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Development and testing of gas samplers in tunnel environments

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Development and testing of gas samplers in tunnel environments

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Abstract

Two gas sampling methods have been tested in selected boreholes and borehole sections at the Äspö Hard Rock Laboratory (Äspö HRL).

- Sampling of groundwater for determination of dissolved gases (H_2, He, Ar, O_2, N_2, CO_2, CO, CH_4 and other hydrocarbon gases).
- Sampling of released gas in order to determine stable isotope ratios in gases (deuterium in H_2 and CH_4, $\delta^{18}O$ in CO_2 as well as $\delta^{13}C$ in CO_2 and CH_4).

The use of boreholes drilled from a tunnel system facilitated the sampling since no pumping was needed due to the pressure gradient out from the boreholes.

Collection of sample series during continuous discharge of water revealed that the amount of dissolved gas in the groundwater initially present in the borehole sections (the first samples in the series) may be larger than the amount in the groundwater directly from the bedrock formation (the latter samples in the series). Furthermore, the size of the pressure drop (back pressure) was found to be important, especially for the amount of dissolved hydrogen. Generally, the results stress the importance of a proper and well tested sampling procedure when investigating dissolved gas concentrations in groundwater.

Another factor that affects primarily the amount of dissolved hydrogen but may also affect gases like carbon dioxide and/or methane, is corrosion of equipment parts in the borehole. Significant differences in the hydrogen concentrations were observed between boreholes with metal parts solely made of stainless steel and those with aluminium parts.

The results from determinations of isotope ratios using samples of released gas from a gas trap generally diverged somewhat from those few samples obtained in earlier investigations using extracted gas from groundwater samples. Additionally, some differences in the isotope signatures were observed in borehole sections affected by corrosion of aluminium. The clearest effect is the higher $\delta^{13}C$ values. The reasons are difficult to deduce and more sampling and analyses have to be done in order to understand the implications of different equipment and establish a reliable procedure for sampling.

Sammanfattning

Två gasprovtagningsmetoder har testats i valda borrhål och borrhålssektioner vid Äspölaboratoriet (Äspö HRL).

- Uttag av grundvattenprov för analyser av lösta gaser (H_2, He, Ar, O_2, N_2, CO_2, CO, CH_4 och andra kolväten i gasform).
- Uttag av gasprov (avgiven gas) för bestämning av isotopkvoter i gaser (deuterium i H_2 och CH_4, $\delta^{18}O$ i CO_2 samt $\delta^{13}C$ i CO_2 och CH_4).

Användningen av borrhål borrade från ett tunnelsystem underlättade provtagningen eftersom vattnet inte behöver pumpas på grund av tryckgradienten ut från borrhålen.

Uttag av provserier under kontinuerligt flöde avslöjade att mängden lösta gaser i det grundvatten som initialt finns i borrhålssektionen (dvs. sektionsvatten som kommer med de första proven i provserien) kan vara större än i grundvattnet från sprickor i bergformationen (dvs. formationsvatten i de senare proven i serien). Vidare visade det sig att tryckfallet (mottrycket) är viktigt och då särskilt för mängden löst väte. Resultaten betonar betydelsen av ett riktigt och väl utprovat provtagningsförfarande för undersökningar av lösta gaser i grundvatten.

En ytterligare faktor som främst påverkar halten löst väte men även kan ha följdverkningar på koldioxid och/eller metan, är korrosion på utrustningsdetaljer i borrhålet. Signifikanta skillnader observerades mellan borrhål med metalldetaljer enbart av rostfritt stål och dem med aluminiumdetaljer.

Resultaten från bestämningar av isotopkvoter i prov på avgiven gas samlad i gasfälla avvek i regel något från de få prov som tagits vid tidigare undersökningar när proven bestod av extraherad gas från grundvattenprov. Dessutom observeras vissa skillnader i isotopsammansättningen när borrhålssektionerna är påverkade av aluminiumkorrosion. Orsakerna är svåra att härleda med så få prov och mer provtagning och analyser är nödvändiga för att förstå innebörden av olika utrustningar och fastställa en tillförlitlig provtagningsprocedur.

Contents

1 Introduction

1.1 Background

The study of gases in groundwater that is presented in this report was carried out at the Äspö Hard Rock Laboratory (Äspö HRL) and constitute a sub-activity within a joint project between SKB (Swedish Nuclear Fuel and Waste Management Co) and Posiva Oy. Information about gases (dissolved gas content and composition as well as isotope ratios in gases) is important in the SKB disposal concept for spent nuclear fuel for several different reasons. The general aim with the overall umbrella project was to assemble data and acquire knowledge on processes that affect the sulphide concentration or the sulphide production rate in groundwater. Sulphide concentrations in groundwater play a key role in the long-term stability of the copper canisters (Tullborg et al. 2010) since it will cause corrosion in an anaerobic environment. This sub-activity concerning gases is relevant for the microbial sulphide production since some gases in groundwater such as H_2 or CH_4 may be the electron donors in the sulphate reduction process. The stable isotope ratios (deuterium) in H_2 and CH_4, $\delta^{18}O$ in CO_2 as well as $\delta^{13}C$ in CO_2 and CH_4 may give information on if these gases result from geological processes, from anaerobic corrosion or from microbial processes and may therefore be helpful when interpreting the dissolved gas results.

Besides the sulphide production issue, the dissolved gas content is important for safety assessment and modelling of radionuclide transport properties, as well as for understanding and modelling of the conditions in the groundwater including effects due to the future construction of the Final Repository for Spent Nuclear Fuel. The analytical data, especially those from H_2, CH_4, are for example used in the inorganic geochemical modelling calculations (e.g. speciation-solubility calculations) related with the redox processes.

The usefulness and applicability of different methods concerning dissolved gases and isotopes in gases was evaluated also as a part of a project (DETUM) designed to develop equipment and methods for the coming detailed investigations during the construction phase of the planned repository in Forsmark. Gas determinations of interest for the future detailed investigations are:

- Amount and composition of dissolved gas in groundwater.
- Carbon, oxygen and hydrogen isotopes in different gases (CH_4, CO_2, O_2, H_2) in groundwater.
- Stable and radioactive noble gas isotopes in groundwater.
- The gases SF_6 (sulphur hexafluoride) and CFC (chlorofluorocarbon or Freon) in groundwater.

The two last points/determinations were not included in this study but may become useful complements when interpreting residence times in the future.

1.2 Objectives and scope

The reported gas investigation aimed to serve two general purposes. Firstly, there is a need to obtain more gas data (concentrations and isotope signatures) and this study is intended to be an initial step using a supposedly improved sampling technique that may give more reliable values at the preceding conditions in the bedrock. It is crucial to better understand possible impacts from different sampling conditions and equipment and a reliable quality is necessary in order to better understand the transport processes that involves H_2 and other gases that can be used by sulphate reducing bacteria (SRB). A second purpose was to develop improved sampling techniques for dissolved gas as well as for isotopes in gases for the coming detailed investigations in Forsmark.

Hydrogen gas is the preferred energy source for many microbes such as SRB and methanogens and it is consumed rapidly if these are active. Because of its light weight it may degas quickly which also obstructs the sampling and could result in too low concentrations. Furthermore, the reliability may be questioned also for other analysed gases since the sampling conditions and sampling procedure may have large influence on the results (for example on CH_4 and CO_2). A specific objective was therefore to test different sampling procedures and to increase the understanding of their implications in order to find a suitable sampling method. The analyses of dissolved gas included the more or less complete gas composition and not only the electron donor candidates hydrogen and methane, see Table 1-1. This ensured full control of the gas composition and possibilities to compare the new data with previous results.

A different piece of sampling equipment for isotope ratios in gases than the previously used was tested in order to obtain samples with a larger gas volume and thereby better possibilities to determine also stable isotope ratios in gases with a low concentration. The isotope ratios listed in Table 1-1 may give information on the origin of the gases i.e. if they result from geological processes, from anaerobic corrosion or from microbial processes and this is a first step also here towards the final aim to obtain a sufficient amount of isotope data (including also earlier data) and get a thorough understanding of how to interpret the origin of the gases.

Table 1-1. Gas analyses and determinations of isotope ratios in gases.

Dissolved gas		Isotope
Hydrogen	(H_2)	δ^2H
Helium	(He)	
Argon	(Ar)	
Oxygen (should be below DL)	(O_2)	
Nitrogen	(N_2)	
Carbon oxide	(CO)	
Carbon dioxide	(CO_2)	$\delta^{13}C$, $\delta^{18}O$
Methane	(CH_4)	δ^2H, $\delta^{13}C$
Ethane	(C_2H_6)	
Ethene	(C_2H_4)	
Ethyne	(C_2H_2)	
Propane	(C_3H_8)	
Propene	(C_3H_6)	
Propyne	(C_3H_4)	

1.3 Strategies and methods

1.3.1 Dissolved gas

The sampling was performed in different boreholes drilled from the tunnel system of Äspö HRL (Äspö Hard Rock Laboratory), see Table 1-2 and Figure 2-1. This location was selected since the sampling conditions are similar to the ones that will prevail during the coming detailed investigations when constructing the planned repository for spent nuclear fuel in Forsmark. The use of subsurface boreholes also implied that the sampling could be conducted without pumping, just by the opening of valves, due to the pressure gradient out from the boreholes. Boreholes with available flow logging data were selected as a first criterion. However, it was also the intension to represent different depths and water types. Flow logs were used for plug flow calculations (cf. Appendix 3) to estimate the required purging prior to sampling. Borehole sections were regarded as unsuitable if they are located close to the borehole orifice or if the hydraulic transmissivity is too low ($T > 1 \times 10^{-8}$ m^2/s is preferred). The purging and sampling have to be performed with as small pressure drop as possible, therefore if the transmissivity is not high enough, the flow rate will be very low. More detailed information about the fixed equipment used to isolate different borehole sections in boreholes drilled from tunnel systems, about estimation of volumes to be purged and about section specific plug flow volumes is given in Appendix 3.

The sampling equipment consisted of a container with a piston, see Section 2.2.1. The groundwater was flowing through the piston to facilitate complete exchange of water in the container during sampling. Back-pressure behind the piston ensured a slow water flow into the container. Water was used instead of gas to maintain the pressure and avoid the risk for gas to move beside the piston into the sample. Furthermore, using water ensures a prompt response in start and stop of the piston when opening/closing valves due to the incompressibility of water.

Sample series of four sample pairs (duplicates) were collected during continuous purging to test the effect of exchanged water volume prior to the sampling. The samples were collected after exchanging 1) the tube volume, 2) two plug flow volumes, 3) three plug flow volumes and 4) five plug flow volumes. This was done in two of the totally four sampled borehole sections. Another factor that may affect the gas amount or composition is the size of the pressure drop during purging and sampling since a too large pressure drop may cause gas release (especially H_2 is easily degassed) in the borehole section. In one borehole section, the collection of samples series was therefore repeated at two different pressure drops. The remaining two target sections were sampled (also duplicates) according to what was judged to be the best sampling procedure after evaluation of the three previous sample series. The borehole sections and the collected samples are summarised in Table 1-2.

1.3.2 Isotope ratios in gases

Initially, the intension was to sample the same borehole sections for dissolved gas and for isotope ratios in gases. However, not surprisingly, it was observed that groundwater from boreholes with equipment parts made of aluminium contained significantly higher concentrations of hydrogen gas then boreholes with stainless steel parts probably due to ongoing corrosion processes. The selection was therefore reconsidered and two borehole sections with aluminium parts were replaced to make it possible to obtain hydrogen isotope signatures representing initial dissolved hydrogen rather than the hydrogen gas formed from reduction of water. The borehole sections and the collected samples are summarised in Table 1-2.

Table 1-2. Summary of borehole sections and collected samples.

Borehole: section	**Section (m along borehole)**	**Permanent equipment material**	**Pressure drop (dissolved gas sampl.)**	***No of samples* × *duplicates* for dissolved gas**	**Comment**	**N*o of samples* for isotope determ.**
KA2511A:4	111–138	Al				1
KA2563A:1	242–246	Al	150 KPa	4 × 2	The sampl. was repeated at two different pressure	–
KA2563A:1	242–246	Al	750 KPa	4 × 2	drops (totally 16 vessels)	–
KA2563A:4	187–190	Al	–	–		1
KA2051A01:5	120–135	Stainless Steel	300 KPa	1 × 2		1
KA2051A01:9	51–67	Stainless Steel	150 KPa	4 × 2		Not enough gas
KA3510A:2	110–124	Al	200 KPa	1 × 2		1
KA3385A:1	32–34	Stainless Steel	–	–	Sampling in 2010–2011, Al in equip.	1
K08028F01:1	84–94	Stainless Steel	–	–		1

The sample container was a simple gas trap with water seal to prevent air from intruding through the water outlet, see Section 2.2.2. The collection of gas in the trap was performed at atmospheric pressure to ensure that the gas was released as efficiently as possible. The purged volume prior to sampling was not considered as crucial (at the time) for the dissolved gas and the most important was to obtain a sufficient gas volume for the determinations of isotope ratios. The hydrogen gas concentration was expected to be critical for the tritium and deuterium analyses.

2 Experimental

2.1 Targets for sampling

Eight target sections in six boreholes were sampled. Table 2-1 summarises detailed information about each borehole and Figure 2-1 shows the locations along the tunnels while Table 2-2 lists detailed information about each borehole section. Generally, there is one tubing with pressurised water (by N_2 gas) for inflating the packers, passing through each section except for the inner section denoted no.1. Most studied borehole sections have dummies that are used to decrease the section volume, cf. Appendix 3.

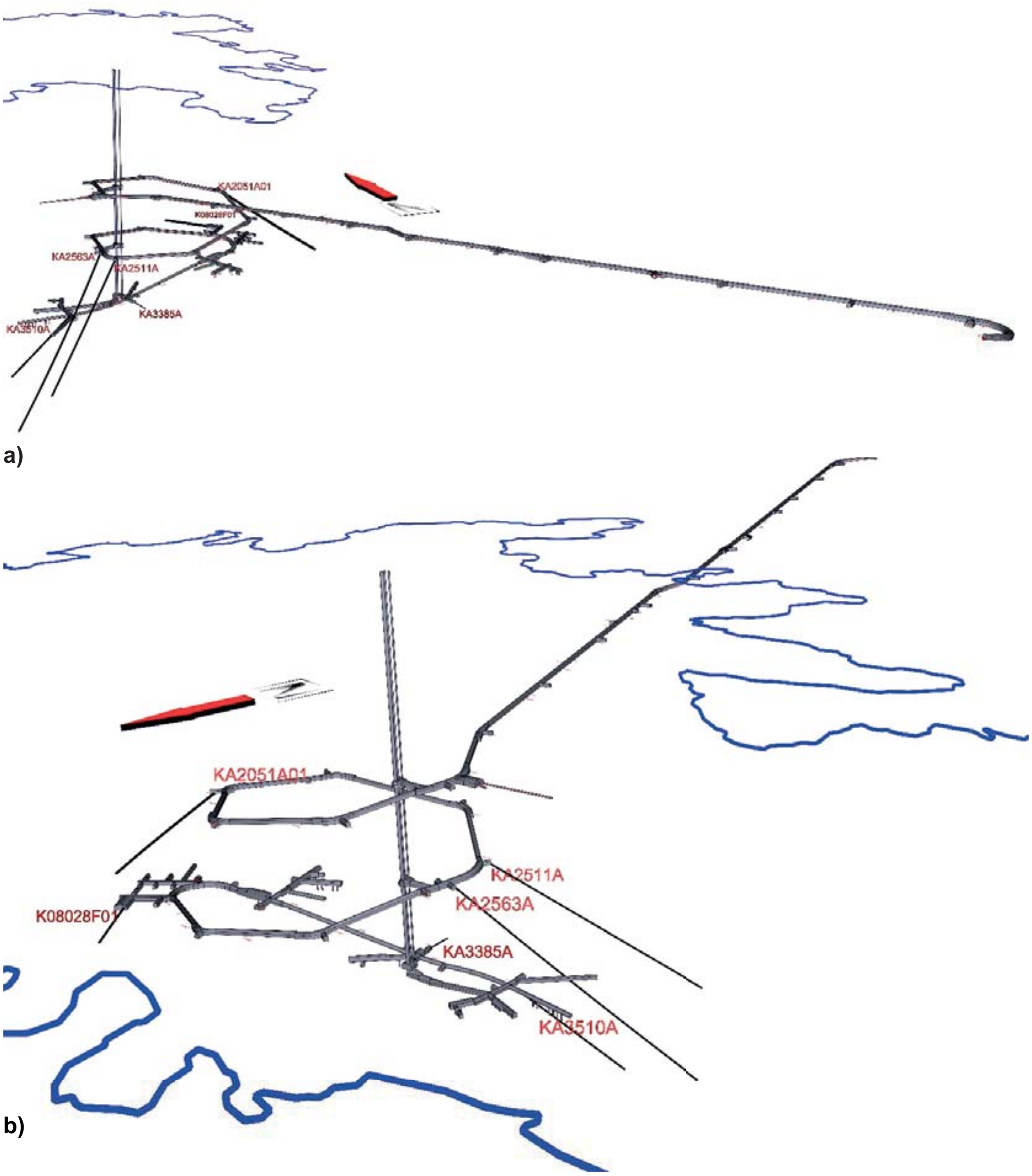

Figure 2-1 a and b. *Borehole locations along the tunnel system in the Äspö HRL. Red text show the sampled boreholes.*

Table 2-1. Summary of information about boreholes.

Borehole idcode	Vertical depth of borehole entrance (masl)	Borehole direction	Borehole diameter (mm)	Permanent equipment material	Equipment installation year
KA2051A01	−276.6	Downwards −35.01°	76	Stainless steel	2001
KA2563A	−340.8	Downwards −42.5°	56	Al	1999
KA3510A	−448.7	Downwards −30.2°	76	Al	2001
KA2511A	−335.9	Downwards −33.3°	56	Al	1999
KA3385A	−446.0	Downwards −4.10°	56	Al	1995
KA3385A	−446.0	Downwards −4.10°	56	Stainless steel	2014
K08028F01	−396.6	Upwards 2.18°	76	Stainless steel	2014

Table 2-2. Summary of information about borehole sections.

Borehole: section no.	Vertical depth at Secmid (masl)	Plug flow volume (L)	Distance to tunnel orifice	Equipment (see Figure A3-1a) dummy (yes/no)	Sampling
KA2051A01:9	−310.2	23	51 to 67 m	Yes (15 m long)	Diss. gas
KA2051A01:5	−349.1	89	120 to 135 m	Yes (14 m long)	Diss. gas, isotope ratios
KA2563A:1	−502.6	7	242 to 246 m	Yes (3.6 m long)	Diss. gas
KA2563A:4	−466.5	15	187 to 190 m	No	Isotope ratios
KA3510A:2	−507.2	792	110 to 124 m	No	Diss. gas, isotope ratios
KA2511A:4	−404.7	297	111 to 138 m	No	Isotope ratios
KA3385A:1	−448.3	–	32 to 34 m	Yes	Isotope ratios
K08028F01:1	−393.4	–	84 to 94 m	Yes	Isotope ratios

2.2 Samplers

2.2.1 Water sampler for dissolved gas

Microbial Analytics Sweden AB has developed and tested a flow-through sampler for dissolved gas. This sampler can take up to 400 mL water sample (Figure 2-2). There are four complete samplers available for this work. These are still prototypes that may need to be fine-tuned and some connectors can be made permanent. However, at present, the sampler can easily be dismantled into individual parts and cleaned. On the other hand, many connections imply an increased risk of leakage. Later versions can be fitted with fully welded joints when the prototype is put into production. The sampler must hang vertically, free from the tunnel wall. Water is led through the hose from the lower end of the sampler in Figure 2-2 and out through the pressure reducer on top of the sampler (cf. Figure 2-3). During sampling, the pressure on the lower pressure reducer is set to a higher level than the formation pressure so that it closes. The upper pressure reducer is set so that a required flow of water through the sampler is obtained after which the sampler tube is filled with sample water. When the sample is to be collected, the top pressure regulator is closed and the lower is set open to a slow flow that will let out the counter pressure water. The sampler can now be slowly filled with the desired volume of water at a pressure slightly below formation pressure. The lower back pressure can be fine-tuned in relation to the flow rate and the valves can be used if necessary for the immediate closure or opening during the sampling. Pressures are read on the pressure gauge. The samplers are shipped two and two in black boxes. The optimal back pressure and flow must be tested on site in the tunnel environment.

The sampler principle is shown in Figure 2-3. It is provided with a piston that is of a flow-through type, which means that the hydraulic line is going through the piston rod. The volume is 400 ml. The sampled volume of groundwater can be varied depending on the gas content of the ground-water. When sampling, tap water should be used for maintaining the back pressure behind the piston.

The sampled water volume is reflected by the piston tube position and the sampled amount of water can also be gauged by the volume of how much of the backpressure water that is discharged during sampling. The counter pressure on the piston in the sample chamber is controlled by the pressure regulator valve so that the pressure in the sample will be approximately similar to the pressure in the sampled section. Adjustment of this pressure regulator will adjust the filling flow rate through the sampler.

Figure 2-2. *Left: Flow-through sampler for dissolved gas dismantled for transport. Right: A mounted sampler with the piston in a position corresponding to a full sample (400 mL) with pressure reducers, manometer, valves and connectors.*

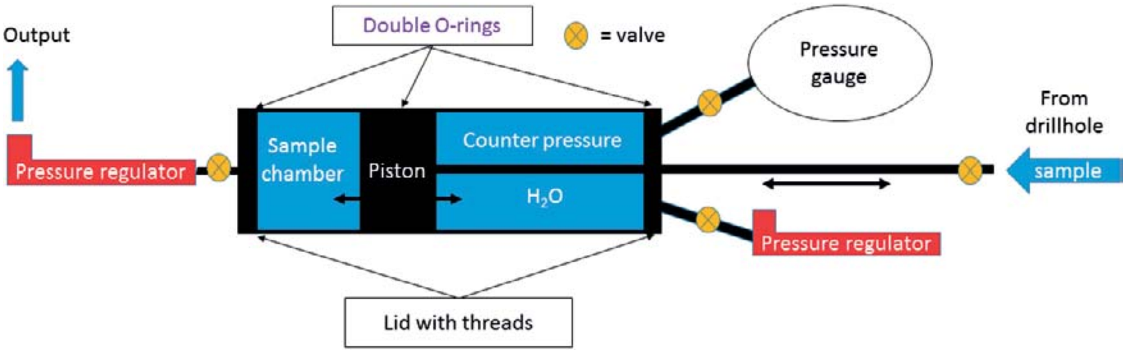

Figure 2-3. *Schematic outline of the sampler for dissolved gas. The details are listed below.*

Specifications for the water sampler for dissolved gas

Material in samplers, tubes and valves: Stainless steel.

Lids on both sides of the sampler tube can be screwed on and off independently.

Seals on the lids and the piston consist of double O-rings.

Valves: Swagelok ball valves SS-42GS6MM (6 mm).

Pressure to get piston movement: < 100 kPa.

Pressure regulators: Swagelok Pressure overload valves SS 6R3A-MM with springs R3A series, 177-R3A-K1-A and 177-R3A-K1 B.

Pressure gauge: WIKA EN-837-1 60 mm 0–4 MPa, oil filled.

2.2.2 Sampler for collection of gas for isotopic analysis

The sampler (Figure 2-4) is first completely filled with the groundwater to be sampled for gas and then the same groundwater is continuously let in from the top valve and out through the swan neck tube while releasing the gas. The sampler can be weighed by a spring balance and when a weight equivalent to the volume of the water in a full container is lost, the sampling is completed.

Specifications

Containers: Swagelok 300 mL or 500 mL stainless steel cylinder which is Teflon coated on the inside. HDF4-300 304L-304L and T-T HDF4-500.

Valves: Swagelok SS 140KV4-S6MM (316 stainless steel).

Tube: 6 mm, 316 stainless steel.

Rail: PVC and stainless steel.

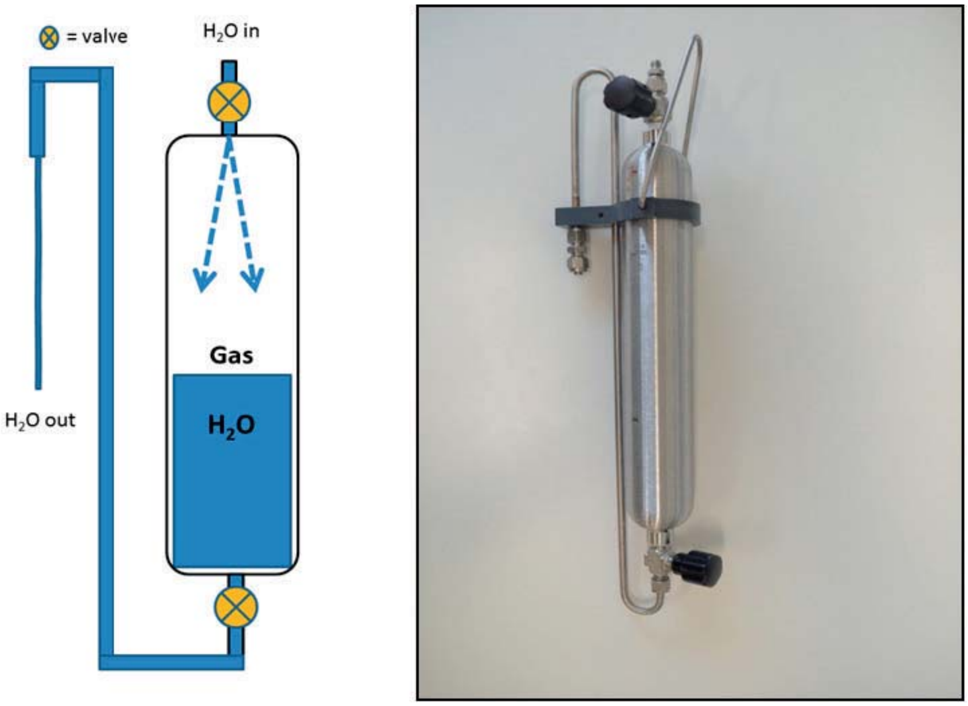

Figure 2-4. *Left: Schematic drawing of sampler for the collection of gases for determinations of isotope ratios. Right: Sampler for the collection of gases for determinations of isotope ratios. The details are listed above.*

2.3 Sampling of groundwater for dissolved gas

The sampling processes are summarised in Table 2-3, Table 2-4 and Table 2-5. The gas transfer to the appropriate sample vessels and the compression of the gas, is conducted in the laboratory.

Table 2-3. Sampling in KA2563A:1. The extracted volume record restarted at zero the second sampling day. Sampling details were collected from the daily logs. The pressure drops are the ones read on the sampler manometers. Graphs showing continuous pressure registrations from the borehole section during purging and sampling are presented in Appendix 2.

Gas sample	Sample date	Sample time	Flow rate (mL/min)	Pressure drop during flowing (KPa)	Pressure drop during sampling (KPa)	Total extracted water volume prior to sampling (L)	Sample volume (mL)	Flow
1a	2014-11-24	11:11	100	150	150	4	160	start
1b	2014-11-24	11:13	100	150	150	4	170	flowing
2a	2014-11-24	12:55	100	150	150	18	160	flowing
2b	2014-11-24	13:02	100	150	150	18	170	stop
	2014-11-24	*13.11*	*sampling*	*for*	*chemistry*			*intermittent*
3a	2014-11-24	16:20	100	150	150	25	250	start
3b	2014-11-24	16:20	100	150	150	25	255	flowing
4a	2014-11-24	17:41	150	150	150	39	260	flowing
4b	2014-11-24	17:43	150	150	150	39	270	stop
5a	2014-11-25	08:35	600	1 250	750	4	275	start
5b	2014-11-25	08:36	600	1 250	750	4	270	flowing
6a	2014-11-25	09:03	600	1 250	750	18	265	flowing
6b	2014-11-25	09:06	600	1 250	750	18	280	stop
	2014-11-25	*09:11*	*sampling*	*for*	*chemistry*			*intermittent*
7a	2014-11-25	11:41	600	1 250	750	25	290	start
7b	2014-11-25	11:44	600	1 250	750	25	295	flowing
8a	2014-11-25	12:13	600	1 250	750	39	265	flowing
8b	2014-11-25	12:15	600	1 250	750	39	270	stop

Table 2-4. Sampling in KA2051A01:9. Sampling details were collected from the daily logs. The pressure drops are the ones read on the sampler manometers. Graphs showing continuous pressure registrations from the borehole section during purging and sampling are presented in Appendix 2.

Gas sample	Sample date	Sample time	Flow rate (mL/min)	Pressure drop during flowing (KPa)	Pressure drop during sampling (KPa)	Total extracted water volume prior to sampling (L)	Sample volume (mL)	Flow
	2015-02-02	13:42						start
1a	2015-02-02	13:50	400	150	150	1.5	330	flowing
1b	2015-02-02	13:52	400	150	150	1.8	310	flowing
2a	2015-02-02	16:16	400	150	150	58	305	flowing
2b	2015-02-02	16:21	400	150	150	58	320	flowing
			52		*slow flow*	*over*	*night*	
3a	2015-02-03	07:48	400	150	150	106	305	flowing
3b	2015-02-03	07:52	400	150	150	106	320	flowing
	2015-03-03	*08:07*	*sampling*	*for*	*chemistry*			*intermittent*
4a	2015-02-03	10:13	400	150	150	160	325	flowing
4b	2015-02-03	10:20	400	150	150	160	310	flowing
	2015-02-03	10:20						stop

Table 2-5. Sampling in KA2051A01:5 and KA3510A:2. Sampling details were collected from the daily logs. A graph showing continuous pressure registrations in the borehole section during purging and sampling is presented in Appendix 2.

Gas sample	Sample date	Sample time	Flow rate (mL/min)	Pressure drop during flowing (KPa)	Pressure drop during sampling (KPa)	Total extracted water volume prior to sampling (L)	Sample volume (mL)	Flow
KA2051A01:5								
	2015-05-25	07:12	290	200	*Flowing* 852 L *for 49 h*			start
1a	2015-05-27	08:05	not registered	–	300	0	325	–
1b	2015-05-27	08:12	not registered	–	300	0	290	-–
	2015-05-27	08:20	1350	not registered	*Sampling for chemistry*			intermittent
	2015-05-27	08:34	0					stop
KA3510A:2								
	2015-05-26	07:31	480	300	*Flowing 720 L for 25 h*			start
1a	2015-05-27	08:54	Not registered	–	200	0	300	–
1b	2015-05-27	08:59	Not registered	–	200	0	300	–
	2015-05-27	09:09	630	not registered	*Sampling for chemistry*			intermittent
	2015-05-27	09:25	0					stop

2.4 Sampling gas for determination of isotope ratios

Gas from six borehole sections have been sent for analysis 2014-12-05 (2 samples), 2014-12-18 (1 sample) and 2015-12-15 (3 samples). The sampled boreholes and the status of the samples are given in Table 2-6. The groundwater from borehole section KA2051A01:9 did not release gas to the sample vessel; repeated sampling gave the same results. It is obvious that the groundwater from this section has too little gas to be released under atmospheric pressure for isotope ratios.

Table 2-6. Samples for isotope analysis. Bottle 1 and 2 represent the 120 mL glass bottles with butyl rubber stoppers to which the sampled gas was transferred for transport to the analysing laboratory. The required minimum total volume was 120 mL gas.

Sampled borehole	sample date	SKB no	Total volume of gas in sample vessel (ml)	Gas volume in bottle 1 (ml)	Gas volume in bottle 2 (ml)
KA2051A01:9	2014-12-03	24011	7	–	–
KA2511A:4	2014-12-03	24012	313	140	144
KA2563A:1	2014-12-03	24013	391	142	154
KA2563A:4	2014-12-16	24022	505	145	165
KA2051A01:9	2014-12-16	–	No gas	–	–
KA3385A	2015-11-26	24277	526	183	178
K08028F01	2015-11-26	24278	504	212	179
KA2051A01:5	2015-12-02	24290	320	173	–

2.5 Extraction for gas analysis

Water samples from the pressurized sampler vessels were transferred within a couple of hours to a vacuum container and any gas in the water was boiled off under vacuum (i.e., at water vapour pressure). The extraction time was 2 × 10 min at room temperature (RT; 20 °C). The extracted gas volume was compressed and transferred to a 10 mL syringe (SGE Analytical Science, Melbourne, Victoria, Australia) and subsequently to a 6.6 mL glass vial with butyl rubber stoppers and sealed with aluminium crimp seals. A dehydrate was added to the sample containers to adsorb any traces of water in the gas sample. The vials were evacuated and flushed twice with nitrogen (N_2), in two cycles, and left under high vacuum (1 Pa), prior to sampling. The volumes of sample water and the extracted gas were measured and the volume of gas at 20 °C was recalculated with the ideal gas law at 100 kPa. Samples with an extracted gas volume of less than 6.6 mL (all samples except sample 1 for KA2563A:1 and 1 and 2 for KA2051A01:9) were diluted with N_2.

2.6 Extraction for isotope ratios

Gas from the gas traps (Figure 2-4) were transferred to 120 mL glass bottles with butyl rubber stoppers and sealed with aluminium crimp seals and sent for analysis.

2.7 Analysis with gas chromatography

Helium (He), hydrogen (H_2), argon (Ar), nitrogen (N_2), oxygen (O_2), methane (CH_4) and carbon oxide (CO) at concentrations < 20 ppm were analysed on a Dani Master GC gas chromatograph (Kovalent AB) using a micro Thermal Conductivity Detector (µTCD). The temperatures of the oven, the detector, and on the filament were 30, 140, and 190 °C respectively. The gases were separated using a MXT-Plot column (30 m × 0.53 mm × 50 µm) with Ar as the carrier gas for He and H_2 and He as the carrier gas for the others. N2, O_2, Ar and CH_4 concentrations >20 ppm were analysed on Varian CP-3800 gas chromatograph (Agilent Technologies Inc., CA, USA) with a 30 m high resolution capillary column (Bruker, SELECT PERMANENT GASES/CO2 HR, CP7430) using He as carrier gas. The gases were detected using a thermal conductivity detector (TCD) at detector temperature 120 °C, with a filament temperature of 220 °C and a column temperature of 45 °C. Methane (CH_4) and hydrocarbon gases (C1-C3) < 20 ppm were analysed on Varian CP-3800 gas chromatograph using carboxen column (2 m × 1/8 inch diameter) and analysed on the flame ionization detector (FID) with N_2 as the carrier gas. A Bruker 450 gas chromatograph equipped with a CP7355 PoraBOND Q (50 m x 0.53 mm, ID) and a CP7536 MOLSIEVE 5A PLOT (25 m × 0.32 mm, ID) and a Pulsed Discharge Helium Ionization Detector (PDHID) was employed for trace concentrations of H_2, O_2, Ar, CO_2 and hydrocarbon gases (C1– C3), (Bruker Daltonics Scandinavia AB, Vallgatan 5, SE-17067 Solna, Sweden). All chromatographs were calibrated using certified gas mixtures that mimic the gas composition of the analysed samples.

The uncertainty of the instruments and repeated injections is low, typically from 0 up to 4 %. The used calibration gases has a maximum accepted mixing uncertainty of ± 2 %.

Contamination by air and O_2 content

The procedures of sampling, extraction and analysis were all performed in air. It is consequently a challenge to avoid a small contamination of air. For instance, small volumes of air may be captured in the syringe needle during transfer of the sample from the vial to the injector on the gas chromatographs which results in additional O_2 that were not present in the gas phase in the vials or the groundwater. Furthermore, the transfer of samples and gas to and from the extraction equipment, respectively, may cause a small inlet of air. These contaminations are usually in the range between 200–700 µL air. Samples with large gas volumes >100 mL are not significantly influenced, but for samples in the range from 3.5–7.6 mL the contamination is significant. Therefore, the gas data are always reported with and without correction for oxygen contamination. In this particular project, it cannot be excluded that there was O_2 in some of the water samples and, therefore, all data in the report are given without correction for possible contamination. The issue of O_2 contamination during analysis has been discussed in detail by Bengtsson et al. (2013) and Johansson et al. (2015). Gas results are shown both with and without possible air contamination in the appendix. Correction was done by subtracting volumes of argon and nitrogen and oxygen in proportions present in air.

3 Results

3.1 Borehole section KA2563A:1

3.1.1 Total volumes of gas

The total volumes of extracted gas are presented in Table 3-1 and illustrated in Figure 3-1. The volume decreased over the two first samples (duplicates) and levelled out at approximately 18 mL of dissolved gas per litre of groundwater. It should be remembered though that the duplicates were collected with some difference in time and discharged volume. The data in Table 3-1 are only for sample wise comparison since they are not corrected for the air contamination. The air contribution was approximately constant to the samples, see O_2 values in Figure 3-2.

The higher amounts of dissolved gas in sample 1a and 1b was mainly due to more N_2, see Figure 3-1. Since this is the inner section of the borehole there are no tubes through the section for transfer of water under high pressure to packers. Therefore, diffusion of N_2 gas used to maintain the pressure of the water is not a possible cause for the N_2 contribution. The reason could be that lowered pressure in the section at previous water sampling occasions has caused higher gas content in the section water (i.e. the water initially present in the borehole section prior to opening of the valve for purging/sampling) compared to the formation groundwater in the bedrock. The lowered pressure in the borehole section during discharge could cause gas release followed by dissolution when the pressure is retained. Nitrogen will contribute the most to the increased gas concentration since it is the clearly dominating gas in groundwater. A higher N_2 concentration in the section will then probably be maintained due to a slow equilibrium process. This would possibly explain why the first two samples, representing the groundwater present in the borehole section, were overrepresented with N_2.

Table 3-1. Results from the extraction and analysis of gas in target KA2563A:1. The total gas volumes are not corrected for contamination by air.

Gas sample	Sample date	Sample time	Sample volume (mL)	Extracted total volume of gas (mL/L groundwater)	H_2 (μL/L groundwater)
1a	2014-11-24	11:11	160	47.5	303
1b	2014-11-24	11:13	170	32.4	329
2a	2014-11-24	12:55	160	21.3	174
2b	2014-11-24	13:02	170	18.2	126
3a	2014-11-24	16:20	250	20.0	590
3b	2014-11-24	16:20	255	18.4	365
4a	2014-11-24	17:41	260	19.2	103
4b	2014-11-24	17:43	270	17.8	100
5a	2014-11-25	08:35	275	17.5	148
5b	2014-11-25	08:36	270	18.5	137
6a	2014-11-25	09:03	265	17.0	32
6b	2014-11-25	09:06	280	17.9	39
7a	2014-11-25	11:41	290	17.9	
7b	2014-11-25	11:44	295	17.3	102
8a	2014-11-25	12:13	265	18.1	28
8b	2014-11-25	12:15	270	17.4	35

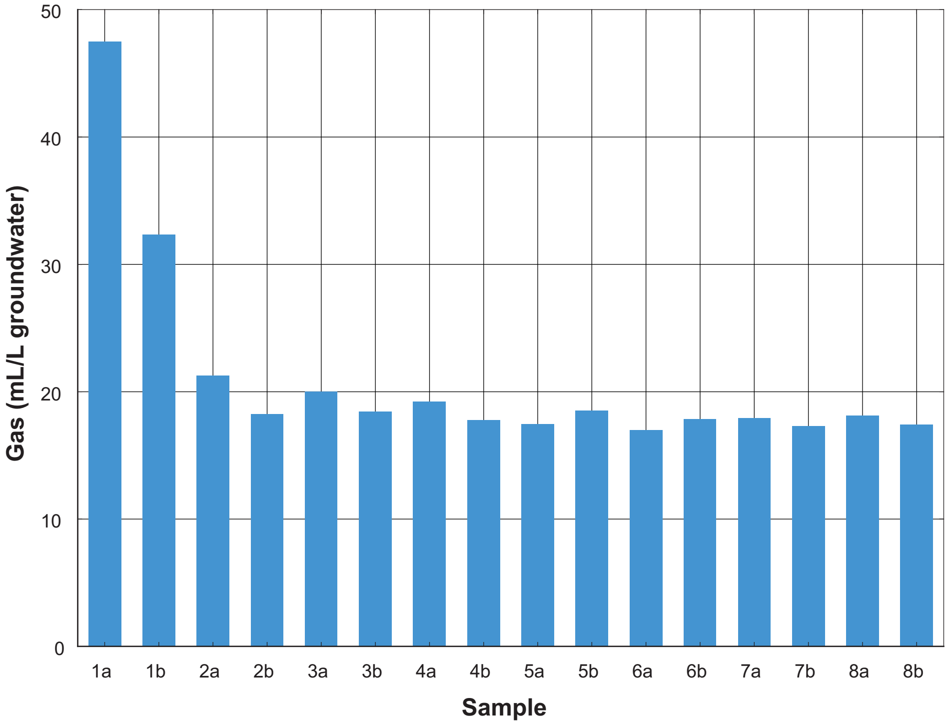

***Figure 3-1.** Total amount of extracted gas from KA2563A:1 calculated as mL of gas per L of groundwater.*

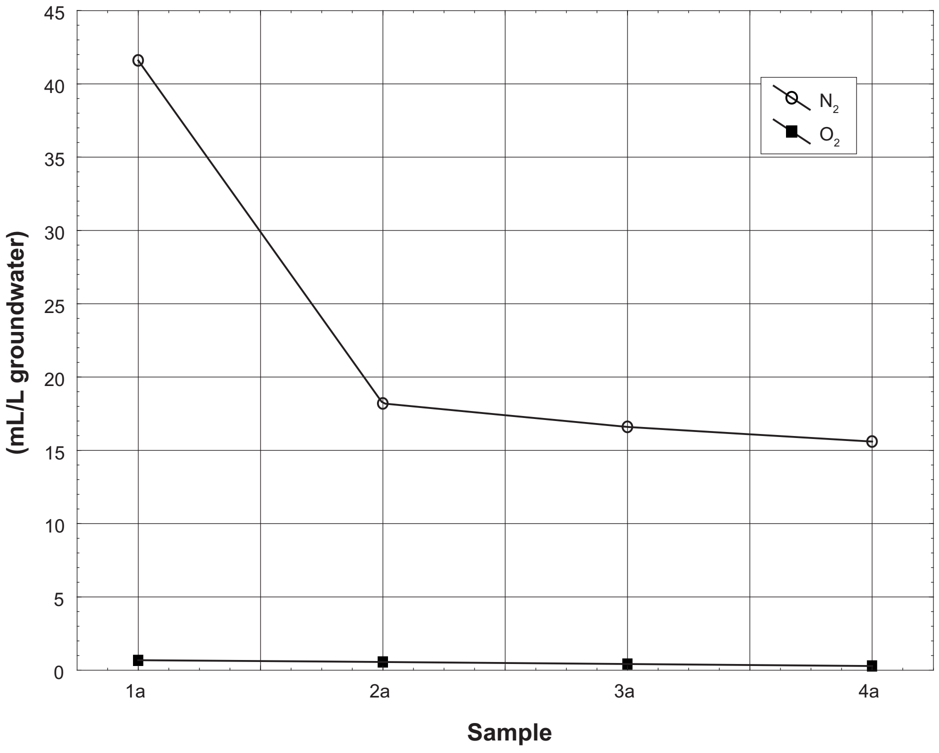

***Figure 3-2.** Distribution of dissolved N_2 and O_2 in KA2563A:1 over the four analysed samples (1a, 2a, 3a and 4a) in the series.*

3.1.2 Volumes of dissolved H_2

Sample number 7a was lost during transfer to the sample vial due to extraction operators 'technical' mistake. It is clear that the amount of analysed dissolved H_2 was very influenced by the purging and sampling procedures. The H_2 concentration was relatively high in the samples from this borehole section compared to some of the other sampled sections and it was highest after periods without withdrawal of water, see Figure 3-3. The concentration decreased significantly when the borehole was drained. A faster flow rate was used the second day which further lowered the concentrations of H_2. The results from the two samplers representing each sampling occasion and flow-pressure combination generally reproduced as well as could be expected.

3.1.3 Complete analysis of gas

N_2 and O_2 data are presented in Figure 3-2 and He, Ar, CO_2 and CH_4 data are presented in Figure 3-4. The result protocols are given in Appendix 1. The concentrations of Ar and CH_4 did not change over the sample series but CO_2 increased with increasing extracted volume, see Figure 3-4. Helium showed a decreasing trend over the three first sampling occasions and increased again in the last sample. As discussed above, N_2 was overrepresented in the first two samples (1a and b) that represented water from the borehole section.

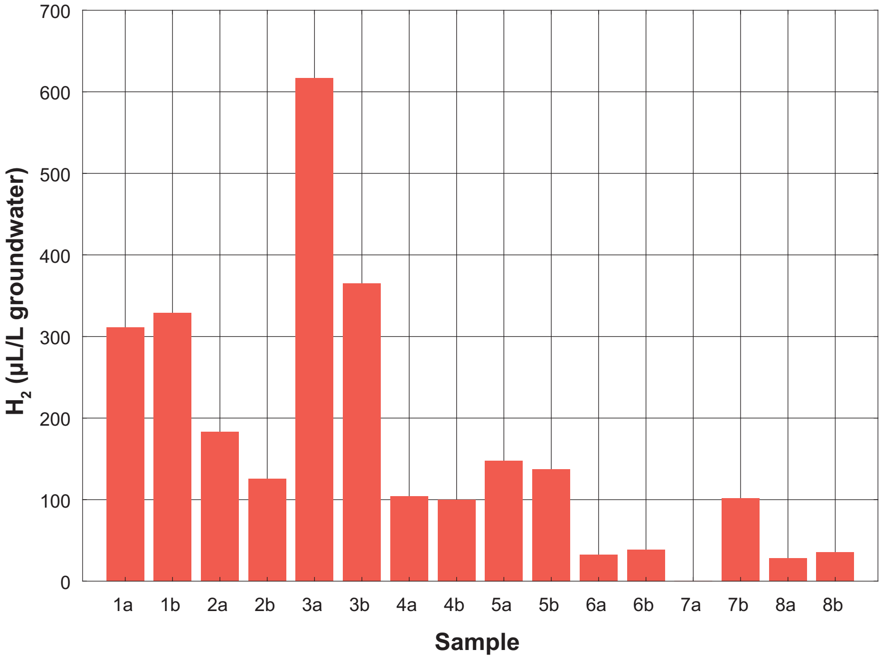

Figure 3-3. *The volumes of dissolved H_2 in sampled groundwater from KA2563A:1.*

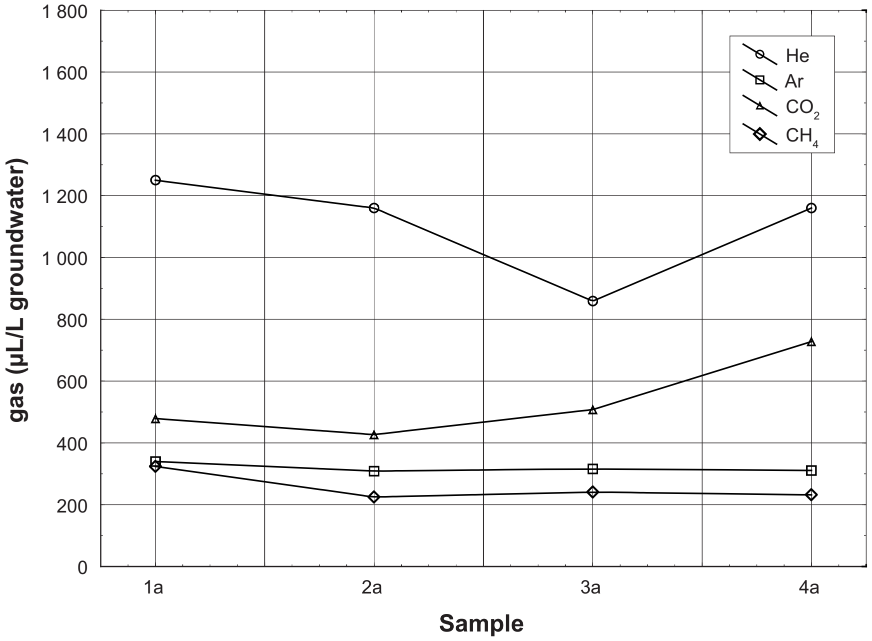

Figure 3-4. *Distribution of analysed gas from KA2563A:1 over the four analysed samples (1a, 2a, 3a and 4a) in the series.*

3.2 Borehole section KA2051A01:9

3.2.1 Total volumes of gas

The total volumes of extracted gas are given in Table 3-2 and Figure 3-5. The volume decreased over the three first samples and levelled out at approximately 18 mL of dissolved gas per litre of groundwater, which is in the same range as observed for KA2563A:1. These volumes are not corrected for air contamination and are only intended for sample wise comparison. The air contamination is approximately constant, see O_2 contribution in Figure 3-6.

The larger gas volumes in samples 1a, 1b and 2a are mainly due to more of N_2 and O_2 as shown in Figure 3-6. The reason for this is probably that the section groundwater has been in contact with air, either through the 4/6 mm plastic tube that passes through the section or the fracture system since this borehole section is located close to the borehole orifice (51–67 m from the tunnel face). Just as for the samples from KA2563A:1, this overrepresentation of contaminating gases decreased with the drained volume.

Table 3-2. Results from the extraction and analysis of gas in target KA2051A01:9. The total gas volumes are not corrected for contamination by air.

Gas sample	Sample date	Sample time	Sample volume (mL)	Extracted total volume of gas (mL/L groundwater)	H_2 (µL/L groundwater)
1a	2015-02-02	13:50	330	24.2	1.52
1b	2015-02-02	13:52	310	29.7	1.71
2a	2015-02-02	16:16	305	21.6	0.96
2b	2015-02-02	16:21	320	18.7	1.61
3a	2015-02-03	07:48	305	18.0	1.51
3b	2015-02-03	07:52	320	17.5	1.16
4a	2015-02-03	10:13	325	16.9	1.15
4b	2015-02-03	10:20	310	18.1	4.08

3.2.2 Volumes of dissolved H_2

The content of dissolved H_2 was approximately 100 times lower in KA2051A01:9 compared to KA2563A:1, see Figure 3-7. Because the values were close to the detection limit for H_2 by gas chromatography, the variability in this sample series may just reflect the analytical error. The last sample, 4b, contained three times more H_2 than the preceding seven samples. However, the reason cannot, be deduced for just one observation. The groundwater in borehole section KA2563A:1, instrumented with an aluminium rod, consequently contained much more gas than the groundwater from borehole KA2051A01:9 with a stainless steel rod.

3.2.3 Complete analysis of gas

N_2 and O_2 data are presented in Figure 3-6 and He, Ar, CO_2 and CH_4 data are presented in Figure 3-8. The result protocols are given in Appendix 1. The concentrations of He, Ar and CH_4 were stable in the sample series but CO_2 decreased with increasing extracted volume. This concentration trend for CO_2 was opposite to the observations for samples from KA2563A:1. However, the values in the final samples from the two sections are similar. The high content of CO_2 in the initial samples from KA2051A01:9 is probably related to the closeness to the tunnel face and sampling of air contaminated section water. The CO_2 content decreases when the contribution of section water to the samples decreases, due to discharge of water. He was approximately 10 times lower in concentration compared to KA2563A:1. He and H_2 generally should show an increase with residence time (for example Laaksoharju et al. 2008). However, in this case the use of pull rods made of aluminium seems to have a significant and superimposed effect which is of decisive importance for the H_2 content. This is most probably due to ongoing corrosion processes in the borehole section where aluminium is oxidised while water is reduced according to $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ giving H_2 development in the borehole section.

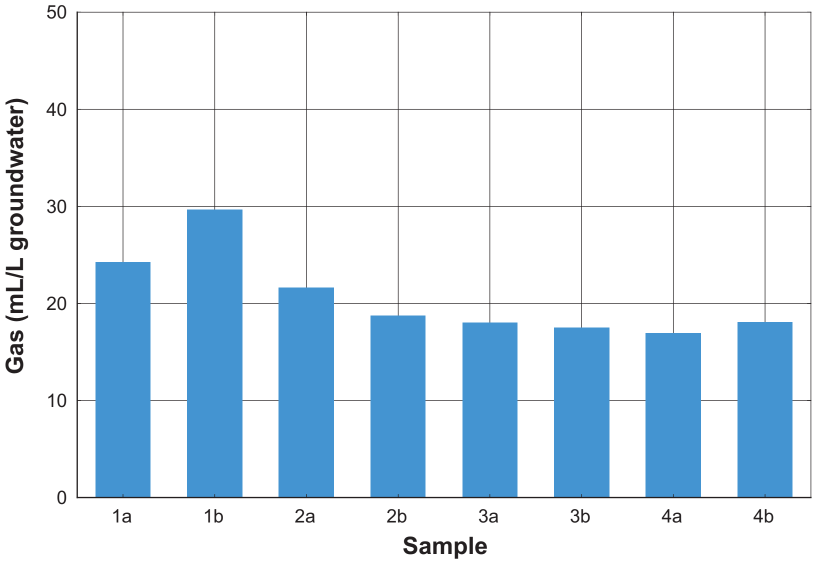

Figure 3-5. *Total amount of extracted gas calculated as mL of gas per L of groundwater from KA2051A01:9.*

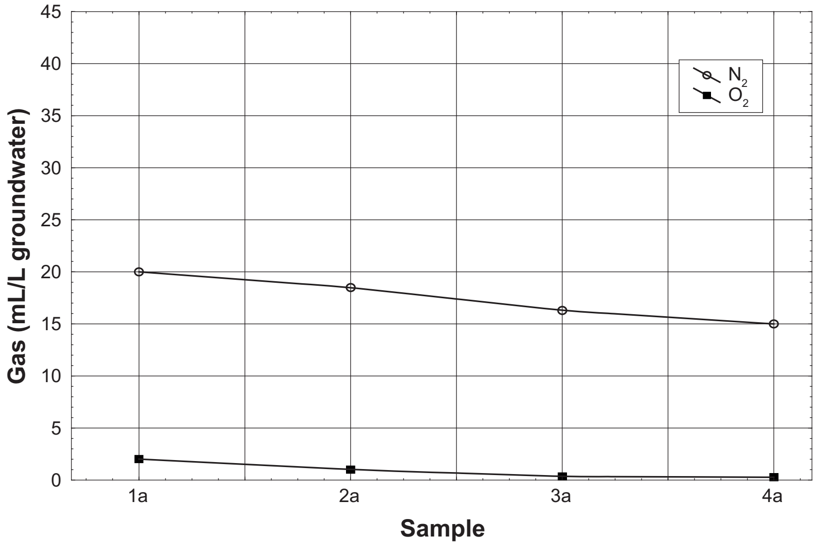

Figure 3-6. *Distribution of dissolved N_2 and O_2 in KA2051A01:9 over the four analysed samples (1a, 2a, 3a and 4a) in the series.*

3.3 Borehole sections KA2051A01:5 and KA3510A:2

3.3.1 Total volumes of gas

The two samples from each one of the borehole sections KA2051A01:5 and KA3510A:2 were collected as duplicates without a significant discharge of groundwater in between filling of the two samplers. Furthermore, the discharged volumes prior to the sampling (Table 2-3) were rather large i.e. almost ten times the estimated plug flow volumes of 89 L and 75 L, respectively. Therefore, ideally, each pair of samplers should contain the same gas volumes. The total volumes of extracted gas are presented in Table 3-3 and Figure 3-9. In KA2051A01:5 the volume of dissolved gas was 19.1 mL/L of groundwater in sample 1a compared to 32.9 mL/L in sample 1b. The total volumes of extracted gas in Table 3-3 (but not the data in Figure 3-6) are corrected for air contamination. The range is the same as observed for KA2051A01:9. It is not clear why the results diverge between the two samples but as observed previously, it is the amount of nitrogen that makes up this difference. On the other hand, there was only a minor difference in the total volumes of extracted gas between samples 1a and 1b from KA3510A:2 which is in line with the expectations.

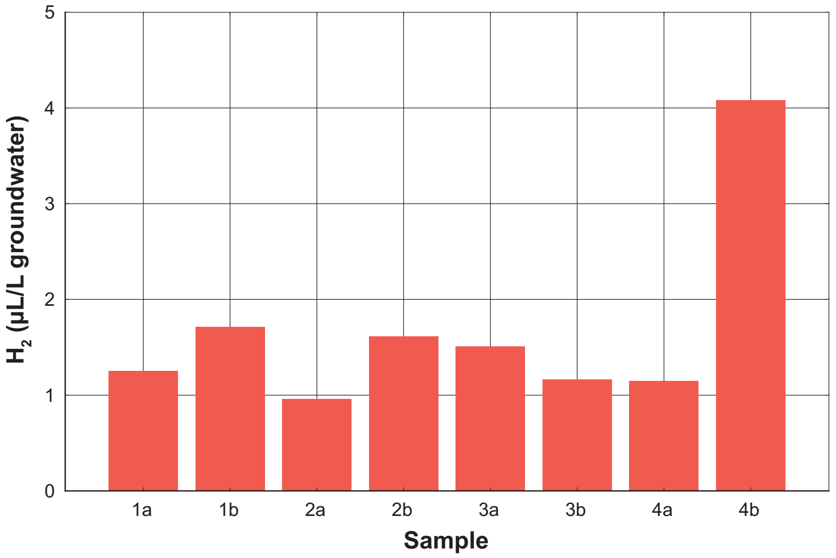

Figure 3-7. *The volumes of dissolved H_2 in sampled groundwater from KA2051A01:9.*

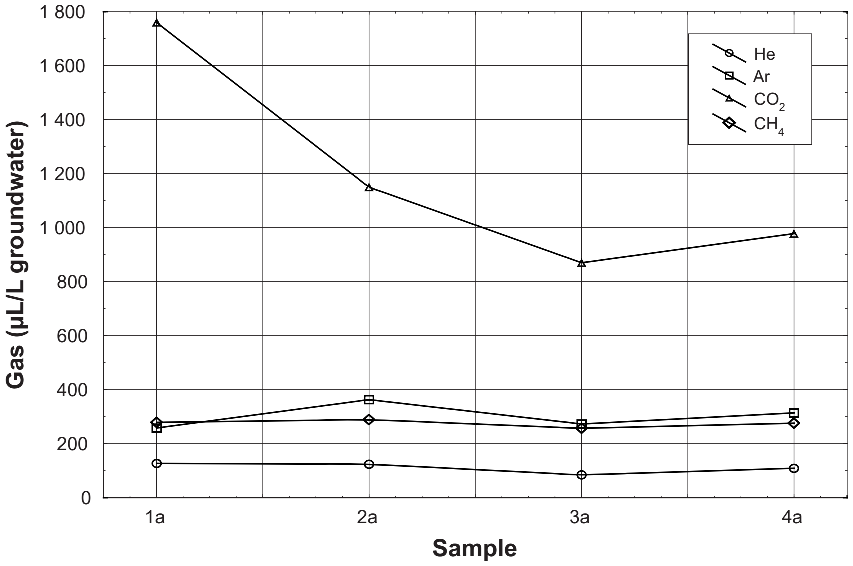

Figure 3-8. *Distribution of analysed gas over the four analysed samples (1a, 2a, 3a and 4a) from KA2051A01:9 in the series.*

Table 3-3. Results from the extraction and analysis of gas in borehole sections KA2051A01:5 and KA3510A:2. The total gas volumes are corrected for contamination by air.

Gas sample	Sample date	Sample time	Sample volume (mL)	Extracted total volume of gas (mL/L groundwater)	H_2 (µL/L groundwater)
KA2051A01:5					
1a	2015-11-27	08:05	325	19.1	1.8
1b	2015-11-27	08:12	305	32.9	1.3
KA3510A:2					
1a	2015-11-27	08:54	300	43.2	30.3
1b	2015-11-27	08:59	300	39.4	43.4

3.3.2 Volumes of dissolved H_2

Groundwater from KA3510A:2 contained 10 to 30 times more hydrogen compared to KA2051A01:5 (Figure 3-10). Again, the borehole KA3510A:2, instrumented with an aluminium rod, showed a higher gas content than the groundwater from borehole KA2051A01:5 with a stainless steel rod.

3.3.3 Complete analysis of gas

The results for the two duplicate samples collected from each one of the two boreholes are presented in Table 3-3 and Figure 3-11. The N_2 and CO_2 concentrations were higher in sample 1b compared to sample 1a for borehole KA2051A01:5. The dissolved He and CH_4 concentrations were higher in the deeper borehole KA3510A:2 (–507 masl) than in KA2051A01:5 (–349 masl) which may be expected since these concentrations depend on residence time and usually increase with depth.

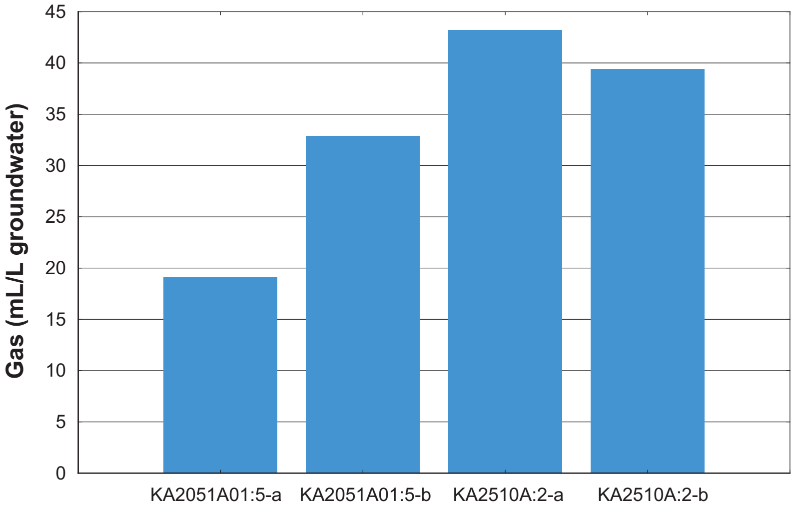

Figure 3-9. *Total amount of extracted gas calculated as mL of gas per L of groundwater from KA2051A01:5 and KA3510A:2. Sampling was performed in November 2015 with two samplers in series for each borehole section.*

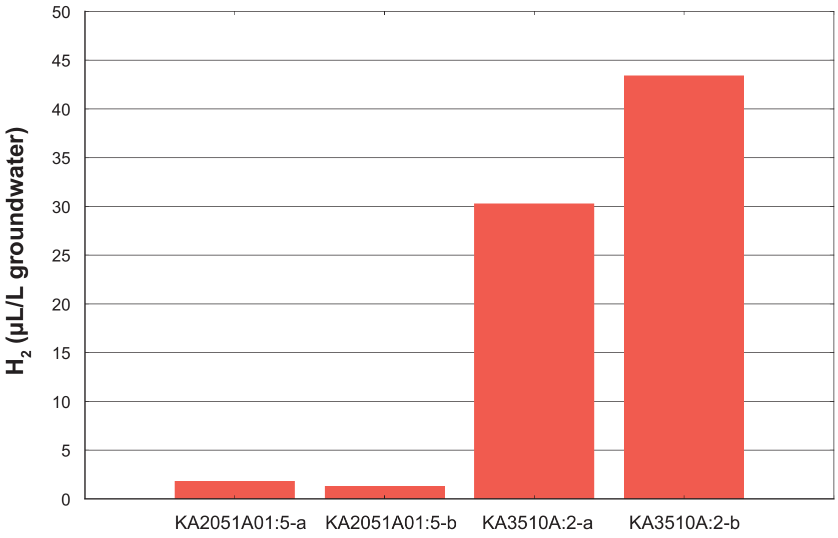

Figure 3-10. *The volumes of dissolved H_2 in sampled groundwater from KA2051A01:5 and KA3510A:2. Sampling was performed in November 2015 with the two duplicate samplers for each borehole section connected in series.*

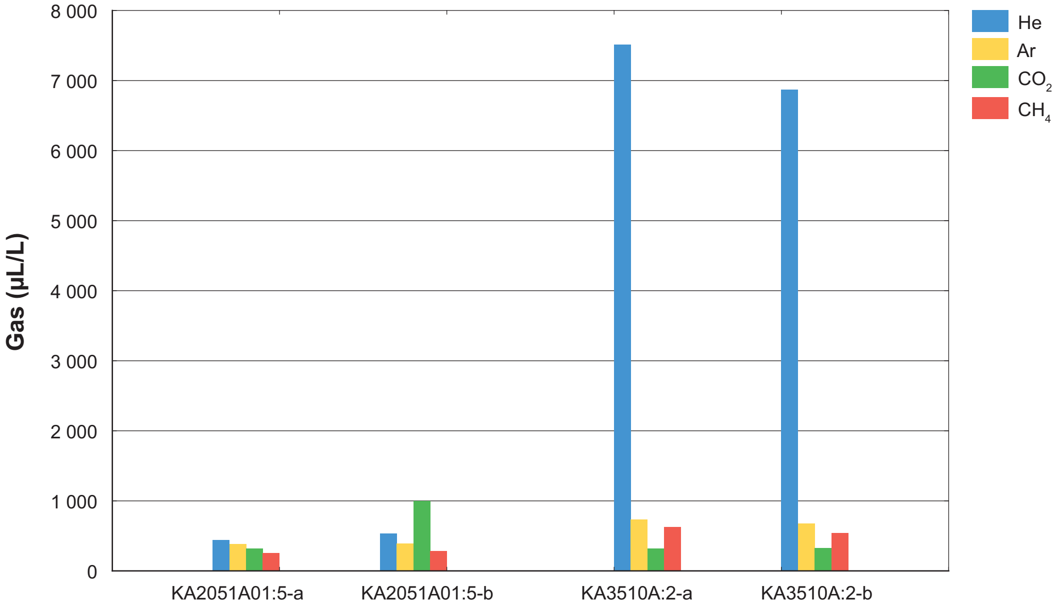

Figure 3-11. *The volumes of dissolved gases in sampled groundwater from KA2051A01:5 and KA3510A:2. Sampling was performed in November 2015 with the two duplicate samplers for each borehole section connected in series.*

3.4 Result summary

- The samples of gas extracted from the water standing in the borehole were overrepresented with N_2 in all targets and also with O_2 and CO_2 in KA2051A01:9.
- The gas samplers performed well and reproduced volumes of extracted gas were obtained after approximately a volume twice the individual plug flow volume (see Appendix 3) of each borehole section was flushed out.
- The gases Ar, CH_4, CO_2 and He all reproduced well over 4 discrete sampling occasions representing borehole section water and water obtained after flushing 2, 3 and 5 times the plug flow volumes of each sampled borehole section.
- The analysis of H_2 was performed on pairwise samples and each pair generally reproduced very well which attests the precision in sampling, extraction and analysis of the applied methods.
- H_2 was the gas that varied most in concentration in target KA2563A:1 when pressure and sample flow rate were altered. The larger flow rate, the less H_2 was detected. It appeared important to have a slow flow rate and as small pressure drop as possible prior to and during the sampling to obtain relevant concentrations since H_2 is easily degassing. Furthermore, the borehole sections may contain enhanced H_2 concentrations due to corrosion processes if the equipment contain parts made of aluminium. Therefore, to exchange a sufficient but not too large water volume prior to sampling is important to ensure samples representing groundwater from the bedrock fractures.
- H_2 and He were the two gases that differed most in concentrations between the targets. Both the H_2 and He contents are usually related to the residence times of the groundwaters. However, the H_2 contents of these sampled boreholes are more significantly affected by the material in the equipment and boreholes equipped with pull rods made of aluminium show 10 to 100 times higher H_2 concentrations in the groundwater. If the two sections (KA205A01:5 and KA205A01:9) from the borehole equipped with acid resistant steel parts are compared the totally 8+2 samples vary within 0.96 to 4.08 µL/L (both extreme values are from section no. 9). This may also be values that are impacted by the discharge of water prior to sampling and it may be the case that they are too low. However, the first sample in the series from section no. 9 is collected after discharge of only the tube volume and it is still a rather low value (1.52 µL/L).

- The diverging gas concentrations obtained by small variations in the sampling procedure indicate that the sampling performance has a significant impact on the results (especially for H_2 and He). It cannot be excluded that some of the previous results indicating large differences in the amount and composition of dissolved gases between the Äspö groundwaters may be due to inadequate control of the sampling procedures. The percentage of the different gases in borehole section KA2563A:1 and KA2051A01:9 are presented in Figures 3-12 and 3-13, respectively, in order to check if and how the proportions of the different gases are affected by purged volume and counter pressure. The diagrams generally show that the first samples in the series diverge the most from the others which may be expected since these samples represent the groundwater present in the borehole sections.

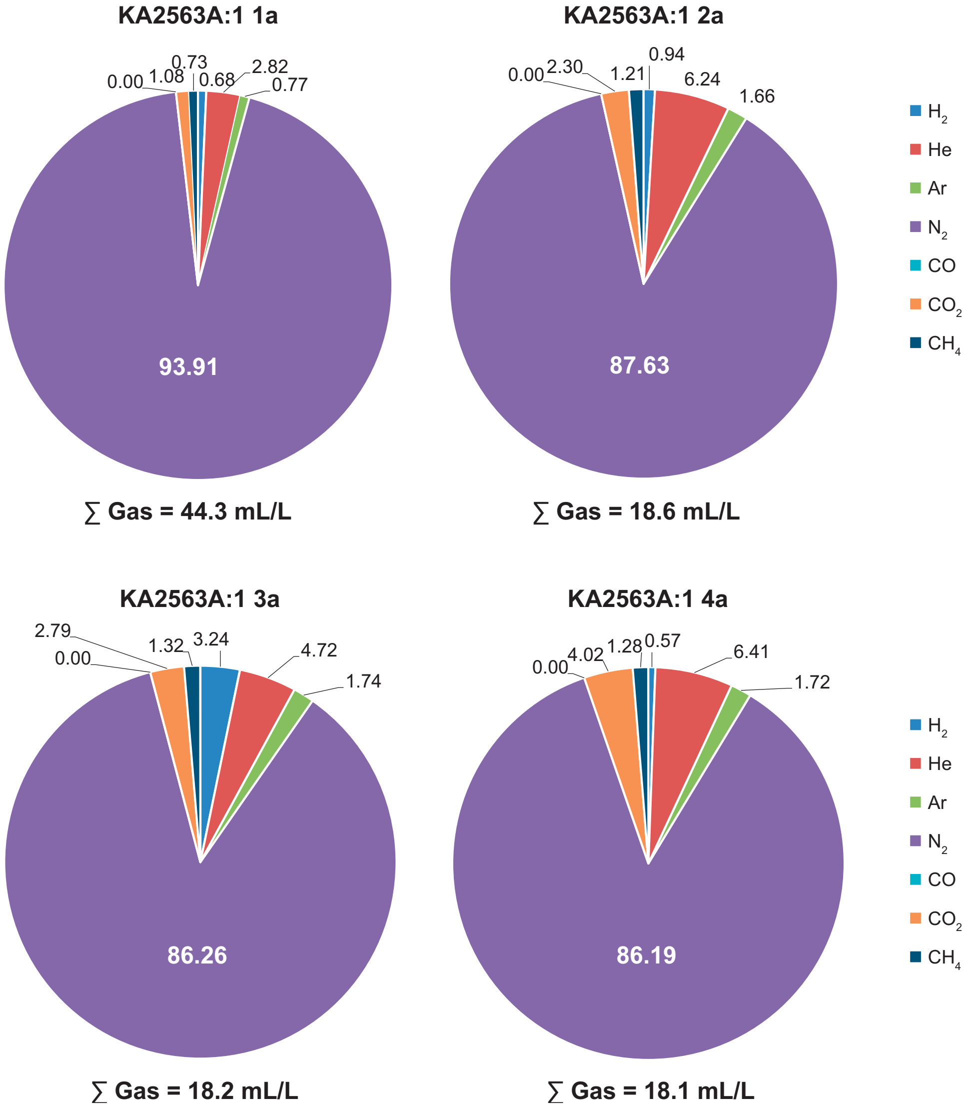

Figure 3-12. *Percentage of different gases in the four samples (1a, 2a, 3a and 4a) from borehole KA2563A section no. 1. The proportions of hydrogen are significant but carbon monoxide is too low to be shown.*

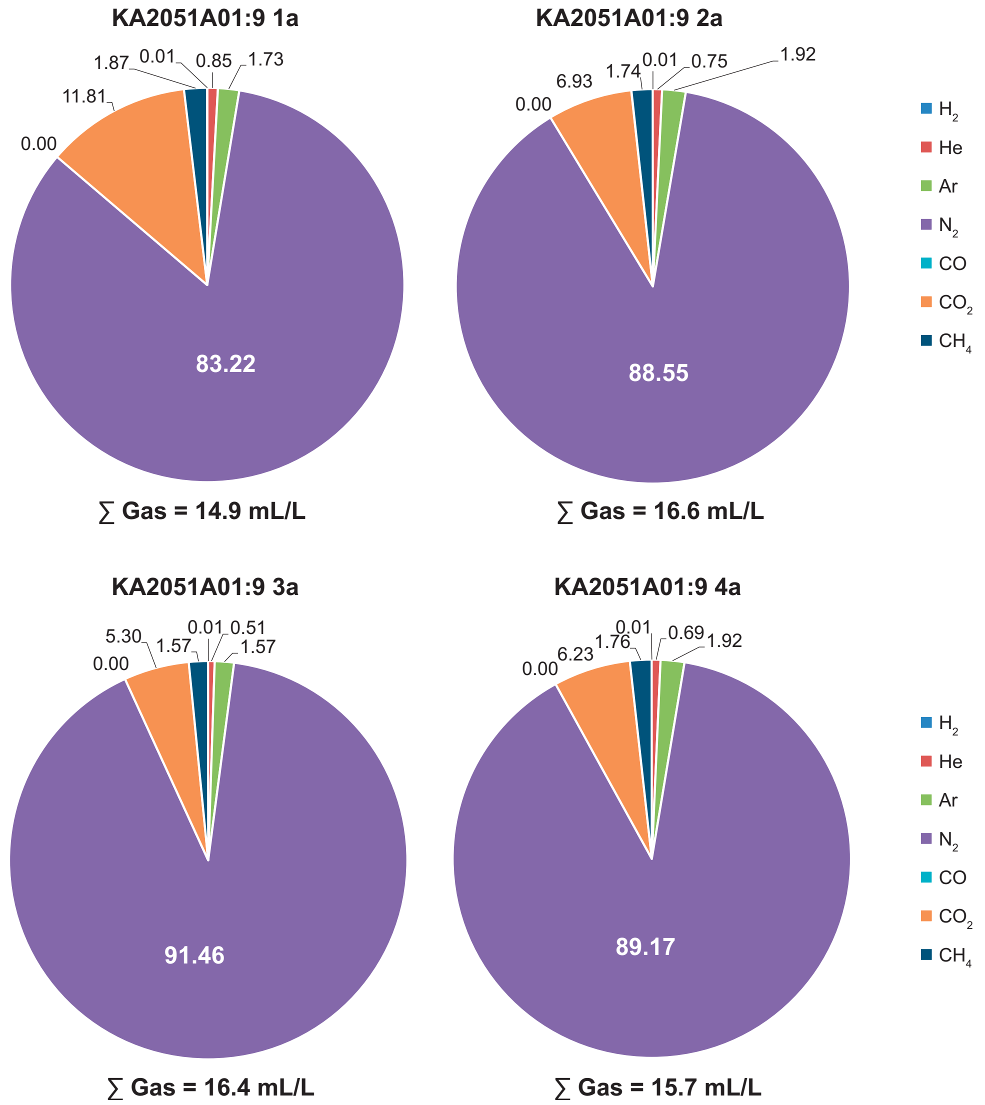

Figure 3-13. *Percentage of different gases in the four samples (1a, 2a, 3a and 4a) from borehole KA2051A01 section no. 9. The proportions of hydrogen and carbon monoxide are too low to be shown.*

3.5 Gas content and composition in Äspö groundwater and correlation with groundwater chemistry

Long series of gas observations relate to the so called MICROBE site in the Äspö Hard Rock Laboratory (HRL), from which several reports present gas data from KJ0050F01, KJ0052F01 and KJ0052F03 (Pedersen 2000, 2005a, b, 2013). Furthermore, gas was analysed in conjunction with the MINCAN experiment (Lydmark and Hallbeck, 2011) and gas was also sampled and analysed during a project focussing on microbial sulphide production in boreholes (Drake et al. 2014) as well as within a few other projects in the Äspö HRL. Additional gas data originate from boreholes drilled from the ground surface during the preinvestigation on Äspö as well as from the site investigations in Laxemar. In order to evaluate the reliability of the new gas dataset from this study, the set was compared to these earlier dissolved gas data. The comparison and evaluation included also possible correlation with the groundwater chemistry. Unfortunately, this reduces the amount of data to treat considerably since very few samples have both groundwater chemistry and gas data. In the following text some expected trends and relations are discussed.

The dissolved carbon dioxide content is expected to correlate with the alkalinity of the groundwater (HCO_3^-). Figure 3-14 presents the CO_2 content versus the alkalinity for all available sets of data from the Äspö area including Laxemar. Furthermore it differentiates between the data obtained in this study (new data) and earlier data (existing data). The increasing trend with the alkalinity is, however, not very clear. Generally, the CO_2 content is high for the samples with high alkalinity but some samples show low CO_2 content even if the alkalinity is high. This is the case for the new as well as the earlier data sets. PHREEQC calculations for the bicarbonate system suggests CO_2 degassing at near surface conditions during sampling (i.e. too large pressure drop) as a possible explanation. This could happen also at low CO_2 partial pressures since the samples have high total gas concentrations and some amounts of CO_2 may be forced to evacuate together with the other gases.

The depth dependence for the dissolved He and CH_4 gas concentrations is examined in Figure 3-15. As can be seen there He shows high values from intermediate depth and downwards while the highest CH_4 concentrations appear at intermediate depths and decrease below approximately −500 masl. Also in this case the new as well as the earlier data sets show the same behaviour. The concentrations of these gases as well as H_2 are expected to be related to the residence time of the groundwater rather than depth. Figures 3-16, 17 and 18 presents H_2, CH_4 and He concentration ranges given as colour coding on plots of $\delta^{18}O$ (‰ V-SMOW) versus chloride concentration. The isotope ratio and the chloride are selected to indicate the water type and thereby the residence time of the groundwaters. The isotope ratio ($\delta^{18}O$) depends on the prevailing climate conditions at the time when the groundwater was formed and is therefore an indicator of the groundwater origin. The chloride concentration, on the other hand, varies according to marine or non-marine origin as well as depth (Laaksoharju et al. 2008).

From Figure 3-16 it is difficult to see any correlation with residence time for the hydrogen gas. Since the H_2 data from this study show increased concentrations for boreholes with equipment parts made of aluminium and most early boreholes have this type of equipment it is reasonable to assume that most of the earlier values are more or less affected by corrosion of aluminium and this effect is superimposed on other possible trends and relations.

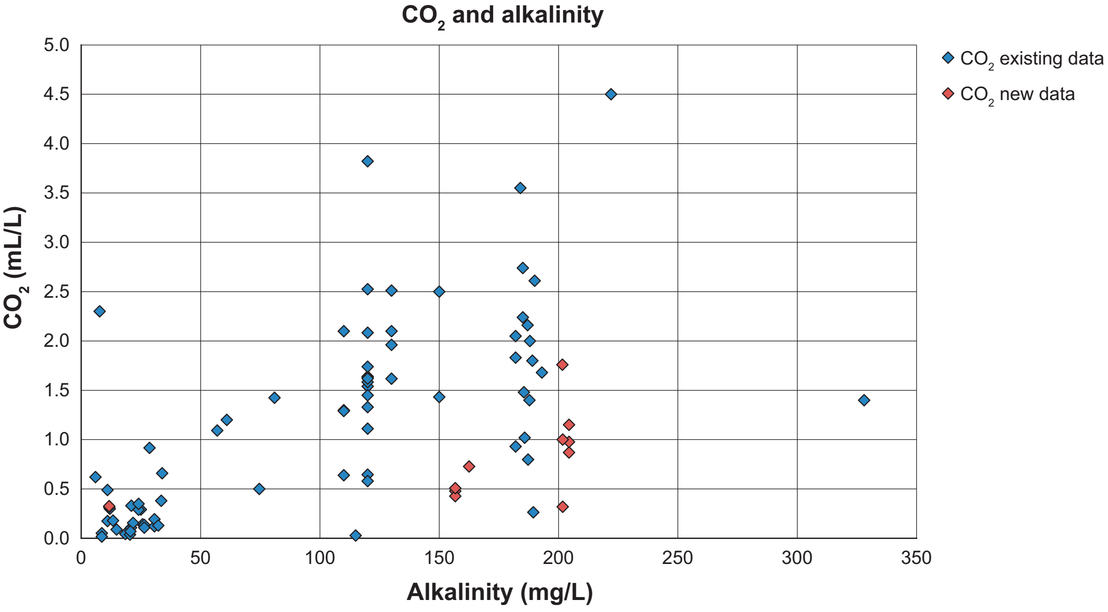

Figure 3-14. *Dissolved CO_2 gas concentration versus the alkalinity of the groundwater for all complete datasets from the Äspö area including Laxemar (data from Sicada).*

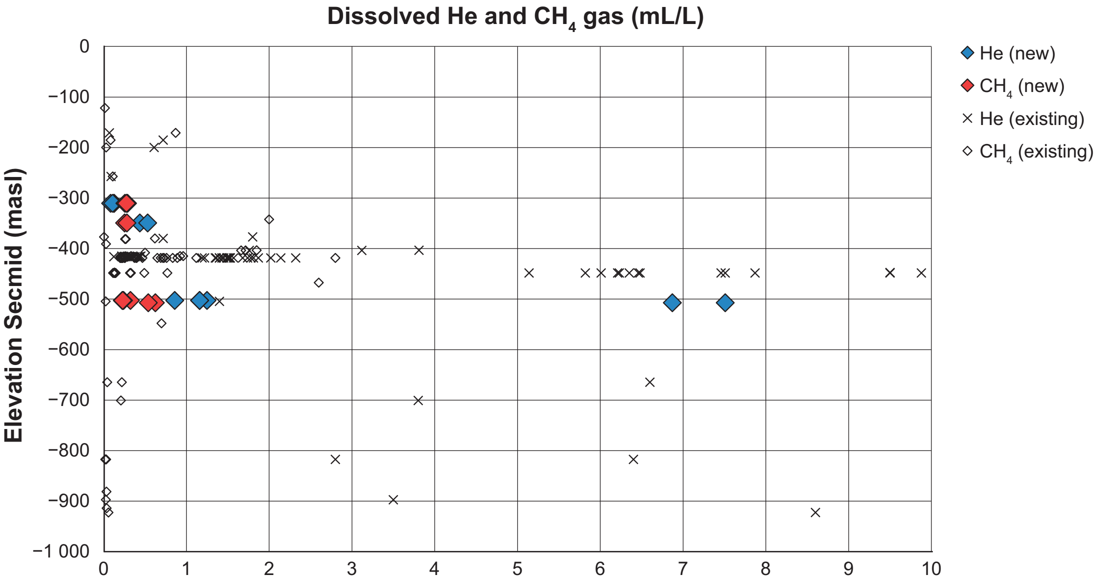

***Figure 3-15.** Dissolved He and CH_4 gas concentrations versus elevation for all complete datasets from the Äspö area including Laxemar (data from Sicada).*

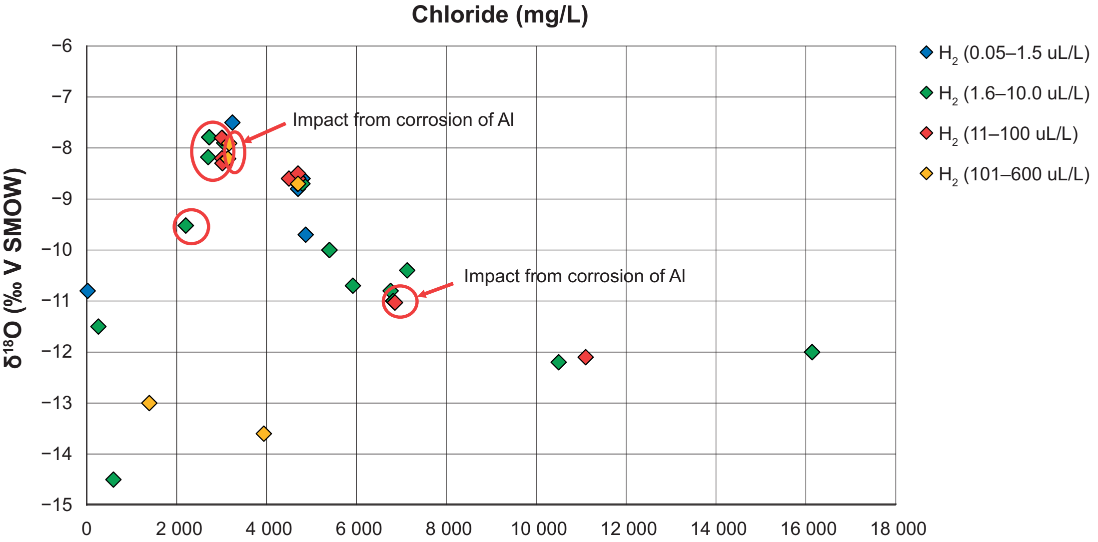

***Figure 3-16.** $\delta^{18}O$ plotted versus chloride concentration to indicate the groundwater type associated to the sample. The dissolved H_2 gas concentration range is given by the colour coding of each sample for all complete datasets from the Äspö area including Laxemar (data from Sicada). The red circles mark the new samples in this study.*

Figure 3-17 show a somewhat more logical pattern for CH_4 although many of the earlier data points seem to diverge. The high concentrations are generally related to intermediate chloride concentrations or low $\delta^{18}O$ (‰ V-SMOW) indicating groundwater of older non-marine and glacial types while deep saline water as well as more diluted water have lower concentrations.

Helium shows the clearest concentration pattern, see Figure 3-18. The highest concentration range is found among the deep saline waters and some of the groundwaters with a pronounced glacial signature, i.e. the groundwaters with the longest residence times, while the low and intermediate chloride concentration range generally show lower contents.

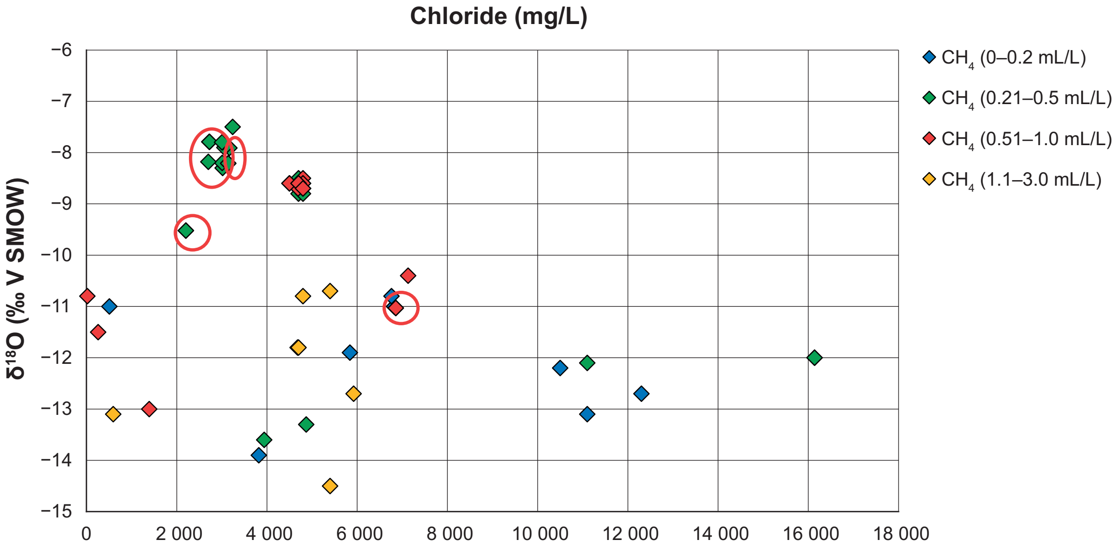

***Figure 3-17.** $\delta^{18}O$ plotted versus chloride concentration to indicate the groundwater type associated to the sample. The dissolved CH_4 gas concentration range is given by the colour coding of each sample for all complete datasets from the Äspö area including Laxemar (data from Sicada). The red circles mark the new samples in this study.*

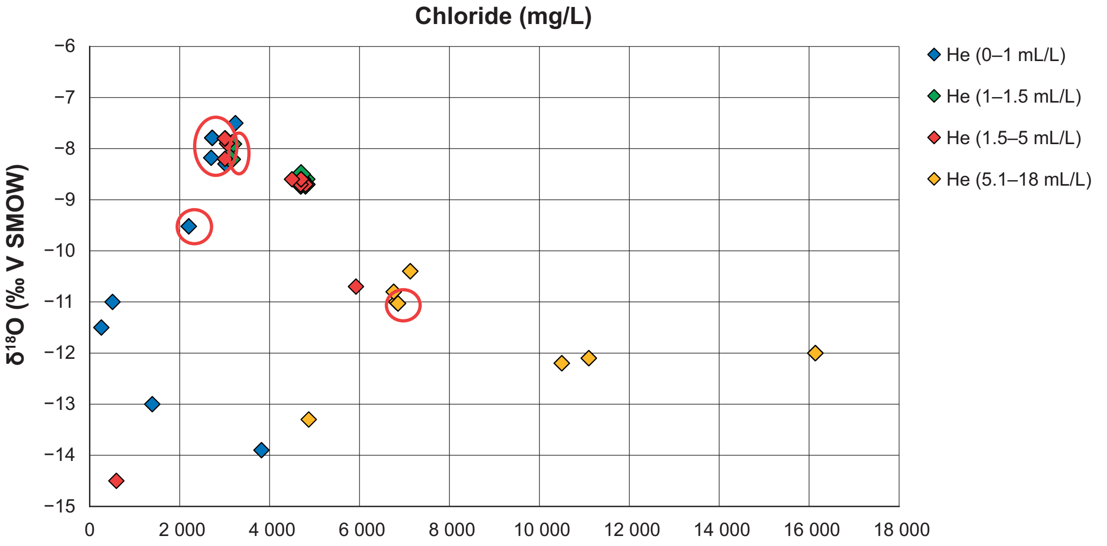

***Figure 3-18.** $\delta^{18}O$ plotted versus chloride concentration to indicate the groundwater type associated to the sample. The dissolved He gas concentration range is given by the colour coding of each sample for all complete datasets from the Äspö area including Laxemar (data from Sicada). The red circles mark the new samples in this study.*

3.6 Isotope composition of collected gases

The isotope ratios obtained by isotope ratio mass spectrometry are presented in Table 3-4. As feared the hydrogen gas contents were too low in many cases to obtain δ^2H values. The few available H_2 gas ranges are given in the Table. The borehole sections having pull rods made of aluminium generally showed measurable ratios, since they have enhanced hydrogen gas concentrations caused by corrosion. These results are, however, less interesting since they are due to artefacts and the ratios will not be further commented here

Borehole section KA3385A:1 has isotope results also from 2010 and 2011. These values are given for comparison since they were obtained with the previous instrumentation including aluminium parts. Despite the aluminium and in contrast to the expectations these three samples showed very low hydrogen gas contents and consequently it was not possible to obtain the δ^2H ratios. This may be due to large discharged volumes prior to sampling, giving lowered concentrations in the samples or the sampling equipment/method that differed from the one documented in this report.

Concerning isotope analyses of other gases than hydrogen, methane was analysed for δ^{13}C and δD and carbon dioxide was analysed for δ^{13}C and δ^{18}O. Six samples from different borehole sections were analysed during this campaign (Table 3-4) and these results are compared with the only available previous results of isotopes in gases from Äspö derived from KA3385A:1 (cf. Table 3-4) and borehole section KA3110A:1, both sampled during the sulphide project at Äspö (Drake et al. 2014). Old and new data are plotted together in Figures 3-19, 3-20 and 3-21.

Based on the very few analyses and the different circumstances during sampling it is difficult to make interpretations about processes and origin. A number of factors that may have influenced the results are discussed below.

Analyses from different laboratories: The samples taken from KA3385A:1 and KA3110A:1 during the sulphide project were analysed at Heidelberg University or at the Laboratory of Ion Beam Physics, in Zurich whereas the samples taken during the present sampling campaign were analysed at Hydroisotop, in Germany.

The sulphide project: The samples taken from KA3385A:1 and KA3110A:1 were part of the sulphide project (cf. Drake et al. 2014) involving different circulation experiments and also possibly influenced by the addition of ethanol (by mistake) at one occasion during the project. The borehole installation involved aluminium-rods (see below).

The instrumentation in the boreholes: It is well known that the combination of the aluminium rods and the steel details in the packers in the instrumentation originally used (and still present in many boreholes) at Äspö causes corrosion and produces H_2. This will also affect other redox systems and microbial activity in a way that theoretically could affect both methane and carbon dioxide contents as well as isotopic signatures. In borehole KA3385A the aluminium rods were replaced by steel so that the three samples taken 2010 represent the period with aluminium and the sample taken 2015 represent steel rods. The samples are marked in Figure 3-19, 3-20 and 3-21. It is obvious that there are differences in isotope ratios between the two sampling occasions mainly concerning δD in the methane (lower values in the 2015 sampling) and δ^{13}C in the carbon dioxide (higher values in the 2015 samples). Also the δ^{18}O values are different (higher values in the 2015 sampling). On the other hand there are other circumstances (see above) that may also have influenced the changes in isotopic composition.

Among the six sections sampled for isotopic composition of gases within the present study, three represent boreholes with aluminium rods and three have steel rods. The Al-samples are encircled in red in Figures 3-19, 3-20 and 3-21 and differ by showing higher δ^{13}C in both methane and carbon dioxide compared with the samples from sections with steel rods. This is not in accordance with the observations from KA3385A:1, so it is not possible to deduce the type of processes that may have affected the isotope ratios based on the available data set.

Available gas and groundwater data from same section: The need of having analysis of gas content (composition), isotope ratios of the gases and also the groundwater chemistry from the same section sampled at the same time cannot be stressed enough. This is crucial for the possibility to judge the quality of the samples and also to interpret the processes responsible for the gas composition.

Despite all the above given potential reasons for deviations a look at the results shows that δ^{13}C of the methane is within the interval −55 to −40 ‰ (VPDB) and δD values between −250 to −150 ‰ VSMOW. These are relatively high values to be microbial methane formed from carbonate reduction which usually have values lower than −60 ‰ VPDB for δ^{13}C (Whiticar 1999). Methane formed via methyl-type formation on the other hand may have δ^{13}C in the measured interval and this may be an explanation especially for the samples with the lowest δ^{13}C and δD values (−55 and −250 ‰, respectively) because low δD values are generally expected during metyl-fermation. Bacterial oxidation of methane increases the δ^{13}C and δD values in the remaining methane and this may have influenced the present samples. The isotope enrichment factor between δ^{13}C (methane) and δ^{13}C (carbon dioxide) is relatively low in all the measured samples (34–36 ‰) further indicating that bacterial methane oxidation may have occurred (cf. Whiticar 1999). In the evaluation of the sulphide project (Drake et al. 2014) the combination of methane formed via methyl-type formation and probable effects of methane oxidation was discussed as well and were also supported by isotopes in the groundwater. Worth mentioning is that the δ^{13}C (carbon dioxide) from the present study is higher (in the range −20 to −15 ‰) than in the sulphide project (KA 3110A and KA3385A; −28 to −19 ‰) possibly indicating that the effect of methane oxidation is even less obvious in the samples from the present study. Concerning supporting information from isotope analyses in calcite, precipitates on the equipment in KA3385A (and KA3105A) show no conclusive influence of methane oxidation (Drake et al. 2014). However, in the fractures at Laxemar there are several clear evidences of fossil methane oxidation so it has indeed occurred in the crystalline basement, although not from present groundwater (Drake et al. 2015).

In summary it is not possible to give any comprehensive interpretations of the hitherto obtained isotopic results as gas composition and other supporting data from the same section is only available for a few samples. It is therefore strongly supported that further sampling includes both groundwater chemistry, gas analyses and isotope ratios on gases and δ^{18}O, δD, δ^{13}C of the groundwater and dissolved carbonate from the same sections and sampled at the same time**.** This should add important information and make interpretations of the gas-groundwater system and the related microbial processes possible.

For the continuation of gas sampling tests it is recommended that series of gas sampling also should be combined with series of gas isotope sampling. In samples were corrosion occurs such sampling series can significantly increase the understanding of the processes going on.

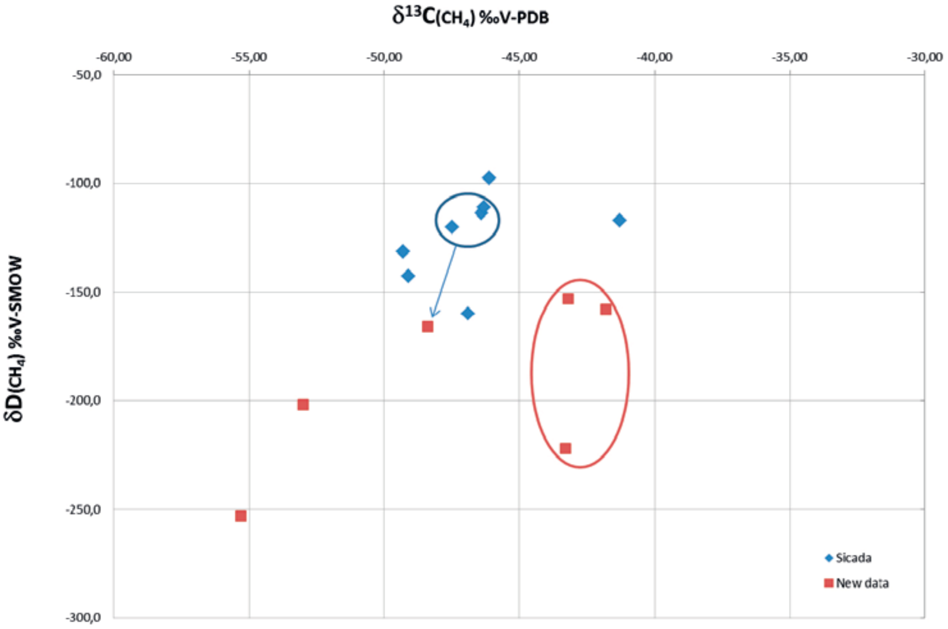

Figure 3-19. *δ^{13}C in methane plotted versus δD in methane. Samples from the present study (red) and from Sicada belonging to the Sulphide project; boreholes KA3110A:1 and KA3385A:1(blue). Encircled in red are the samples from the presented study with Al-rods in the borehole installations. Encircled in blue are samples from KA3385A:11 analysed during the Sulphide project and resampled in the present study (red sample connected with an arrow).*

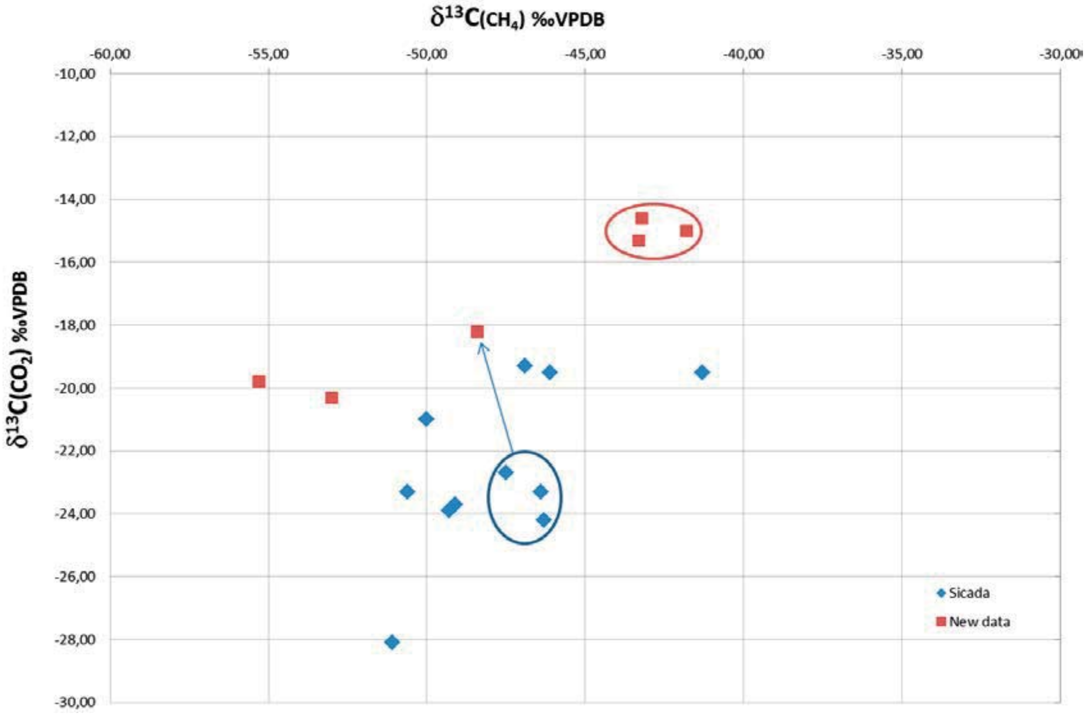

Figure 3-20. $\delta^{13}C$ *in methane plotted versus* $\delta^{13}C$ *in carbon dioxide. Samples from the present study (red) and from Sicada belonging to the Sulphide- and Microbe projects at Äspö (blue). Encircled in red are the samples from the presented study with Al-rods in the borehole installations. Encircled in blue are samples from KA3385A:1 analysed during the sulphide project and resampled in the present study (red sample connected with an arrow).*

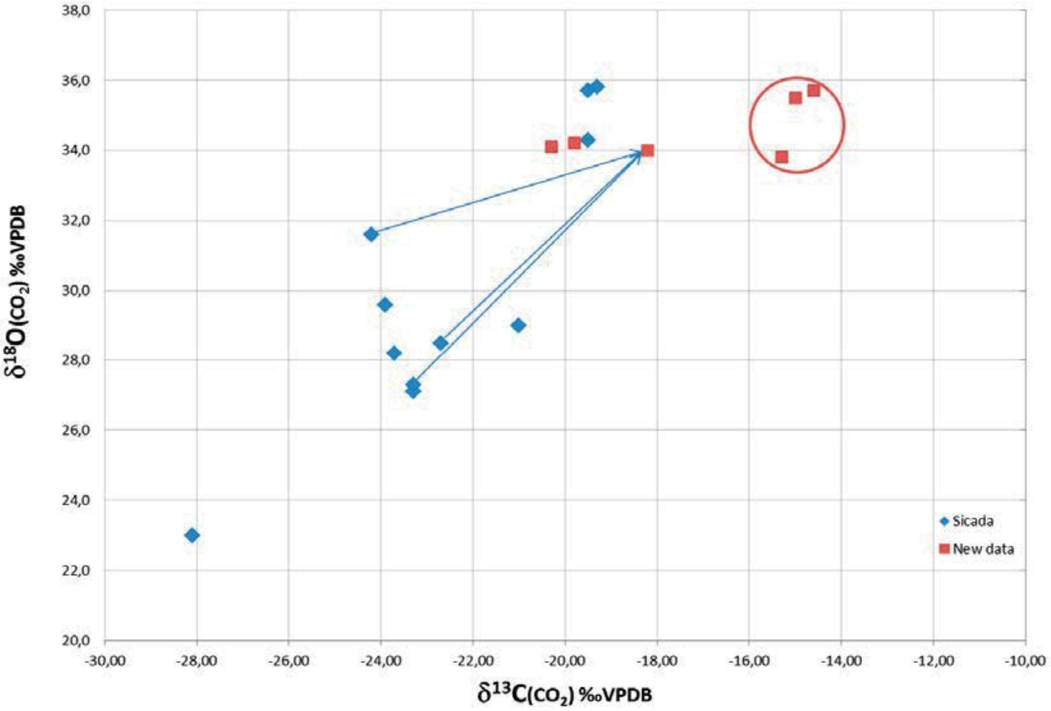

Figure 3-21. $\delta^{18}O$ *in carbon dioxide plotted versus* $\delta^{13}C$ *in carbon dioxide***.** *Samples from the present study (red) and samples from Sicada belonging to the Sulphide- and Microbe projects at Äspö (blue). Encircled in red are the samples from the presented study with Al-rods in the borehole installations. Samples from KA3385A:1 analysed during the sulphide project and resampled in the present study are connected with arrows).*

Table 3-4. Isotope results by isotope ratio mass spectrometry. δ^2H values that may be influenced by corrosion of aluminium are marked (Al).

Isotopes	**KA2511A:4** **Sample no. 24012**	**KA2563A:1** **Sample no. 2013**	**KA2563A:4** **Sample no. 24014**	
Sampling date	2014-12-03	2014-12-03	2014-12-16	Unit and error
H_2 conc. (µL gas/L water)		30–300		
Deuterium (δ^2H-H_2)	−788 (Al)	−780 (Al)	−773 (Al)	‰ VSMOW; ±10 ‰
Deuterium (δ^2H-CH_4)	−222	−158	−153	‰ VSMOW; ±10 ‰
Carbon-13 ($\delta^{13}C$-CH_4)	−43.3	−41.8	−43.2	‰ VPDB; ±1.5 ‰
Carbon-13 ($\delta^{13}C$-C_2H_6)*	−31.8	−30.8	−31.8	‰ VPDB; ±1.5 ‰
Carbon-13 ($\delta^{13}C$-CO_2)	−15.3	−15.0	−14.6	‰ VPDB; ±0.3 ‰
Oxygen ($\delta^{18}O$-CO_2)	33.8	35.5	35.7	‰ VSMOW; ±0.2 ‰

Isotopes	**KA3385A:1** **Sample no. 24277**	**KO8028F01** **Sample no. 24278**	**KA2051A01:5** **Sample no. 24290**	
Sampling date	2015-11-26	2015-11-26	2015-12-02	Unit and error
H_2 conc. (µL gas/L water)			1.3–1.8	
Deuterium (δ^2H-H_2)	n.m.	n.m.	n.m.	
Deuterium (δ^2H-CH_4)	−166	−253	−202	‰ VSMOW; ±10 ‰
Carbon-13 ($\delta^{13}C$-CH_4)	−48.4	−55.3	−53.0	‰ VPDB; ±1.5 ‰
Carbon-13 ($\delta^{13}C$-CO_2)	−18.1	−19.8	−20.3	‰ VPDB; ±0.3 ‰
Oxygen ($\delta^{18}O$-CO_2)	34.0	34.2	34.1	‰ VSMOW; ±0.2 ‰

Isotopes		**KA3385A:1** **Sample no. 20348** **Fract. water**	**KA3385A:1** **Sample no. 20573** **Sect. water**	
Sampling date		2010-10-06	2011-01-20	Unit and error
H_2 conc. (µL gas/L water)		4.0	2.4	
Deuterium (δ^2H-H_2)		n.m. (Al)	n.m. (Al)	‰ VSMOW; ±10 ‰
Deuterium (δ^2H-CH_4)		−113.9	−111.1	‰ VSMOW; ±10 ‰
Carbon-13 ($\delta^{13}C$-CH_4)		−46.40	−46.30	‰ VPDB; ±1.5 ‰
Carbon-13 ($\delta^{13}C$-CO_2)		−23.30	−24.20	‰ VPDB; ±0.3 ‰
Oxygen ($\delta^{18}O$-CO_2)		27.1	31.6	‰ VSMOW; ±0.2 ‰

* Generally δ13C in C2H6, C3H8, C4H10 and C4H10 were not possible to measure. This was due to too low gas concentrations.

4 Discussion and conclusions

Despite the additional new dataset, the total amount of useful gas data is still too small to allow a comprehensive evaluation and discussion about the reliability of the values. The fact that so many of the early gas data points lack corresponding groundwater composition data is an aggravating circumstance. This makes them less useful for the type of evaluation considering also possible correlation with water types and residence times.

The most momentous achievement from this gas study is the improved understanding of the importance of the sampling conditions and how they affect the samples, especially the N_2, H_2 and He concentrations. For example, the purged volume prior to sampling is of outmost importance since the dissolved gas concentrations in the borehole section probably differ from that of the groundwater in the bedrock fractures. However, it may not be obvious whether a small or a large purged volume is the most favourable in order to get representative results. 1) If the borehole section water is influenced by H_2 gas development from corrosion of aluminium or, to a lesser extent, stainless steel parts of the packer equipment in the borehole, it is necessary to discharge at least two to three plug flow volumes to obtain more plausible H_2 gas values and it is still difficult to judge their representativity. 2) On the other hand, if the pressure drop during purging and sampling causes gas (most easily H_2) to be released from the water and trapped in the borehole section this will result in a too low gas content in the water samples. In this case it would be more favourable with discharge of a very small volume. Both situations may occur at the same time causing a more complex situation. Furthermore, the recent history of the borehole section implying pressure drops etc prior to the sampling occasion may also play a significant role for the dissolved concentration of gas in the groundwater present in the borehole section.

It is a general impression that the handling of the sampling equipment and the method for dissolved gas is somewhat too complicated for routine sampling. However, with some minor measures and improvements on the design of the equipment and the procedure this could probably be solved. It is of utmost importance though, to develop and test equipment for gas extraction at the site. It is not an optimal procedure to send the sampling equipment to another laboratory for extraction.

The few determinations of isotope ratios in gases that have been carried out prior to this study were all of them from a previous sulphide project in the Äspö HRL (Drake et al. 2014). The new data show differences between borehole sections with aluminium and stainless steel equipment which is what could be expected, although the causing processes are not fully known. Furthermore, there is generally a systematic difference between the new dataset from this study and the earlier dataset, however, the data are too few to deduce an explanation. More isotope determinations in gases have therefore to be performed in order to improve the understanding and the reliability. An aggravating circumstance is the often quite long time needed to collect a sufficient gas volume for the determinations. For the moment there is no solution proposed to this problem. Although the present procedure seems unfavourably time consuming it is still recommended to collect more sample series and vary the purged volume, to use more than one laboratory for the analyses and to compare different sampling equipment.

Regular yearly sampling for dissolved gas as well as isotope ratios in gases is suggested in order to overcome the lack of data and estimate the optimal sampling conditions. A few carefully selected boreholes without equipment parts made of aluminium and collection of sample series including at least two samples, one initial sample and one sample after discharge of at least two plug flow volumes is recommended.

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Appendix 1

Gas data reporting

Sample: **KA2563A:1**
Sample vessel 1
MICANS sample nr: **140277:1**
Section: 242–246 m, at 340 m level
Sampling date: 2014-11-24
Extraction date: 2014-11-24
Volume water: 160 mL
Volume extracted gas: 7.6 mL
Gas L^{-1} groundwater: 47.5 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater: 47.5 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater: 44.3 mL (sum of analysed gases without air contamination)
Analysis volume agreement: 100 (sum of analysed gas versus extracted gas)
Air contamination: 6.9 %
Volume of air in the extracted gas: 525 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	6 380	303	6 860	303
Helium	(He)	26 300	1 250	28 300	1 250
Argon	(Ar)	7 800	371	7 690	340
Oxygen	(O_2)	14 500	688	–	–
Nitrogen	(N_2)	929 000	44 100	940 000	41 600
Carbon monoxide	(CO)	15.0	0.71	16.1	0.71
Carbon dioxide	(CO_2)	10 100	479	10 800	479
Methane	(CH_4)	6 810	324	7 320	324
Ethane	(C_2H_6)	< 1.00	< 0.05	< 1.08	< 0.05
Ethene	(C_2H_4)	< 2.00	< 0.10	< 2.15	< 0.10
Ethyne	(C_2H_2)	< 2.00	< 0.10	< 2.15	< 0.10
Propane	(C_3H_8)	< 1.00	< 0.05	< 1.08	< 0.05
Propene	(C_3H_6)	< 2.00	< 0.10	< 2.15	< 0.10
Propyne	(C_3H_4)	< 4.00	< 0.20	< 4.30	< 0.20
	Σ	**1 000 000**	**47 500**	**1 000 000**	**44 300**

Date: Approved by:

Karsten Pedersen

Sample: **KA2563A:1**
Sample vessel 3
MICANS sample nr: **140277:3**
Section: 242–246 m, at 340 m level
Sampling date: 2014-11-24
Extraction date: 2014-11-24
Volume water: 160 mL
Volume extracted gas: 3.4 mL
Gas L^{-1} groundwater: 21.3 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater: 21.3 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater: 19.7 mL (sum of analysed gases without air contamination)
Analysis volume agreement: 100 (sum of analysed gas versus extracted gas)
Air contamination: 12.7 %
Volume of air in the extracted gas: 432 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas ($\mu L\ L^{-1}$)**	**Gas (ppm)**	**Gas ($\mu L\ L^{-1}$)**
Hydrogen	(H_2)	8 170	174	9 360	174
Helium	(He)	54 400	1 160	62 300	1 160
Argon	(Ar)	15 700	335	16 700	309
Oxygen	(O_2)	26 700	567	–	–
Nitrogen	(N_2)	867 000	18 400	879 000	16 300
Carbon monoxide	(CO)	< 3.19	< 0.07	< 3.47	< 0.07
Carbon dioxide	(CO_2)	20 100	427	23 000	427
Methane	(CH_4)	10 600	225	12 100	225
Ethane	(C_2H_6)	< 1.60	< 0.04	< 1.74	< 0.04
Ethene	(C_2H_4)	< 3.19	< 0.07	< 3.47	< 0.07
Ethyne	(C_2H_2)	< 3.19	< 0.07	< 3.47	< 0.07
Propane	(C_3H_8)	< 1.60	< 0.04	< 1.74	< 0.04
Propene	(C_3H_6)	< 3.19	< 0.07	< 3.47	< 0.07
Propyne	(C_3H_4)	< 6.38	< 0.14	< 6.94	< 0.14
	Σ	**1 000 000**	**21 300**	**1 000 000**	**18 600**

Date:

Approved by:

Karsten Pedersen

Sample:	**KA2563A:1**
Sample vessel	1
MICANS sample nr:	**140277:5**
Section:	242–246 m, at 340 m level
Sampling date:	2014-11-24
Extraction date:	2014-11-24
Volume water:	250 mL
Volume extracted gas:	5.0 mL
Gas L^{-1} groundwater:	20.0 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater:	20.2 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater:	18.2 mL (sum of analysed gases without air contamination)
Analysis volume agreement:	101 (sum of analysed gas versus extracted gas)
Air contamination:	10.1 %
Volume of air in the extracted gas:	505 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	29 500	590	32 800	590
Helium	(He)	42 900	859	47 800	859
Argon	(Ar)	16 700	335	17 600	316
Oxygen	(O_2)	21 400	428	–	–
Nitrogen	(N_2)	864 000	17 300	872 000	15 700
Carbon monoxide	(CO)	< 3.6	< 0.07	< 4.0	< 0.07
Carbon dioxide	(CO_2)	25 400	508	28 300	508
Methane	(CH_4)	12 100	241	13 400	241
Ethane	(C_2H_6)	< 1.8	< 0.04	< 2.0	< 0.04
Ethene	(C_2H_4)	< 3.6	< 0.07	< 4.0	< 0.07
Ethyne	(C_2H_2)	< 3.6	< 0.07	< 4.0	< 0.07
Propane	(C_3H_8)	< 1.8	< 0.04	< 2.0	< 0.04
Propene	(C_3H_6)	< 3.6	< 0.07	< 4.0	< 0.07
Propyne	(C_3H_4)	< 6.12	< 0.14	< 8.00	< 0.14
	Σ	**1 010 000**	**20 200**	**1 010 000**	**18 200**

Date:

Approved by:

Karsten Pedersen

Sample: **KA2563A:1**

Sample vessel 3

MICANS sample nr: **140277:7**

Section: 242–246 m, at 340 m level

Sampling date: 2014-11-24

Extraction date: 2014-11-24

Volume water: 260 mL

Volume extracted gas: 5.0 mL

Gas L^{-1} groundwater: 19.2 mL (volume extracted from the groundwater sample)

Gas L^{-1} groundwater: 19.5 mL (sum of analysed gases with air contamination)

Gas L^{-1} groundwater: 18.1 mL (sum of analysed gases without air contamination)

Analysis volume agreement: 101 (sum of analysed gas versus extracted gas)

Air contamination: 7.1 %

Volume of air in the extracted gas: 353 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	5 350	103	5 760	103
Helium	(He)	60 300	1 160	64 900	1 160
Argon	(Ar)	16 800	323	17 400	311
Oxygen	(O_2)	15 000	288	–	–
Nitrogen	(N_2)	865 000	16 600	871 000	15 600
Carbon monoxide	(CO)	13.5	0.26	14.5	0.26
Carbon dioxide	(CO_2)	37 900	728	40 700	728
Methane	(CH_4)	12 100	232	13 000	232
Ethane	(C_2H_6)	< 1.8	< 0.04	< 1.94	< 0.04
Ethene	(C_2H_4)	< 3.6	< 0.07	< 3.87	< 0.07
Ethyne	(C_2H_2)	< 3.6	< 0.07	< 3.87	< 0.07
Propane	(C_3H_8)	< 1.8	< 0.04	< 1.94	< 0.04
Propene	(C_3H_6)	< 3.6	< 0.07	< 3.87	< 0.07
Propyne	(C_3H_4)	< 6.12	< 0.14	< 7.74	< 0.14
	Σ	**1 010 000**	**19 500**	**1 010 000**	**18 100**

Date:

Approved by:

Karsten Pedersen

Sample: **KA2051A01:9**
Sample vessel 1
SKB sample nr: 24052
MICANS sample nr: **150019:1**
Section: 1 m
Sampling date: 2015-02-02 13:50
Extraction date: 2015-02-02
Volume water: 330 mL
Volume extracted gas: 8.0 mL
Gas L^{-1} groundwater: 24.2 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater: 24.5 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater: 14.9 mL (sum of analysed gases without air contamination)
Analysis volume agreement: 101 % (sum of analysed gas versus extracted gas)
Air contamination: 39.4 %
Volume of air in the extracted gas: 3 150 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	62.8	1.52	104.0	1.52
Helium	(He)	5 250	127	8 660	127
Argon	(Ar)	14 300	348	17 600	258
Oxygen	(O_2)	83 500	2 020	–	–
Nitrogen	(N_2)	825 000	20 000	847 000	12 400
Carbon monoxide	(CO)	< 2.0	< 0.05	< 3.3	< 0.05
Carbon dioxide	(CO_2)	72 600	1 760	120 000	1 760
Methane	(CH_4)	11 500	279	19 000	279
Ethane	(C_2H_6)	< 1.0	< 0.03	< 1.7	< 0.03
Ethene	(C_2H_4)	< 2.0	< 0.05	< 3.3	< 0.05
Ethyne	(C_2H_2)	< 2.0	< 0.05	< 3.3	< 0.05
Propane	(C_3H_8)	< 1.0	< 0.03	< 1.7	< 0.03
Propene	(C_3H_6)	< 2.0	< 0.05	< 3.3	< 0.05
Propyne	(C_3H_4)	< 4.0	< 0.1	< 6.6	< 0.1
	Σ	**1 010 000**	**24 500**	**1 010 000**	**14 900**

Date:

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Sample:	**KA2051A01:9**
Sample vessel	1
SKB sample nr:	24054
MICANS sample nr:	**150019:3**
Section:	1 m
Sampling date:	2015-02-02 16:16
Extraction date:	2015-02-02
Volume water:	305 mL
Volume extracted gas:	6.6 mL
Gas L^{-1} groundwater:	21.6 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater:	21.4 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater:	16.6 mL (sum of analysed gases without air contamination)
Analysis volume agreement:	99 % (sum of analysed gas versus extracted gas)
Air contamination:	22.6 %
Volume of air in the extracted gas:	1 491 µL

Gas		Not corrected for air contamination		Corrected for air contamination	
		Gas (ppm)	Gas (µL L^{-1})	Gas (ppm)	Gas (µL L^{-1})
Hydrogen	(H_2)	44.3	0.96	57.3	0.96
Helium	(He)	5 750	124	7 420	124
Argon	(Ar)	16 800	363	19 000	318
Oxygen	(O_2)	46 900	1 010	–	–
Nitrogen	(N_2)	855 000	18 500	878 000	14 700
Carbon monoxide	(CO)	< 3.12	< 0.07	< 4.03	< 0.07
Carbon dioxide	(CO_2)	52 900	1 150	68 400	1 150
Methane	(CH_4)	13 400	289	17 300	289
Ethane	(C_2H_6)	< 1.56	< 0.04	< 2.02	< 0.04
Ethene	(C_2H_4)	< 3.12	< 0.07	< 4.03	< 0.07
Ethyne	(C_2H_2)	< 3.12	< 0.07	< 4.03	< 0.07
Propane	(C_3H_8)	< 1.56	< 0.04	< 2.02	< 0.04
Propene	(C_3H_6)	< 3.12	< 0.07	< 4.03	< 0.07
Propyne	(C_3H_4)	< 6.24	< 0.14	< 8.06	< 0.14
	Σ	**991 000**	**21 400**	**991 000**	**16 600**

Date:

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Sample: **KA2051A01:9**

Sample vessel 1

SKB sample nr: 24056

MICANS sample nr: **150019:5**

Section: 1 m

Sampling date: 2015-02-03

Extraction date: 2015-02-03

Volume water: 305 mL

Volume extracted gas: 5.5 mL

Gas L^{-1} groundwater: 18.0 mL (volume extracted from the groundwater sample)

Gas L^{-1} groundwater: 18.1 mL (sum of analysed gases with air contamination)

Gas L^{-1} groundwater: 16.5 mL (sum of analysed gases without air contamination)

Analysis volume agreement: 100 % (sum of analysed gas versus extracted gas)

Air contamination: 9.2 %

Volume of air in the extracted gas: 507 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas ($\mu L\ L^{-1}$)**	**Gas (ppm)**	**Gas ($\mu L\ L^{-1}$)**
Hydrogen	(H_2)	83.7	1.51	92.2	1.51
Helium	(He)	4 680	84.4	5 160	84.4
Argon	(Ar)	15 100	273	15 700	257
Oxygen	(O_2)	19 400	350	–	–
Nitrogen	(N_2)	903 000	16 300	915 000	15 000
Carbon monoxide	(CO)	< 3.05	< 0.06	< 3.36	< 0.06
Carbon dioxide	(CO_2)	48 300	870	53 200	870
Methane	(CH_4)	14 200	257	15 700	257
Ethane	(C_2H_6)	< 1.53	< 0.03	< 1.68	< 0.03
Ethene	(C_2H_4)	< 3.05	< 0.06	< 3.36	< 0.06
Ethyne	(C_2H_2)	< 3.05	< 0.06	< 3.36	< 0.06
Propane	(C_3H_8)	< 1.53	< 0.03	< 1.68	< 0.03
Propene	(C_3H_6)	< 3.05	< 0.06	< 3.36	< 0.06
Propyne	(C_3H_4)	< 6.10	< 0.12	< 6.72	< 0.12
	Σ	**1 000 000**	**18 100**	**1 000 000**	**16 400**

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Sample: **KA2051A01:9**

Sample vessel	1
SKB sample nr:	24058
MICANS sample nr:	**150019:7**
Section:	1 m
Sampling date:	2015-02-03 10:30
Extraction date:	2015-02-03
Volume water:	325 mL
Volume extracted gas:	5.5 mL
Gas L^{-1} groundwater:	16.9 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater:	17.0 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater:	15.6 mL (sum of analysed gases without air contamination)
Analysis volume agreement:	100 % (sum of analysed gas versus extracted gas)
Air contamination:	7.8 %
Volume of air in the extracted gas:	428 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	67.7	1.15	73.4	1.15
Helium	(He)	6460	109	7000	109
Argon	(Ar)	18500	314	19300	301
Oxygen	(O_2)	16300	276	–	–
Nitrogen	(N_2)	887000	15000	896 000	14000
Carbon monoxide	(CO)	< 3.45	< 0.06	< 3.75	< 0.06
Carbon dioxide	(CO_2)	57800	978	62600	978
Methane	(CH_4)	16300	276	17700	276
Ethane	(C_2H_6)	< 1.73	< 0.03	< 1.88	< 0.03
Ethene	(C_2H_4)	< 3.45	< 0.06	< 3.75	< 0.06
Ethyne	(C_2H_2)	< 3.45	< 0.06	< 3.75	< 0.06
Propane	(C_3H_8)	< 1.73	< 0.03	< 1.88	< 0.03
Propene	(C_3H_6)	< 3.45	< 0.06	< 3.75	< 0.06
Propyne	(C_3H_4)	< 6.90	< 0.12	< 7.50	< 0.12
	Σ	**1000000**	**17000**	**1000000**	**15700**

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Sample: KA2051A01:5

Sample vessel 1
SKB sample nr: 24143
MICANS sample nr: 150090
Section: 120–135 m
Sampling date: 2015-05-27
Extraction date: 2015-05-28
Volume water: 325 mL
Volume extracted gas: 6.7 mL
Gas L^{-1} groundwater: 20.6 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater: 20.5 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater: 19.1 mL (sum of analysed gases without air contamination)
Analysis volume agreement: 99.3 % (sum of analysed gas versus extracted gas)
Air contamination: 6.9 %
Volume of air in the extracted gas: 464 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	87.5	1.8	94.1	1.8
Helium	(He)	21 300	438	22 800	438
Argon	(Ar)	18 500	381	19 200	368
Oxygen	(O_2)	14 400	297	–	–
Nitrogen	(N_2)	911 000	18 800	921 000	17 700
Carbon monoxide	(CO)	< 18	< 0.4	< 19	< 0.4
Carbon dioxide	(CO_2)	15 500	320	16 700	320
Methane	(CH_4)	12 300	254	13 200	254
Ethane	(C_2H_6)	< 1.8	< 0.04	< 2.0	< 0.04
Ethene	(C_2H_4)	< 3.6	< 0.08	< 3.9	< 0.08
Ethyne	(C_2H_2)	< 3.6	< 0.08	< 3.9	< 0.08
Propane	(C_3H_8)	< 1.8	< 0.04	< 2.0	< 0.04
Propene	(C_3H_6)	< 1.8	< 0.04	< 2.0	< 0.04
Propyne	(C_3H_4)	< 3.6	< 0.08	< 3.9	< 0.08
	Σ	**993 000**	**20 500**	**993 000**	**19 000**

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Sample:	**2051A01:5**
Sample vessel	2
SKB sample nr:	24144
MICANS sample nr:	**150091**
Section:	120–135 m
Sampling date:	2015-05-27
Extraction date:	2015-05-28
Volume water:	290 mL
Volume extracted gas:	9.96 mL
Gas L^{-1} groundwater:	34.3 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater:	34.3 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater:	32.9 mL (sum of analysed gases without air contamination)
Analysis volume agreement:	99.9 % (sum of analysed gas versus extracted gas)
Air contamination:	4.1 %
Volume of air in the extracted gas:	412 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas ($\mu L\ L^{-1}$)**	**Gas (ppm)**	**Gas ($\mu L\ L^{-1}$)**
Hydrogen	(H_2)	38.5	1.32	40.1	1.32
Helium	(He)	15 500	532	16 200	532
Argon	(Ar)	11 300	389	11400	376
Oxygen	(O_2)	8 660	297	–	–
Nitrogen	(N_2)	926 000	31 800	933 000	30 700
Carbon monoxide	(CO)	< 10.0	< 0.3	< 10.4	< 0.3
Carbon dioxide	(CO_2)	29 200	1 000	30 500	1 000
Methane	(CH_4)	8 170	281	8 530	281
Ethane	(C_2H_6)	< 1.00	< 0.03	< 1.04	< 0.03
Ethene	(C_2H_4)	< 2.00	< 0.07	< 2.09	< 0.07
Ethyne	(C_2H_2)	< 2.00	< 0.07	< 2.09	< 0.07
Propane	(C_3H_8)	< 1.00	< 0.03	< 1.04	< 0.03
Propene	(C_3H_6)	< 1.00	< 0.03	< 1.04	< 0.03
Propyne	(C_3H_4)	< 2.00	< 0.07	< 2.09	< 0.07
	Σ	**999 000**	**34 300**	**999 000**	**32 900**

Date:

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Sample:	**KA3510A:2**
Sample vessel	1
SKB sample nr:	24145
MICANS sample nr:	**150092**
Section:	110–124
Sampling date:	2015-05-27
Extraction date:	2015-05-28
Volume water:	300 mL
Volume extracted gas:	13.4 mL
Gas L^{-1} groundwater:	44.8 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater:	45.0 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater:	43.2 mL (sum of analysed gases without air contamination)
Analysis volume agreement:	100 % (sum of analysed gas versus extracted gas)
Air contamination:	4.0 %
Volume of air in the extracted gas:	544 µL

Gas		Not corrected for air contamination		Corrected for air contamination	
		Gas (ppm)	Gas (µL L^{-1})	Gas (ppm)	Gas (µL L^{-1})
Hydrogen	(H_2)	677	30.3	706	30.3
Helium	(He)	168 000	7 510	175 000	7 510
Argon	(Ar)	16 300	732	16 600	715
Oxygen	(O_2)	8 510	381	–	–
Nitrogen	(N_2)	791 000	35 400	791 000	34 000
Carbon monoxide	(CO)	< 10.0	< 0.45	< 10.4	< 0.45
Carbon dioxide	(CO_2)	7 050	316	7 350	316
Methane	(CH_4)	14 000	626	14 600	626
Ethane	(C_2H_6)	< 1.00	< 0.04	< 1.04	< 0.04
Ethene	(C_2H_4)	< 2.00	< 0.08	< 2.08	< 0.08
Ethyne	(C_2H_2)	< 2.00	< 0.08	< 2.08	< 0.08
Propane	(C_3H_8)	< 1.00	< 0.04	< 1.04	< 0.04
Propene	(C_3H_6)	< 1.00	< 0.04	< 1.04	< 0.04
Propyne	(C_3H_4)	< 2.00	< 0.08	< 2.08	< 0.08
	Σ	**1 000 000**	**45 000**	**1 000 000**	**43 200**

Date:

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Sample: **KA3510A:2**
Sample vessel 2
SKB sample nr: 24146
MICANS sample nr: **150093**
Section: 110–124
Sampling date: 2015-05-27
Extraction date: 2015-05-28
Volume water: 300 mL
Volume extracted gas: 13.2 mL
Gas L^{-1} groundwater: 44.1 mL (volume extracted from the groundwater sample)
Gas L^{-1} groundwater: 44.5 mL (sum of analysed gases with air contamination)
Gas L^{-1} groundwater: 39.4 mL (sum of analysed gases without air contamination)
Analysis volume agreement: 101 % (sum of analysed gas versus extracted gas)
Air contamination: 11.5 %
Volume of air in the extracted gas: 1 522 µL

Gas		**Not corrected for air contamination**		**Corrected for air contamination**	
		Gas (ppm)	**Gas (µL L^{-1})**	**Gas (ppm)**	**Gas (µL L^{-1})**
Hydrogen	(H_2)	984	43.4	1 110	43.4
Helium	(He)	156 000	6 870	176 000	6 870
Argon	(Ar)	15 400	678	16 100	630
Oxygen	(O_2)	24 300	1 070	–	–
Nitrogen	(N_2)	793 000	35 000	793 000	31 000
Carbon monoxide	(CO)	< 10.0	< 0.44	< 11.3	< 0.44
Carbon dioxide	(CO_2)	7 390	326	8 350	326
Methane	(CH_4)	12 200	540	13 800	540
Ethane	(C_2H_6)	< 1.00	< 0.04	< 1.13	< 0.04
Ethene	(C_2H_4)	< 2.00	< 0.08	< 2.26	< 0.08
Ethyne	(C_2H_2)	< 2.00	< 0.08	< 2.26	< 0.08
Propane	(C_3H_8)	< 1.00	< 0.04	< 1.13	< 0.04
Propene	(C_3H_6)	< 1.00	< 0.04	< 1.13	< 0.04
Propyne	(C_3H_4)	< 2.00	< 0.08	< 2.26	< 0.08
	Σ	**1 010 000**	**44 500**	**1 010 000**	**39 400**

Date:

Approved by:

Karsten Pedersen

Appendix 2

Pressure registrations during purging and sampling

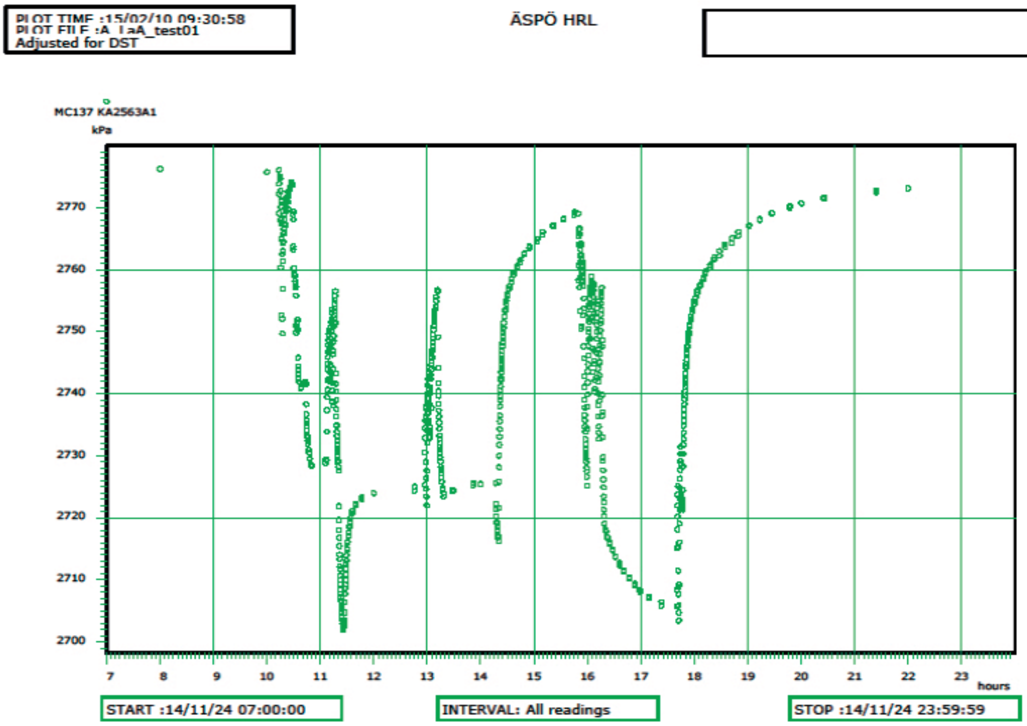


Figure A2-1. *Pressure curve for section 1 in KA2563A, 2014-11-24.*

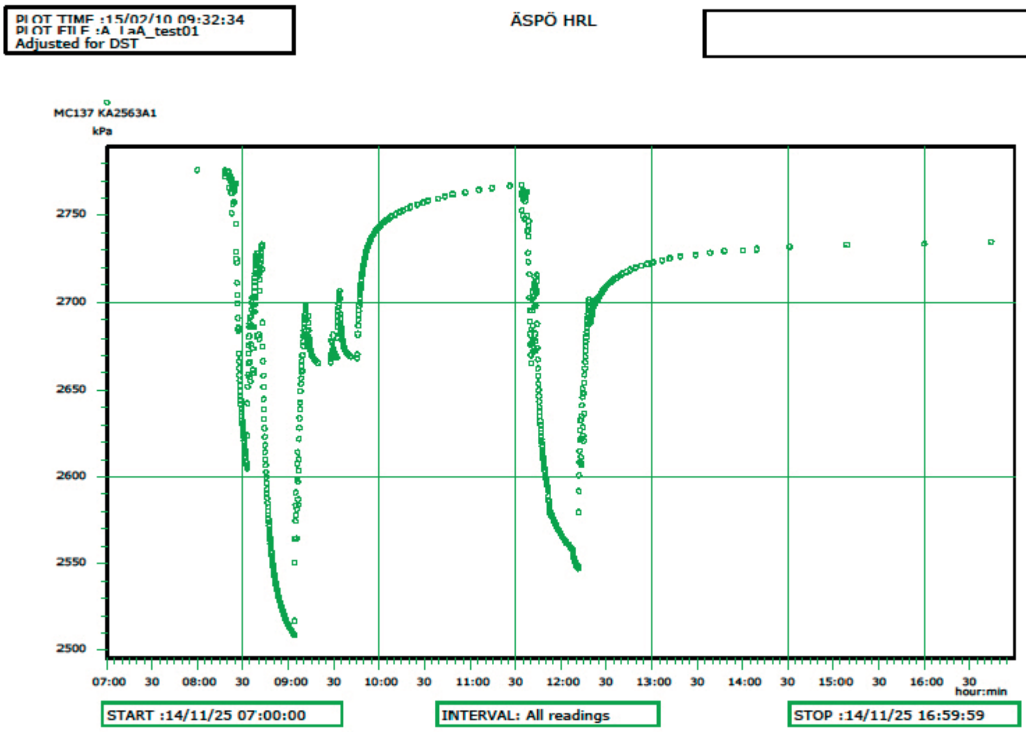


Figure A2-2. *Pressure curve for section 1 in KA2563A, 2014-11-25.*

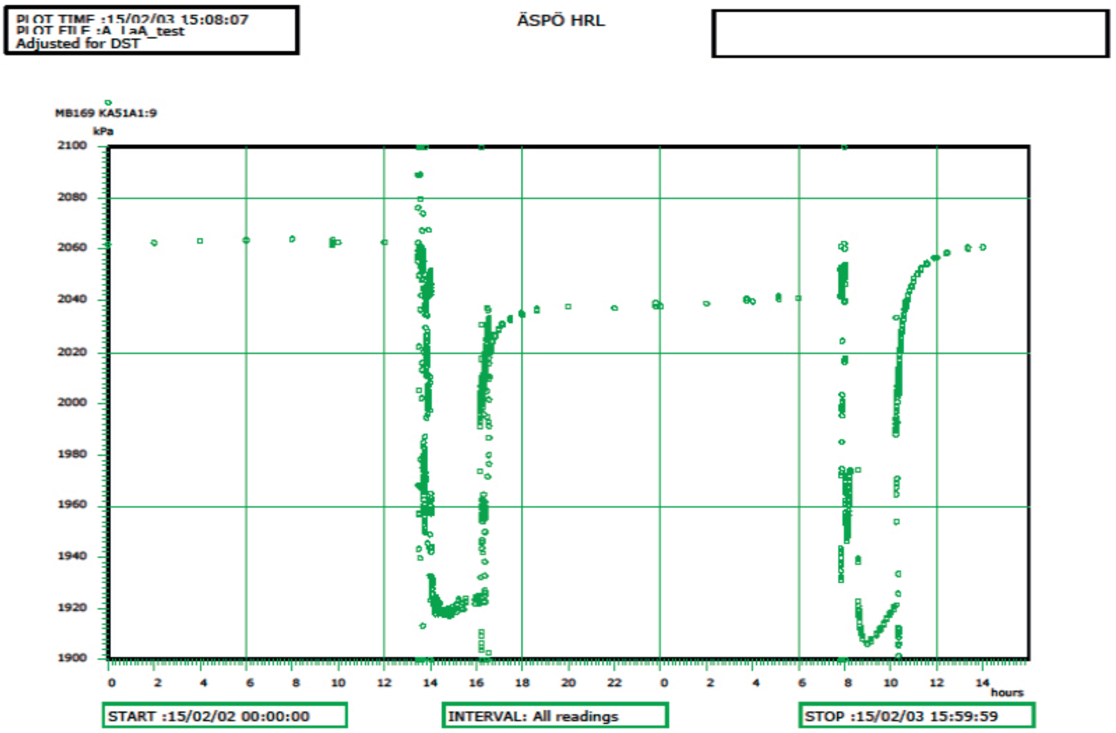


Figure A2-3. *Pressure curve for section 9 in KA2051A01, 2015-02-02/03.*

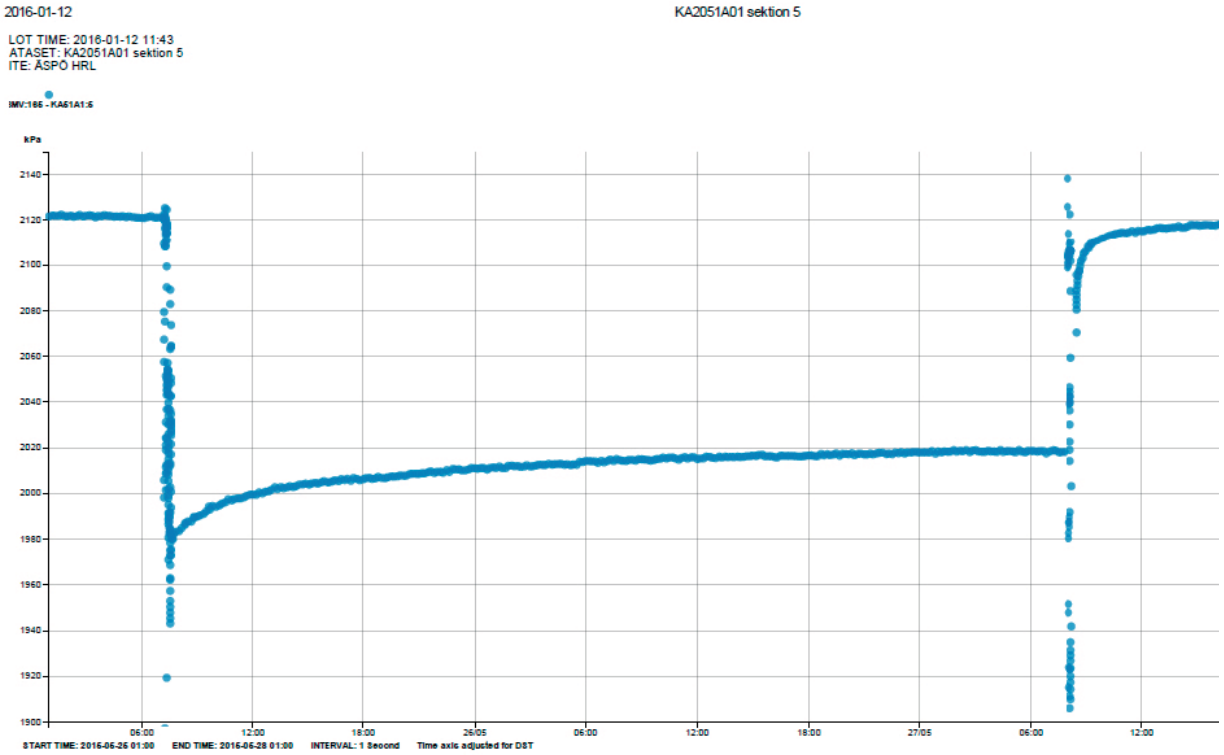


Figure A2-4. *Pressure curve for section 5 in KA2051A01, 2015-06-25/27.*

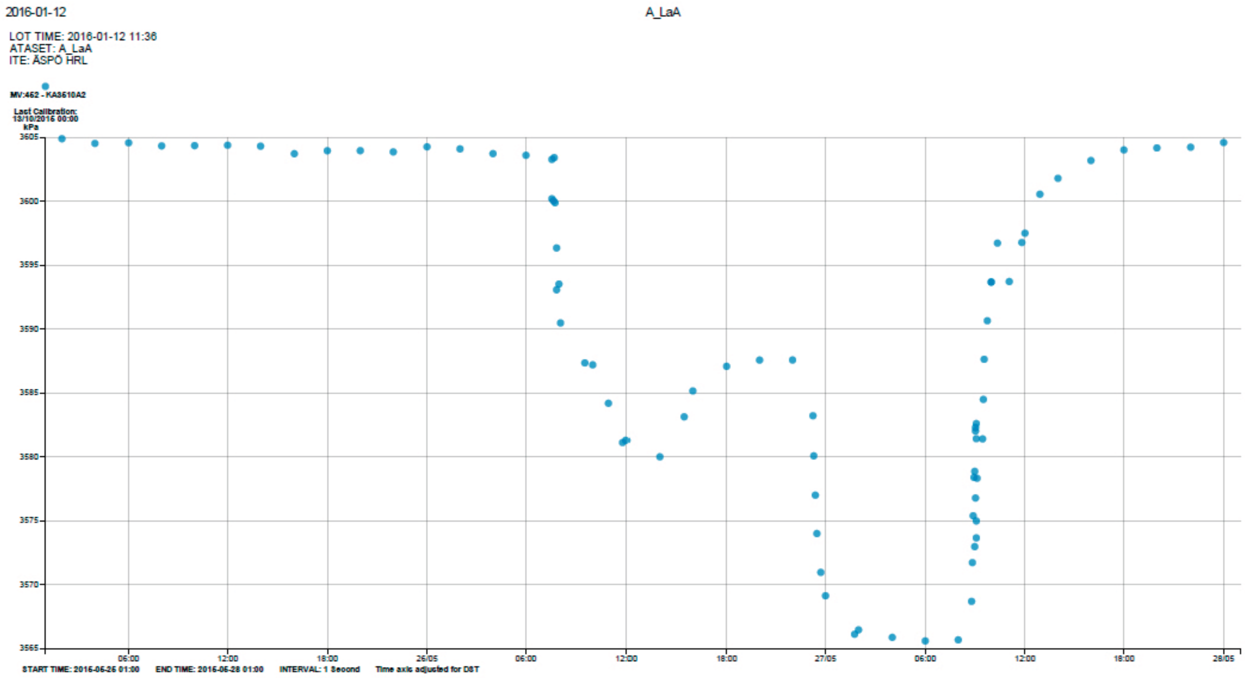


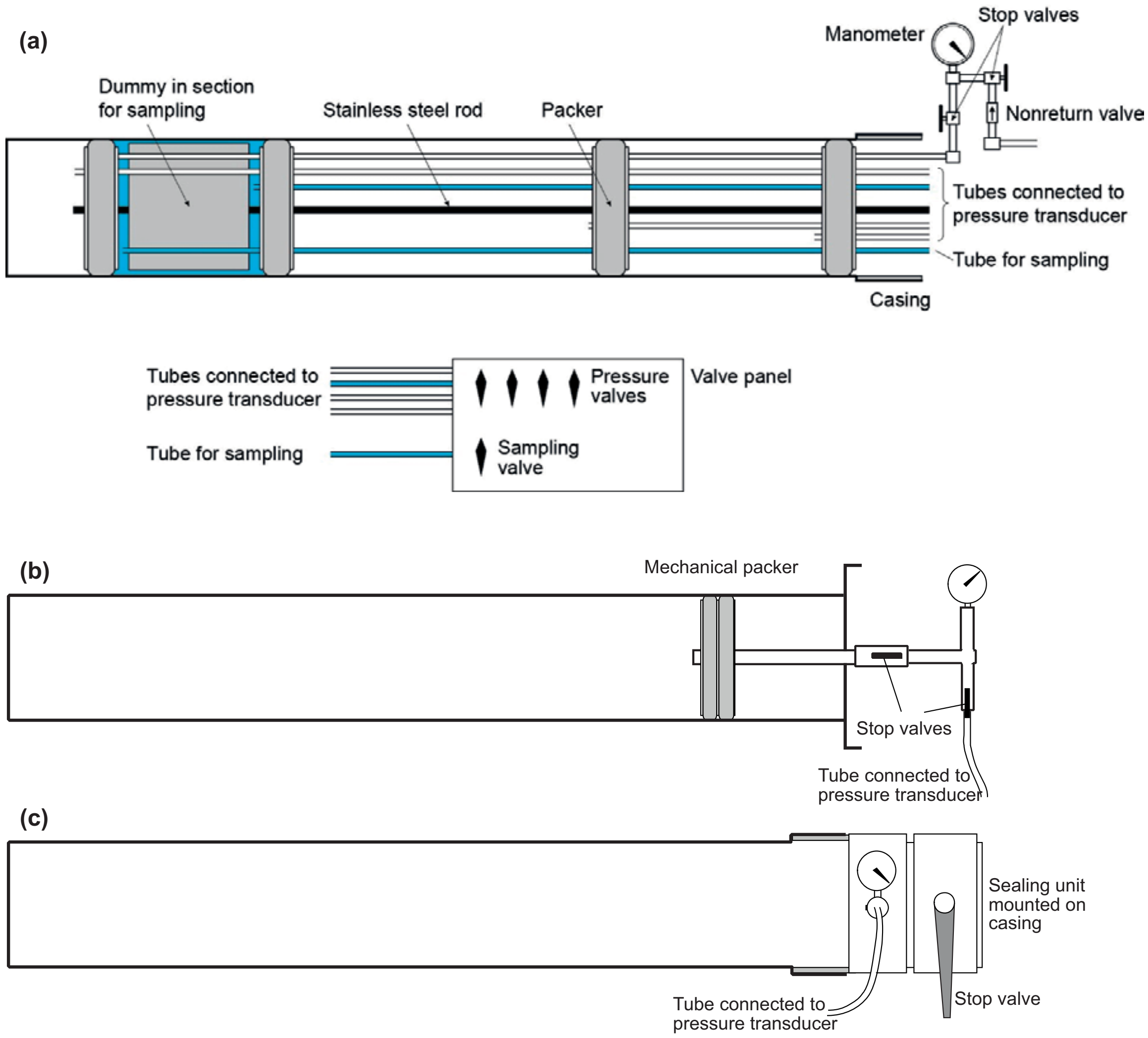
Figure A2-5. *Pressure curve for section 5 in KA3510A:2, 2015-06-25/27.*

Appendix 3

Descriptions of borehole installations and groundwater purging prior to sampling

Fixed borehole installations in subsurface boreholes

Fixed monitoring equipment has been installed in the sampled boreholes after completion of the general investigation activities that were performed directly after drilling. Most boreholes are separated into different isolated borehole sections, see Figure A3-1a, while others have just one section, case b and c. Inflated rubber packers also prevent undesired short circuiting effects that will occur if boreholes are kept open. No pumping is needed to discharge the groundwater due to the pressure gradient.



Figur A3-1. Examples showing different installations in subsurface boreholes. a) A so called circulation section with a dummy to reduce the water volume and two regular sections for pressure measurements. The sections are isolated by inflated rubber packers. b) Non-sectioned borehole with a mechanical packer close to the borehole orifice. c) Non-sectioned borehole with only a stopper mounted on the casing at the orifice. All these installations allow pressure measurements.

Groundwater purging prior to sampling

Groundwater samples should ideally consist of 100 % formation groundwater directly from the water bearing fractures in the adjacent bedrock in order to be fully representative. The need for purging in order to fulfill this condition prior to sampling, depends on the distribution and hydraulic transmissivity of the flow anomalies influencing the borehole section (cf. Figure 3-4). For example, a single water bearing fracture (**A** and **B**) with high hydraulic transmissivity, located in the upper/nearest part of the borehole section close to the outlet from the section is favourable, since the water volume in the part of the borehole section beneath the fracture will stay trapped regardless of the removal of water from the section (i.e. it is a dead volume). If, on the other hand, there are several fractures in the section (**C** and **D**), borehole water between the fractures will contribute to the sample until formation water from the last fracture reaches the outlet. In this case there is a good possibility that some residual water will remain in the borehole section when sampling commences and can be expected also in the final samples. Simple plug flow calculations (Tullborg et al. 2010) can be used in order to estimate the need for purging in each individual borehole section.

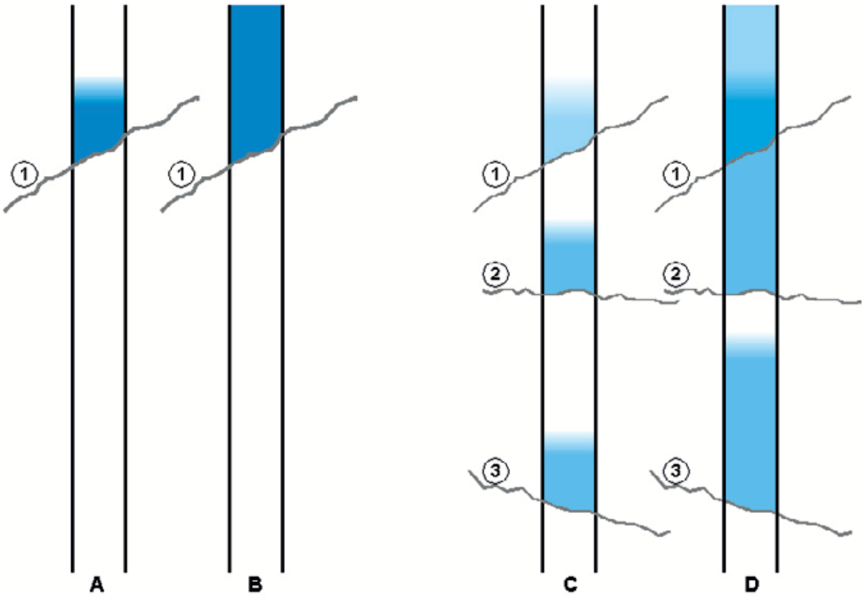


Figure A3-2. *The colour strength illustrates the amount of new formation groundwater in a borehole section during pumping. A and B show a situation with one water yielding fracture. Shortly after pump start (A) the water from the only fracture has not reached the outlet from the section. After a certain time (B), all the water leaving the section is formation water. C and D show a situation with three fractures yielding similar contributions to the total flow. Shortly after pump start (C), no formation water has reached the outlet from the section. After a certain time (D), corresponding to situation B, formation water from fracture 1) has reached the outlet and formation water from fracture 2 has passed fracture 1. Formation water from fracture 3 has not yet reached fracture 2 and the water at the outlet from the borehole is still a mixture between formation water and initial section water since fractures 2) and 3) are not yet contributing.*

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