nd	nd	<b>49</b>
Geol-pvt3-T50	12/02/2020	3	He	<b>20,4</b>	1,0	<b>78,5</b>	0,023	0,102	0,002	0,001	0,002	nd	nd	<b>40</b>
Geol-pvt3-T50	12/02/2020	3	He	<b>20,3</b>	1,1	<b>78,5</b>	0,028	0,114	0,002	0,001	0,003	nd	nd	<b>40</b>
Geol-pvt4	12/02/2020	4	He	<b>18,2</b>	2,6	<b>78,7</b>	nd	0,513	nd	nd	nd	nd	nd	<b>96</b>
Geol-pvt5	12/02/2020	5	-	Non analyzed – too low quantity of gas										



**Table 6: Measurements of low GWR on Well GE\_01**

Date	N°	Depth (m)	Assembly setting type	Sampling/transfert	Inert gas	Water volume (cm <sup>3</sup> )	Gas volume (cm <sup>3</sup> )	GWR
10/02/2020	1	400	B1 + B2	Inox tube	N2	38	12	0,316
10/02/2020	1	400	B1 + B2	On-line analysis	N2			
11/02/2020	2	200	B1 + G	Inox tube GV	N2	277	23	0,083
11/02/2020	2	200	B1 + G	Inox tube PV	N2			
12/02/2020	3	200	B1 + G	On-line analysis	He	193	7,3	0,038
12/02/2020	3	200	B1	On-line analysis	He			
12/02/2020	3	200	B1	On-line analysis	He			
12/02/2020	3	200	B1	On-line analysis	He			
12/02/2020	3	200	B1	On-line analysis	He			
12/02/2020	3	200	B1	On-line analysis	He			
12/02/2020	4	400	B1 + G	Inox tube GV	He	233	7	0,030
12/02/2020	5	400	B1 inversée	Non analysed	-	565	0,5	0,001

### 3.2 SITE TESTS \_ GEO-2

The second field test GEO-2 is located in Bernex (Switzerland). As with the first test, logistical support from SEMM Logging was necessary to deploy the entire device on site (Figure 10).



**Figure 8: Logistic at Bernex site operating GEO-2**

Five samples were recovered from GEO-2 (Table 7). No gas was detected for samples 1 & 3. For samples 2, 4 and 5 composition of the gas phases have been measured (Table 8). The air contamination of the gas phases is less than 3.5%.



**Table 7: GEO-2 sampling and telemetric data**

Samples	Depth (m)	Fluid volume (ml)	T (°C)	P (bars)	Gas volume (ml)	GWR (-)
1	1361	570	51.9	133	No gas	0
2	880	570	39	90	9	0.15
3	996	570	42	101.5	No gas	0
4	880	570	39.1	89.7	9	0.15
5	800	570	37.5	81.5	12	0.2

The gas composition and GWR of same depth samples (2 & 4) present an excellent repeatability, especially as these GWRs are less than 0.2.

**Table 8: Composition of the gas phase (% mol)- \* corrected value relative to the O<sub>2</sub> content in the air**

Name	<sup>2</sup> analyses	He	H <sub>2</sub>	*O <sub>2</sub>	*N <sub>2</sub>	*Ar	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub> S	Total	% air
Test 2 – 880 m	Average	0.08	0.0015	0	38.7	0.92	59.7	0.62	0.016	0.001	0.024	100.000	3.5
	Std dev	0.01	0.0000	0	0.2	0.00	0.2	0.00	0.000	0.000	0,005		
Test 4 – 880 m	Average	0.07	0.0040	0	39.3	0.87	59.1	0.60	0.016	0.002	0.006	100.000	3.4
	Std dev	0.01	0.0003	0	0.3	0.04	0.3	0.06	0.000	0.001	0.001		
Test 5 – 800 m	Average	0.06	0.0103	0	39.1	0.92	59.3	0.55	0.016	0.001	0.005	100.000	1.5
	Std dev	0.00	0.0005	0	0.2	0.03	0.2	0.01	0.000	0.000	0.002		

Gas compositions are mainly constituted of CH<sub>4</sub> and N<sub>2</sub>, with significant proportions of CO<sub>2</sub>, He, Ar and traces of H<sub>2</sub>S, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>. These compositions are coherent with the conceptual model of Guglielmetti et al., (2019) which underline the arrival of a gas containing methane, helium and dihydrogen sulphur from deep tectonic structures.

The samples present similar compositions with an increasing GWR associated to the rise to the surface (Table 7). The compositions of dissolved gases in water (Table 9) at sampling depth conditions were calculated with the thermodynamic model (section 2.2.4). We noted that these measurements are strongly GWR dependent, mainly for low volumes of gas. The accuracy of GWR measurements is therefore crucial for determinations of the dissolved gas composition. The minimum volume of gas that can be measured for the GWR is 0.2 cm<sup>3</sup> (burette limit) and the minimum gas volume of gas required for the μ-GC analysis is 9 cm<sup>3</sup> (2 analyses μ-GC). This required volume implies to add inert gas to the gas extracted (for GWR < 0,01).

The H<sub>2</sub>S and CO<sub>2</sub> do not seem to be significantly more abundant at 800 than at 880 m but we observe a gas inflow/accumulation at 800 m which is mainly composed of CH<sub>4</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, He and Ar (Table 9).



**Table 9: Dissolved gas concentrations in water at P and T of sampling depth**

	Depht	T	P	CO <sub>2</sub>	H <sub>2</sub> S	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	H <sub>2</sub>	He	Ar
	m	°C	bars	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
Test 2	880	39	90	0,29	1,32E-02	3,1	6,88E-04	2,87E-06	0,33	3,90E-05	0,007	0,11
Test 4	880	39,1	89,7	0,29	3,40E-03	3,1	7,10E-04	8,34E-06	0,34	1,05E-04	0,006	0,10
Test 5	800	37,5	81,5	0,36	3,62E-03	35,8	9,57E-03	5,22E-04	21,92	6,04E-03	0,034	0,56

Gas samples were also taken after the GWR measurements for additional laboratory analysis: isotopic composition of carbon and hydrogen for CO<sub>2</sub> and CH<sub>4</sub> with the GCC-IRMS).

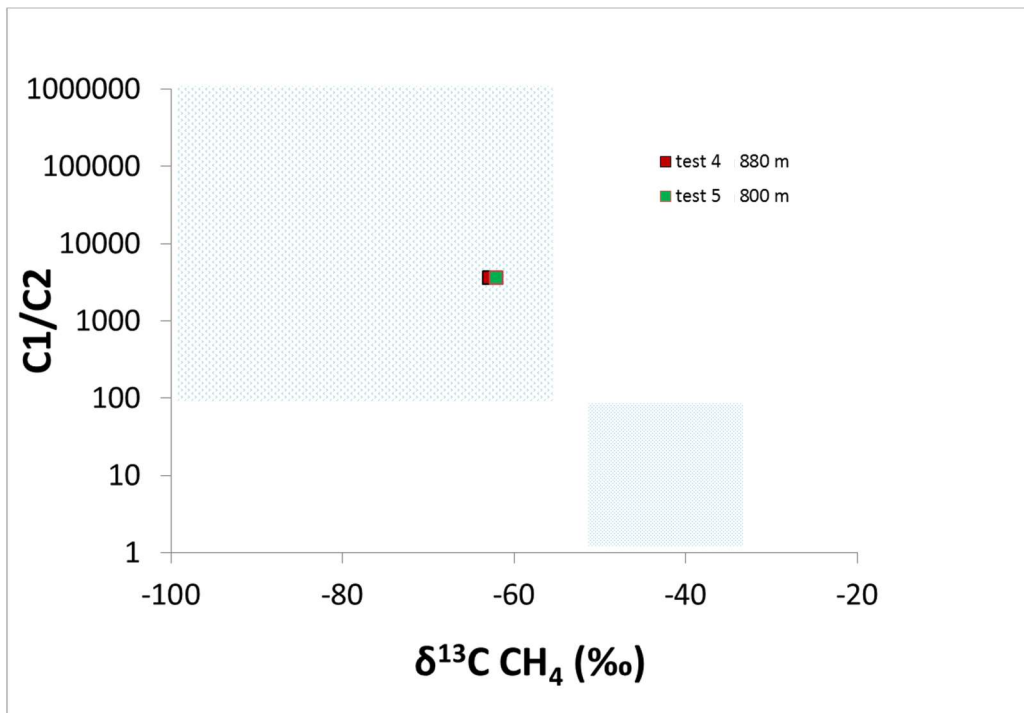
The CO<sub>2</sub> δ<sup>13</sup>C of the surface water sample was -1.5‰ which corresponds to classical values for carbon in equilibrium with carbonate rocks (Assayag, 2006).

The C and H isotopic composition of methane was measured in sample 4 and 5 (Table 10). They are similar with slightly more negative δ<sup>13</sup>C and positive δD in depth.

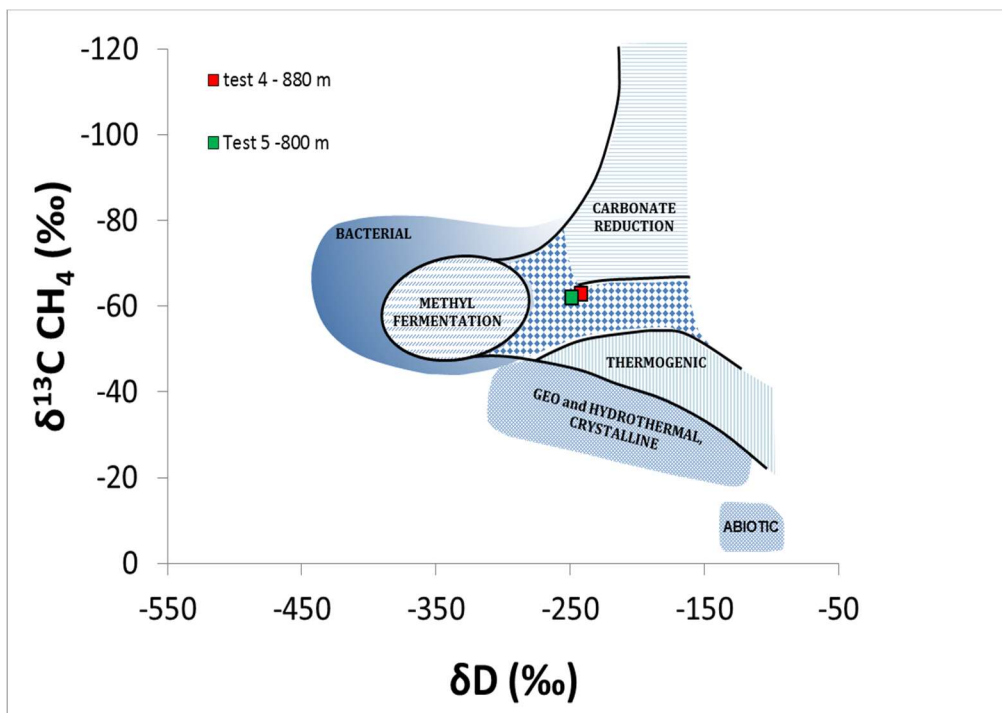
**Table 10: Isotopic compositions in C and H for CH<sub>4</sub> in sample 4 and 5**

	δ <sup>13</sup> C CH <sub>4</sub> (‰) écart type		δD CH <sub>4</sub> (‰) écart type	
Test 4 - 880 m	-62,93	0,11	-242,0	0,9
Test 5 - 800 m	-62,04	0,07	-249,1	0,2

These compositions can be used in classical geochemical diagrams to determine the gas origin (Figure 11 & 12). With these figures we can conclude that CH<sub>4</sub> is from biological origin, resulting from the carbonate reduction and methyl fermentation.



**Figure 9: C Isotopic composition of CH<sub>4</sub> vs CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>**  
- ratio in mol% (modified from Bernard, 1978)



**Figure 10: D Isotopic composition of CH<sub>4</sub> vs C**  
Isotopic composition of CH<sub>4</sub> (modified from Whiticar, 1999)



These samples gave very important information on the origin of the gas and to go further a specific sampling for noble gas isotope composition will be very interesting (as for Helium and Argon).

Hence, the first encouraging data results acquired and associated calculations are key results at this stage for a better understanding of the hydrogeology of the well: this set of data shows a gas arrival or gas accumulation at 800 m depth.

## 4 Conclusion & Perspectives

Developing and validating a downhole sampler and an integrated analysis system at R&D stage is a long process which can take several years. IFPEN has successfully validated the downhole sampler incrementally, first at the specification stage with the help of ANTARES and secondly on the design stage with validation tests performed in their factory.

Two on-site missions have been realized with difficult sanitary conditions. It has to be mentioned that these missions have been possible thanks to both the reactive logistic deployment of SEMM Logging and the contribution of SIG for their acceptance of HSE guidelines on site of GEO-1 and GEO-2 in Switzerland. The field measurements were essential to validate the sampler and the integrated analysis system.

The first mission on GEO-1 has allowed to highlight an important air contamination (>90%) and that the T555 unit was not adapted to fluid with low GWR. Based on these observations, three main modifications have been made:

- a new custom glass burette was designed to adapt the system to low GWR.
- the dead volume between the burette and the  $\mu$ -GC was reduced to maintain the gas pressure as much as possible,
- the tightness of the entire system was improved to prevent air contamination.

The results of the second mission show that our process has been improved between the two on-site field tests and became robust. The atmospheric contamination was reduced from more than 90% to 3.5% and an excellent repeatability of the gas composition measurements was reached (< 5%). The results show an increase in the quality of GWR measurements and specifically for low GWR (value < 0,2).

The analysis of the geochemical composition of the dissolved gas of this second mission gave major information regarding both the origin of the gas and the hydrogeology of the zone with the detection of a gas arrival or accumulation at 800 m depth.

However, the equipment can still be improved:

- 1) It is possible to optimize the air tightness during the transfer of fluids for isotopic analysis of dissolved noble gases. This would require an additional sampling and testing.
- 2) The results have shown it was necessary that the downhole sampler keeps the reservoir pressure to measure the saturation pressure.
- 3) Direct measurement of pH and conductivity with the sampler at reservoir conditions is also necessary for a full understanding of downhole conditions.
- 4) Finally, new field tests will be key for validating the satisfactory performance of the equipment with high gas water to ratio.

In the future, geothermal and gas storage stakeholders can still contribute to developing the downhole sampler as well as improving the digitalization of the compiled results to improve reactivity and presentation of our results directly on the web. Thus, - the US market for well tests in CO<sub>2</sub> reservoirs, as the number of potential wells is large in this country offer multiple interesting opportunities for deployment and partnerships in next years.

We also see lot of opportunities to apply our expertise in gas analysis in the area of climate change to monitor with accuracy the CO<sub>2</sub> absorption in oceans and their consecutive acidification or the methane release due to the permafrost warming.



## Glossary

**GWR :** GAS TO WATER RATIO

**GOR :** GAS TO OIL RATIO

**SEMM LOGGING :** INDUSTRIAL WELL LOG SUBCONTRACTOR OF IFPEN  
(<http://www.semmlogging.com/>)

**ANTARES :** DOWHOLE DESIGN SUBCONTRACTOR OF SEMM LOGGING



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