

## **Oskarshamn site investigation**

**Granitic groundwater colloids sampling  
and characterisation. Colloids analysis  
from KLX17A (416.0 to 437.5 m) and  
KLX15A (623.0 to 634.5 m)**

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September 2008

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## Abstract

Natural ground water colloids from KLX17A and KLX15A were sampled by micro-filtration of water samples collected from a granitic groundwater and maintained at the *in situ* thermodynamic conditions. The methodology avoids the generation of artefacts produced by pH changes due to CO<sub>2</sub> exchange, yielding potential carbonate precipitation, or by O<sub>2</sub> contaminations yielding oxidized insoluble phases. The enhanced pressure and the anoxic conditions are maintained also through the filtering procedure. *In situ* groundwater sampling (followed by micro-filtration of the colloids) were carried out after a period of regular sampling for chemical and physical analyses of the groundwater pumped to the surface. Colloid samples were characterized by scanning electron microscopy. At deep granitic groundwater conditions, natural colloids occur sparsely. The colloid concentration was determined  $C_{col} \sim 20 \mu\text{g}\times\text{L}^{-1}$  (KLX15A) and  $60 \mu\text{g}\times\text{L}^{-1}$  (KLX17A) for sizes ranging from 50 to 200 nm or  $N_{col} \sim 4\times 10^{10}\text{L}^{-1}$  for sizes larger than 50 nm and for both systems (KLX17A and KLX15A). These colloids are suggested to be clay particles with an average size smaller than 200 nm. For the Na-(Ca)-Cl groundwater (pH 7.4–8.0, ionic strength  $\sim 2\times 10^{-1}$  (KLX15A) –  $\sim 2\times 10^{-2}$  (KLX17A) M), the colloid concentration values are comparable with values reported earlier in the literature.

## Sammanfattning

Kolloidprov från naturligt granitiskt grundvatten erhöles genom mikrofiltrering av grundvattenprov. Vattenprovet bibehöll sitt *in situ* termodynamiska tillstånd under provtagningen. Med den använda metoden kan man undvika bildandet av artefakter orsakade av syreinträngning eller pH-förändring, beroende på utbyte av koldioxid. En ändring av pH-värdet kan ge utfällning av karbonater, medan föroreningar av syre orsakar utfällning av olösliga oxider. Tryckförhöjningen, liksom det anoxiska tillståndet, bibehölls även under filtreringsförloppet. Provtagning av *in situ* grundvatten åtföljd av mikrofiltrering av kolloider genomfördes efter en mät- och provtagningsperiod där regelbundna uttag av vattenprov gjordes på det uppumpade grundvattnet för analys av kemiska och fysikaliska parametrar. Kolloidproven analyserades med svepelektronmikroskopi. I djupa granitiska grundvatten är förekomsten av naturliga kolloider sparsam. Kolloidkoncentrationen uppmättes till  $C_{col} \sim 20 \mu\text{g}\cdot\text{L}^{-1}$  (KLX15A) respektive  $60 \mu\text{g}\cdot\text{L}^{-1}$  (KLX17A) i området mellan 50 och 500 nm eller  $N_{col} \sim 4 \times 10^{10} \text{L}^{-1}$  över 50 nm (KLX15A och KLX17A). Kolloiderna bestod av lera med en genomsnittlig storlek på mindre än 200 nm. Kolloidkoncentrationen i Na-(Ca)-Cl grundvattnet vid pH 7,4–8,0 och jonkoncentration  $\sim 2 \times 10^{-1}\text{M}$  (KLX15A) och  $\sim 2 \times 10^{-2}\text{M}$  (KLX17A) befanns vara jämförbar med de värden som tidigare rapporterats i litteraturen.

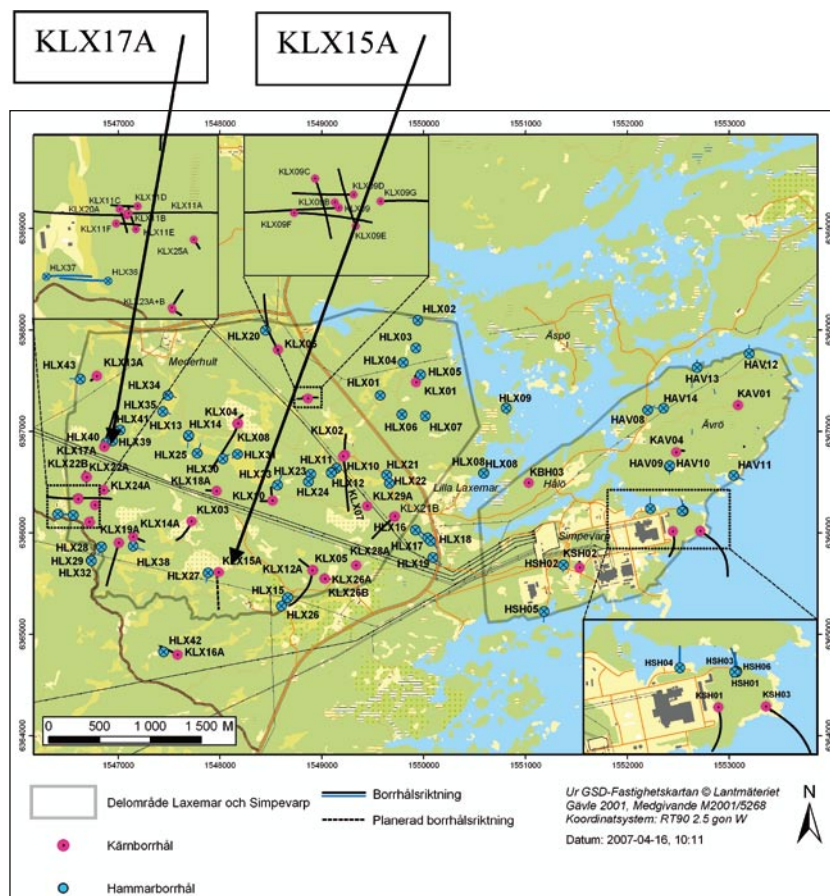
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# 1 Introduction

The ground water colloids are found in all hydrogeochemical systems /Degueldre *et al.* 2000/. These colloids are defined as particles of size ranging from 1 to 1,000 nm /Stumm and Morgan 1996/ varying from inorganic particle, organic colloid and bioorganic features /e.g Degueldre *et al.* 2000/. To evaluate the impact of contaminant transport by colloids, information about colloid concentrations, size distribution and chemical nature are needed / Degueldre 1997/. Accurate studies on groundwater colloids require very careful sampling /e.g. Backhus *et al.* 1992/ and characterisation /McCarthy and Degueldre 1993/ of the colloids as well as accurate analysis of the groundwater.

This document reports the results gained by microscopic investigations on colloids collected on membranes after filtration of groundwaters from boreholes KLX17A (416.0 to 437.5 m) and KLX15A (623.0 to 634.5 m). This study is one of the activities performed within the site investigation at Laxemar, Oskarshamn (Fig.1-1). The work was carried out in accordance to the activity plans AP PS 400-07-053 and AP PS 400-06-138 (complementary addition). Activity plans are SKB's internal controlling documents.



**Figure 1-1.** General overview over Laxemar site investigation area, location of KLX17A and KLX15A boreholes.

The site for the present colloid study is located in the granite Scandinavian mole. At this location the cooperative for the nuclear waste management in Sweden (SKB) is investigating a potential site for a deep repository for spent nuclear fuel. The host rock is metamorphosed granite where water bearing fracture zones or single fractures occur relatively scarcely. The site investigation implies, among other, drilling of boreholes in order to study the geological, hydrogeological and hydrogeochemical e.g. SKB R-06-70 conditions and especially the properties of the few larger zones.

The boreholes selected for the colloid study, KLX17A and KLX15A, intersect locally water bearing zones along borehole length. However, water for this study was pumped/sampled from zones at 416.0–437.5 and 623.0–634.5 m borehole length (~ 360 and 478 m vertical depth) respectively in a fissured part of the bedrock adjacent to this zone. Water sampling for colloid studies was carried out *in situ* in the borehole sections delimited by double-packers. The enclosed water sample was lifted to the surface where it was filtered in a closed system. The entire procedure was performed under argon atmosphere and at maintained pressure and temperature from the borehole section /e.g. Bergelin *et al.* 2007/.

This report presents and discusses the granite groundwater colloids sampling and characterisation results from the borehole test KLX17A (416.0 to 437.5 m) and KLX15A (623.0 to 634.5 m).

## 2 Objective and scope

Since colloids are present in all ground waters, they must be taken into account in the performance assessment studies. Colloid facilitated transport mechanisms are evaluated considering the geosphere as a source of colloids with constant concentration in the groundwater. Their presence is a consequence of solid-water interaction, and they are generated when rocks interact with the groundwater. An attempt to correlate their concentration and their stability is currently in progress since more than a decade /e.g. Degueldre 1997/. These studies are difficult because colloid sampling is not always carefully performed and because the uncontaminated colloid concentration obtained may also be a function of the history of the aquifer prior to sampling /McCarthy and Degueldre 1993/. Numerous colloid data are systematically affected by interfering phases such as precipitates which are generated during sample preparation or additional components induced by perturbation in the aquifer during water collection. These perturbing phases called **artefacts** are often erroneously measured as colloids and thereby falsify the determined concentration.

Colloid sampling and characterization method was reviewed by McCarthy and Degueldre (1993). It was pointed out that sampling must be optimized in all cases prior to characterization. Today various techniques (including single particle counting to colloid bulk analysis) are available involving on-site sampling and characterisation on-line or off-line. For example, samples may flow on-site online in the characterisation unit. Samples may also be taken on site and characterised directly at the site e.g. by light scattering. Or alternatively samples can be separated by filtration and filters can be sent for characterisation. In all cases artefact tracking is required /see also Degueldre *et al.* 1996a/ with assessment of the colloid number/amount by increasing the volume of the groundwater samples. However, this work requires resources that are not always available.

The colloid concentration in deep ground waters is usually of the order of the  $\mu\text{g}\times\text{l}^{-1}$  and thus the contamination risks are obvious during water sampling and colloid sample preparation. Colloidal particles can be generated as artefacts, even proceeding on-line during sample preparation. The sampling errors are due to: excessively high or low pump rates, contamination from borehole activities, complex hydrological situations, contamination from tubes varying the composition of the groundwater, air contamination ( $\text{O}_2$  uptake), losses or uptake of  $\text{CO}_2$ , aggregation-coagulation effects, long storage times prior to analyses, analytical errors etc. Some errors in the sampling and analysis of colloids are easy to avoid, others are difficult or impossible to evaluate. These problems have been addressed among others by Laaksoharju *et al.* (1994).



### 3 Hydrogeochemical system and water analysis

Borehole KLX17A was drilled with a conventional rotary drilling system. The 701 m long borehole drilling was completed at a vertical depth of 607 m in 2006. The bedrock in the 416.00 to 437.51 m borehole length section, from where the water sample for the colloid study was collected, consists of partly altered granite intersected by fissures /e.g. Bergelin *et al.* 2007 and Mattsson and Keison 2007a/.

Borehole KLX15A was also drilled with a conventional rotary drilling system. The 1,000.43 m long borehole was completed at a vertical depth of 701 m in 2007. The bedrock in the 623.0 to 634.5 m borehole length section, from where the water sample for the colloid study was collected, consists of partly altered granite intersected locally by fissures e.g. /Mattsson and Keison 2007b and Nielsen and Ringyard 2007/.

For both systems (KLX15A and KLX17A) the ground waters reach the intervals through open fractures. In these systems, the water bearing fractures contain small amounts of clay minerals e.g. /see Drake *et al.* 2006/.

In borehole KLX17A (416.0–437.5 m) differential flow logging revealed several water bearing fractures along the borehole /e.g. SKB R-06-70/. A water flowing zone at 420–431 m was selected for investigation due to a suitable hydraulic transmissivity and its location for groundwater flow. A down-hole equipment, consisting of from the top; umbilical hose, length mark detector, measurement cell for *in situ* measurements, upper packer, borehole pump, *in situ* water sampler and lower packer, was installed in the borehole and a section at 416.0 to 437.5 m (360 to 380 m bsl) was isolated by the packers.

In borehole KLX15A, differential flow logging revealed also several water bearing fractures along the borehole /e.g. Nielsen and Ringyard 2007/. A water flowing zone at 630 m was selected for investigation due to its hydraulic transmissivity and groundwater flow. Similar down-hole equipments were installed with measurement cell for *in situ* monitoring, upper packer, borehole pump, *in situ* water sampler and lower packer, was installed in the section at 623.0 to 634.5 m (478–485 m bsl).

Water samples (KLX15A and KLX17A) were collected regularly during a period of regular sampling. Prior to lifting the equipment the valves to the *in situ* sampling containers were opened from the surface in order to rinse the system and fill the containers. After some hours the valves were closed and the water sample portions for analyses of colloids, dissolved gases and microbes were secured. Following stopping of the borehole pump and deflation of the packers, the equipment was lifted and the different down-hole units were dismantled.

Prior to the investigation period, and for both KLX17A and KLX15A systems, nitrogen flushing was performed several times from the bottom of the borehole and efficient pumping was maintained from the top of the borehole. At the start of the investigation period in the sampling section, the drilling water content was still some percents. Due to the continuous pumping at a flow rate of about 270 (KLX17) and 100 (KLX15) mL min<sup>-1</sup> for regular water sampling from the section, this content was reduced to about 4.4% (KLX15A) and 2% (KLX15A) at the time of the *in situ* water sampling for colloid filtration.

Regular water sampling (KLX15A and KLX17A) was performed from pumped water and filtration of sample portions for chemical analyses was performed by connecting the filter holders directly to the outlet tubing made by polyamide. Field-pH was measured on-line in the unbroken water line with glass- and Ag/AgCl reference electrodes in measurement cells down-hole in the borehole section as well as at the ground surface. Laboratory pH was measured in batch samples at 25°C using a combined electrode. The pH was measured to ± 0.02 units after careful stand-

ardisation with buffers (4, 7 and 10). The *Eh* was recorded using Au, Pt and carbon electrodes in a cell attached to the pH cell.

Analyses of Fe(II), alkalinity, ammonium, lab-pH and electrical conductivity were performed immediately after each sampling at the site (KLX15A and KLX17A). The other analyses were performed by several consulted laboratories and the water was analysed for its dissolved and suspended solid contents. Mohr titration (chloride) and ion chromatography (Dionex 120) was utilised for assaying major anions. Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) were determined using a carbon analyser, Shimadzu TOC-5000. ICP-AES and ICP-MS techniques were used for major and minor element determination.

## 4 Colloid analysis methodology

### 4.1 Colloid sampling

The *in situ* groundwater samples (two samples from each borehole) were lifted to the surface at maintained pressure from the borehole section. One of the samples from each borehole was used to obtain colloid samples on filters. The colloid filtering system allowed micro-filtering of groundwater followed by rinsing with a small volume of de-oxygenised, de-ionised water through five connected filters in a closed system under argon atmosphere. Furthermore, the filtering was performed at a pressure similar to that of the groundwater in the borehole section and five filters in the pore size order 2, 2, 0.4, 0.2 and 0.05  $\mu\text{m}$  were used. The two first filters were used to prevent clogging. The membranes of diameter 47 mm are mounted with a 1.8 mm O-ring in the filtration cell and the volume of water  $V$  was 150 ml. The system was kept at 12 to 14 and 17 to 18°C (respectively for KLX17A and KLX15A) in isotherm and isobar conditions, and maintained in the *in situ* conditions for filtration. After groundwater filtration, the colloid phase collected on the membrane was contacted with a small volume of ultrapure water (e.g. 10 mL for washing) to avoid salt recrystallization during the drying phase. The filters were stored under argon in welded plastic bags in the fridge before and during transfer to the laboratory.

### 4.2 Colloid analysis

SEM investigations were carried out on 0.2 and 0.05  $\mu\text{m}$  pore size membranes. Particle analysis was carried out by SEM/EDS. The scanning electron microscopy (SEM) investigations were performed with a Zeiss DSM 962 unit under 30 kV. SEM investigations were earlier tested with the gold colloids as recently reported by Degueldre *et al.* (2005). For the present tests the filter membranes were coated with 15 nm Pt layer by Magnetron sputtering prior to microscopic investigation. The energy dispersive spectroscopy (EDS) analysis was performed using the Zeiss unit. This single particle monitoring allows specific counting of 3 size classes from 50 to 100, 100 to 150 and 150 to 200 nm.

### 4.3 Colloid data handling

The number of colloid  $n$  detected on a micrography (surface  $s$ ) of the membrane of surface  $S$  may be translated in number of particle  $N_{col}$  in volume of filtered water  $V$ . The colloid number concentration  $N_{col}$  is simply given by:

$$N_{col} = \frac{n \cdot S}{V \cdot s} \quad (1)$$

The colloid number concentration  $N_{col}$  may be modelled as a function of their size  $d$  using a power law size distribution:

$$\frac{\Delta N_{col}}{\Delta d} = A \cdot d^{-b} \quad (2)$$

where  $A$  and  $b$  are constant for given size ranges.

The colloid mass concentration  $C_{col}$  may be calculated assuming spherical colloids of density  $\rho$ :

$$\frac{\Delta C_{col}}{\Delta d} = \frac{\pi \cdot A \cdot \rho}{6} \cdot d^{3-b} \quad (3)$$

Concentration can be calculated for size range  $d_{min} - d_{Max}$  by integrating the concentration over the size interval. Calculations could be done utilising the COLIAT code based on particle size distribution including shape hypothesis /see Degueldre *et al.* 1996 and Degueldre *et al.* 2000/ when the number of colloid is large enough and when colloids present aggregates, or, simple calculation may be carried out size class wise.

## 5 Results and discussion

### 5.1 Ground water colloid characterisation

The KLX17A ground water chemistry is given in Table 5-1. This granitic water is of Na-Cl type, with an  $Eh$  of  $-297 \pm 13$  mV and a  $pH$  of 8.00.

**Table 5.1 Element/species concentrations ( $C$ , in mass or  $M$ , molality) in the KLX17A (416.0 to 437.5 m) granitic ground water. The water conductivity is  $215 \pm 6$  mS  $m^{-1}$  and its  $pH$   $8.00 \pm 0.1$  *in situ* and  $8.00 \pm 0.2$  at well head, Fe for Fe total. The charge balance is. Temperature  $T$  was  $12^\circ C$  *in situ* and  $14^\circ C$  during filtration,  $Eh = -0.297 \pm 0.013$  V.**

Concentration Element/species	$C$ (mg.L <sup>-1</sup> )	$M$ (M)
Li	0.0543	$7.834 \times 10^{-6}$
Na	332	$1.442 \times 10^{-2}$
K	3.97	$4.016 \times 10^{-4}$
Mg	9.78	$1.027 \times 10^{-4}$
Ca	69.2	$1.729 \times 10^{-3}$
Sr	1.72	$1.965 \times 10^{-5}$
Al	0.00433	$1.607 \times 10^{-7}$
Si	8.35	$1.391 \times 10^{-4}$
Mn	0.108	$1.968 \times 10^{-5}$
Fe	0.76	$1.362 \times 10^{-6}$
Fe(II)	0.76	$1.362 \times 10^{-6}$
F <sup>-</sup>	2.7	$1.423 \times 10^{-4}$
Cl <sup>-</sup>	591	$1.669 \times 10^{-2}$
Br <sup>-</sup>	2.2	$2.757 \times 10^{-5}$
I <sup>-</sup>	0.0221	$1.753 \times 10^{-7}$
HCO <sub>3</sub> <sup>-</sup>	115	$1.887 \times 10^{-3}$
SO <sub>4</sub> <sup>2-</sup>	24.4	$2.543 \times 10^{-4}$
HS <sup>-</sup>	0.028	$8.485 \times 10^{-7}$
P-PO <sub>4</sub> <sup>3-</sup>	0.0041	$1.281 \times 10^{-7}$
TOC	3.3	$2.750 \times 10^{-4}$

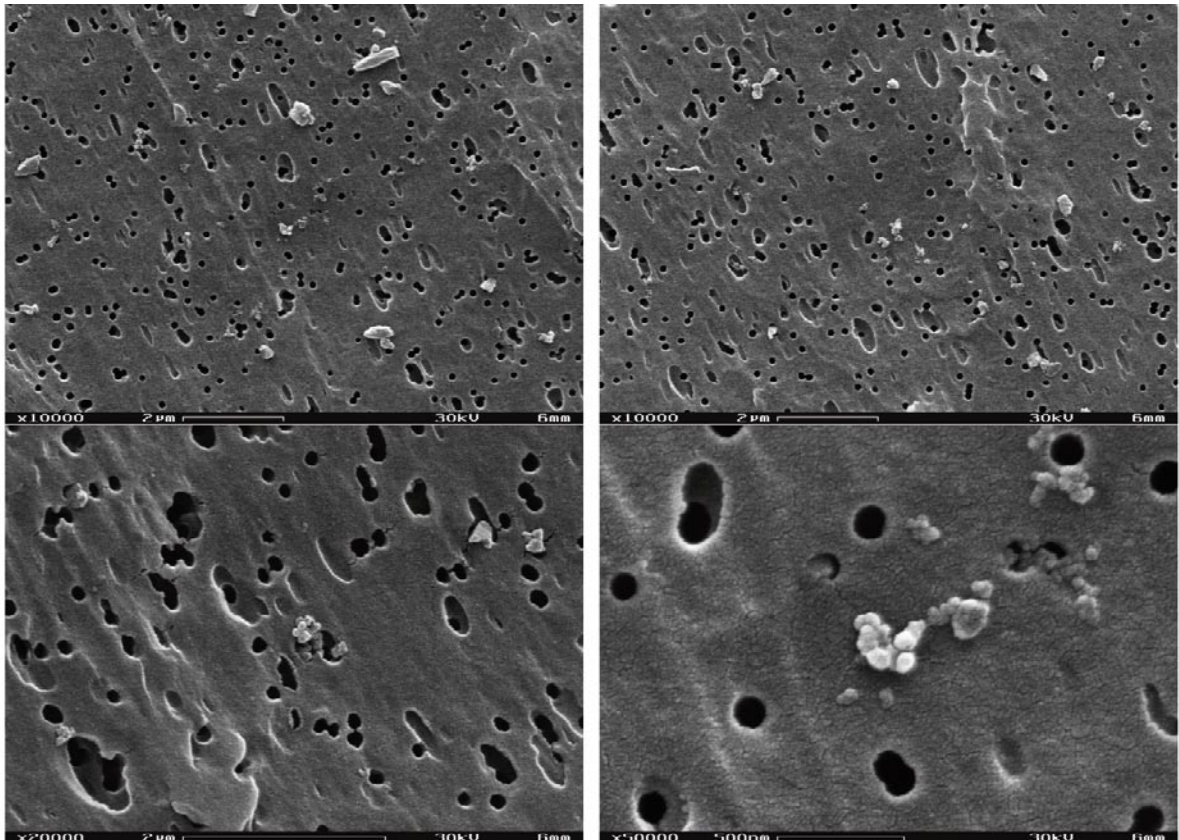
The KLX15A ground water chemistry is given in Table 5-2. This granitic water is of Na-Ca-Cl type, with an estimated  $Eh$  of  $-200$  mV and a  $pH$  of 7.45.

**Table 5.2 Element/species concentrations ( $C$ , in mass or  $M$ , molality) in the KLX15A (623.0 to 634.5 m) granitic ground water. The water conductivity is  $1,690$  mS  $m^{-1}$  and its  $pH$   $7.45 \pm 0.1$  *in situ* and  $7.42 \pm 0.2$  at well head, Fe for Fe total. The charge balance is  $-2.33 \times 10^{-3}$ . Temperature  $T$  was  $17^\circ C$  *in situ* and  $18^\circ C$  during filtration, estimated  $Eh = -0.200$  V.**

Concentration Element/species	$C$ (mg.L <sup>-1</sup> )	$M$ (M)
Li	0.293	$4.265 \times 10^{-5}$
Na	2,080.0	$9.139 \times 10^{-2}$
K	13.8	$3.565 \times 10^{-4}$
Mg	54.0	$2.244 \times 10^{-3}$
Ca	1,540.2	$3.882 \times 10^{-2}$
Sr	27.7	$3.194 \times 10^{-4}$
Al	0.00286	$1.071 \times 10^{-7}$
Si	5.34	$8.978 \times 10^{-5}$
Mn	0.549	$1.009 \times 10^{-5}$
Fe	0.537	$9.589 \times 10^{-6}$
Fe(II)	0.55	$9.948 \times 10^{-6}$
F <sup>-</sup>	2.3	$1.223 \times 10^{-4}$
Cl <sup>-</sup>	5,870.0	$1.673 \times 10^{-1}$
Br <sup>-</sup>	29.0	$3.666 \times 10^{-4}$
I <sup>-</sup>	0.257	$2.025 \times 10^{-6}$
HCO <sub>3</sub> <sup>-</sup>	14.0	$2.318 \times 10^{-4}$
S-SO <sub>4</sub> <sup>2-</sup>	426.0	$4.480 \times 10^{-3}$
HS <sup>-</sup>	0.007	$2.121 \times 10^{-7}$
P-PO <sub>4</sub> <sup>3-</sup>	< 0.040	—
TOC	1.4	$1.166 \times 10^{-4}$

The analysis of the colloid by scanning electron microscopy on the prepared membranes reveals colloids of various sizes, shapes and morphologies as it can be seen Fig. 5-1 and 5-2. Figure 5-1 presents typical micrographies taken for ground water colloid sample in KLX17A (416.0 to 437.5 m) on the 0.2  $\mu\text{m}$  membrane. The 0.2–0.3  $\mu\text{m}$  colloid number  $n$  on the membrane is quite small. These particles for size larger than 0.2  $\mu\text{m}$  are composed mostly of bore hole drilling fragments. They do not play a significant role since they sediment quite rapidly in the *in situ* water bearing fissure (see Section 5.2).

Figure 5-2 presents micrographies taken for ground water colloid sample in KLX17A (416.0 to 437.5 m) on the 0.05  $\mu\text{m}$  membrane. The 0.05–0.2  $\mu\text{m}$  colloid number  $n$  on the membrane is quite large. These particles for size larger than 0.05  $\mu\text{m}$  are composed mostly of *in situ* ground water colloids. Some small bacteria are also identified.

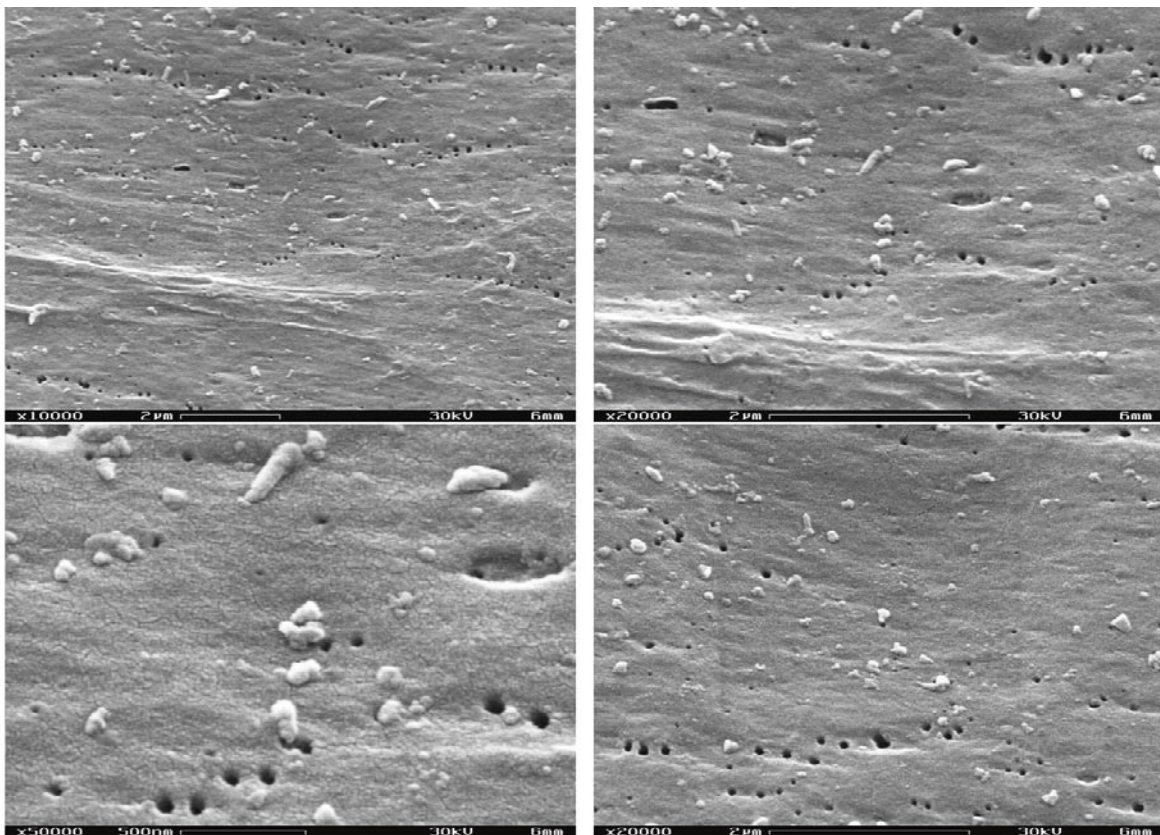


**Figure 5-1.** SEM micrographs of the ground water colloids in KLX17A (416.0–437.5 m) on the 0.2  $\mu\text{m}$  membrane.

The counting of the colloids was carried out systematically for KLX17A. Table 5-3a gives details about the colloid concentration for the investigated sizes. The colloid size distribution for KLX17A is shown in Fig. 5-5 (in comparison with the KLX15A data).

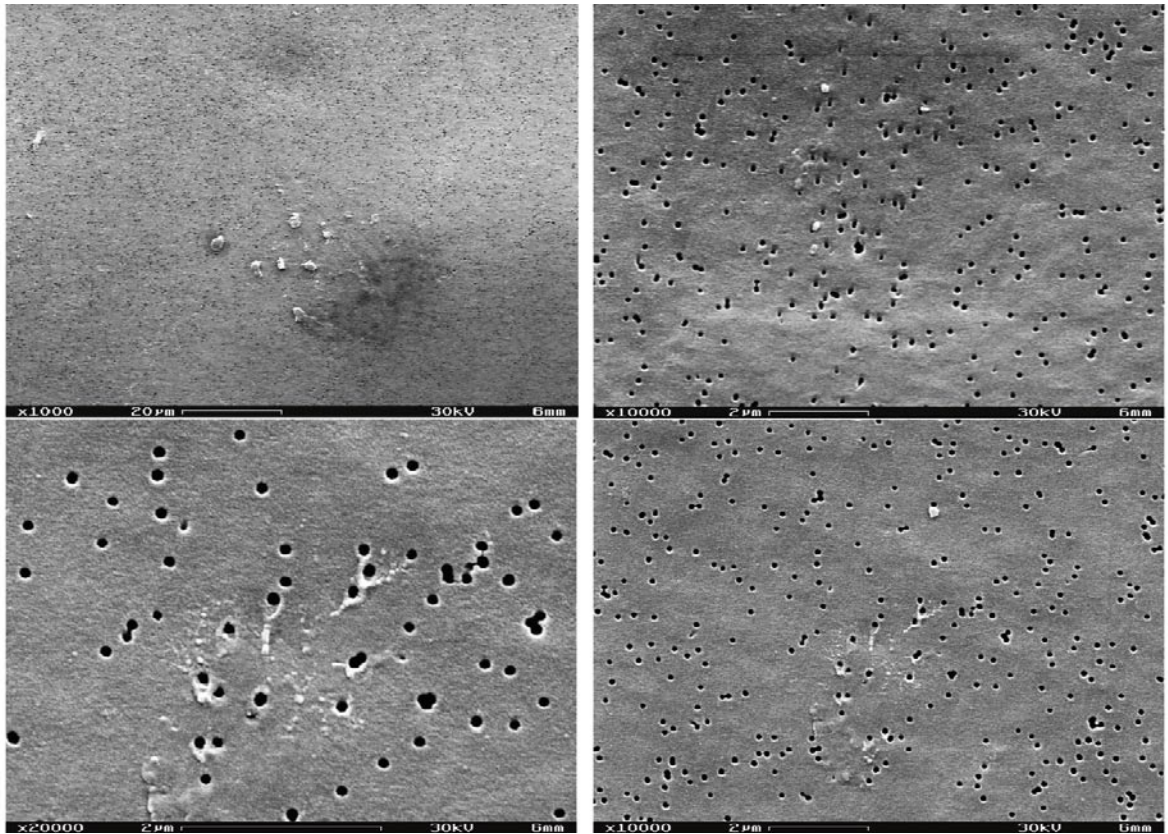
Figure 5-3 presents typical micrographies taken for ground water colloid sample in KLX15A (623.0 to 634.5 m) on the 0.2  $\mu\text{m}$  membrane. The number of colloid larger than 0.2  $\mu\text{m}$  on the membrane is very small. Occasionally one larger particle is found all the 10–100 micrograph field of magnification 10'000. These particles for size larger than 0.2  $\mu\text{m}$  are currently composed of bore hole drilling fragments. They do not play a significant role since they sediment quite rapidly in the *in situ* water bearing fissure.

Figure 5-4 presents typical micrographies taken for ground water colloid sample in KLX15A (623.0 to 634.5 m) on the 0.05  $\mu\text{m}$  membrane. A colloid population for sizes ranging from 0.05–0.1  $\mu\text{m}$  is identified. These particles could be partially a population of specific phase precipitates.

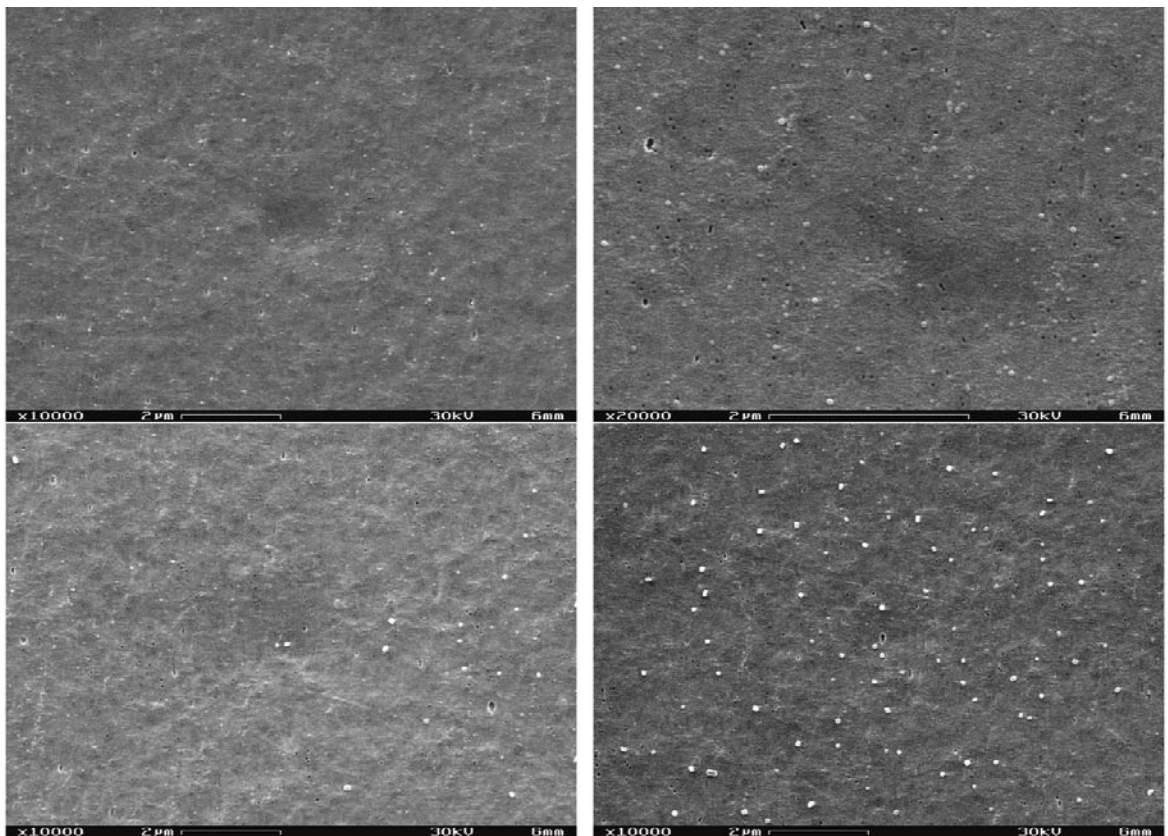


**Figure 5-2.** SEM micrographs of the ground water colloids in KLX17A (416.0–437.5 m) on the 0.05  $\mu\text{m}$  membrane.





*Figure 5-3. SEM micrographs of the ground water colloids (KLX15A (623.0 to 634.5 m)) on the 0.2  $\mu$ m filter:*



*Figure 5-4. SEM micrographs of the ground water colloids (KLX15A (623.0 to 634.5 m)) on the 0.05  $\mu$ m filter:*

The counting of the colloids was carried out systematically for KLX15A. Table 5-3 gives for waters from both boreholes details about the colloid concentration for the investigated sizes. The colloid size distribution is shown in Fig. 5-5 for both boreholes.

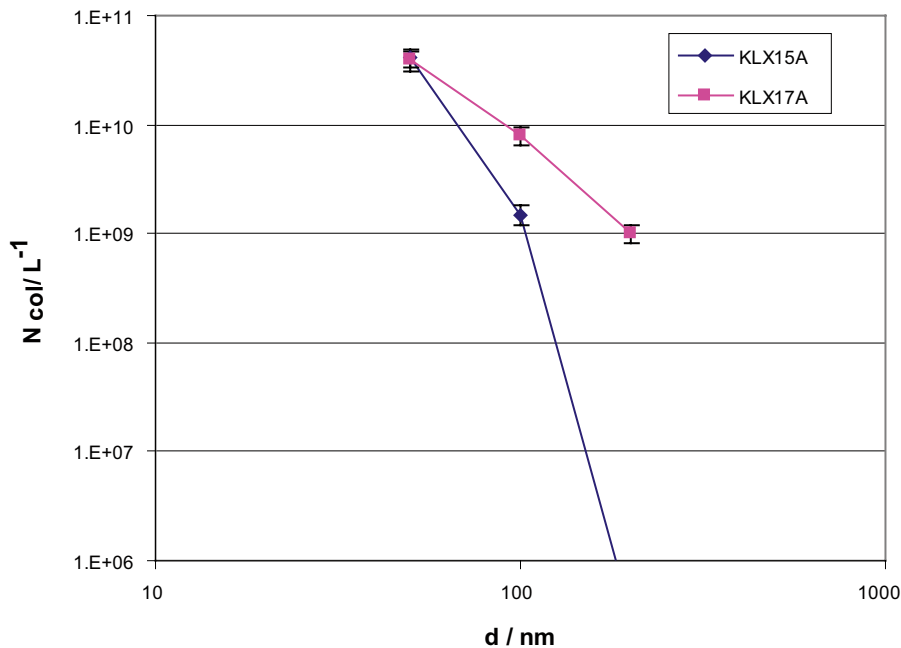
**Table 5-3: Quantification of the colloid specific size distribution for a. KLX17A (416.0–437.5 m) and b. KLX15A (623.0 to 634.5 m). Conditions: for the colloid size  $d$  on the basis of the colloid number  $n$  on the micrograph ( $s = 23.2 \mu\text{m}^2$ ) the colloid number concentration  $N_{col}$  is calculated on the basis of the active membrane size ( $S = 14.25 \text{ cm}^2$ ) and the filtered volume ( $V = 140 \text{ mL}$ ). For the average colloid size  $d_{av}$ , of volume  $V_{av}$  or mass  $m_{av}$  (estimated for a density  $\rho = 2 \text{ g cm}^3$ ) the colloid concentration  $C_{col}$  is calculated.**

**a. For KLX17A (416.0–437.5 m).**

Size $d$ / nm	50	100	150	50–200
<b>Colloid data</b>				
$n$	79–84	9–18	4–4	
$N_{col} / \text{L}^{-1}$	$394 \times 10^8$	$80 \times 10^8$	$20 \times 10^8$	$\sim 500 \times 10^8$
$d_{av} / \text{nm}$	60	120	170	
$V_{av} / \text{cm}^3$	$0.2 \times 10^{-15}$	$1.7 \times 10^{-15}$	$4.8 \times 10^{-15}$	
$m_{av} / \text{g}$	$0.4 \times 10^{-15}$	$3.4 \times 10^{-15}$	$9.5 \times 10^{-15}$	
$C_{col} / \text{mg L}^{-1}$	0.016	0.024	0.018	0.060

**b. For KLX15A (623.0–634.5 m).**

Size $d$ / nm	50	100	150	50–200
<b>Colloid data</b>				
$n$	78–82	2–4	$\ll 1$	
$N_{col} / \text{L}^{-1}$	$399 \times 10^8$	$15 \times 10^8$	$\ll 5 \times 10^8$	$\sim 400 \times 10^8$
$d_{av} / \text{nm}$	60	120	170	
$V_{av} / \text{cm}^3$	$0.2 \times 10^{-15}$	$1.7 \times 10^{-15}$	$4.8 \times 10^{-15}$	
$m_{av} / \text{g}$	$0.4 \times 10^{-15}$	$3.4 \times 10^{-15}$	$9.5 \times 10^{-15}$	
$C_{col} / \text{mg L}^{-1}$	0.016	0.004	$< 0.001$	0.020



**Figure 5-5.** Colloid size distributions estimated from data reported in Table 5-3 a and b.

Based on SEM micrographs, colloid morphology suggests that they consist mostly of clay particles. However, Al and Si are not detectable by EDS, the colloid size being too small to allow analysis. X-ray diffraction XRD analysis of colloids from 0.10–1.00  $\mu\text{m}$  collected on membrane filters should be tempted to analyse their clay nature. These particles are expected from the rock mineralogy described in Section 2.1 for both KLX17A and KLX15A.

## 5.2 Assessing the colloid data

In order to assess the quality of the colloid data, it is imperative to understand if the water quality is affected or not by the borehole construction and packer installation. In principle, the artefacts from borehole construction and packer installation have been discarded and removed by dilution within the flow of water during the weeks of flush out and prior to the colloid sampling. Micro-filtration of the colloids was carried out after a period of regular sampling for chemical and physical parameter determinations.

On site, colloid transit during pumping in the borehole line creates a cut-off (balance between transport upward and sedimentation). The particle of size  $d$  acquires in the bore hole a constant settling velocity  $v$  is given by Stoke's law:

$$v = 0.05556 g d^2 (\rho - \rho_w) \eta^{-1} \quad (4)$$

with  $g$  the gravity acceleration ( $981 \text{ cm} \times \text{s}^{-2}$ ),  $\rho_w$  the water density and  $\eta$  is the fluid viscosity ( $1.0 - 1.4 \text{ cPoise}$ , or  $\times 10^{-3} \text{ Pa} \times \text{s}$ , at  $25$  and  $10^\circ\text{C}$  respectively). For a colloid density of  $2 \text{ g} \times \text{cm}^{-3}$  corresponds to a maximum size that transit from the interval to the container must be determined. Large colloids may concentrate in the interval while small are extracted by pumping. Part of the large may settle in the interval. The remaining part of large particles is however filtered out during the prefiltration process (2 first filtrations through the  $2 \mu\text{m}$  membranes).

On the other side, *in situ* and prior borehole drilling, the presence in the water bearing zone of colloids with sizes larger than  $0.2 \mu\text{m}$  is unlikely because of their sedimentation rate of the order of  $10^{-2} \text{ cm h}^{-1}$  and this rate increases with the square of the colloid size (see Equation 4).

Residence time in the interval from the water bearing zone to the container aperture is also important. During this period, the aggregation of the colloids in the considered size range should not be significant. The aggregation half-time has to be estimated for a colloid concentration level of  $100 \text{ ppb}$  or  $10 \text{ ppb}$  and for attachment coefficients of the order of  $10^{-1}$  (corresponding to the Ca, Mg, Na and K concentration) and size  $100 \text{ nm}$  /see Degueldre *et al.* 1996b/.

From the chemistry point of view the question is: are colloids affected by any carbonate or oxy-hydroxyde precipitation? The generation of artefacts produced by pH changes due to  $\text{CO}_2$  exchange, yielding potential carbonate precipitation, or by  $\text{O}_2$  contaminations yielding oxidised insoluble phases was evaluated running the code PHREEQ /e.g. Plummer *et al.* 1983/ for the data reported in Table 5-1 and 5-2. The results are given in Table 5-4 and 5-5.

The water pH's and the concentrations of bicarbonate make the carbonates of Ca, Mg, Sr, Fe and Mn undersaturated. The calculated partial pressure of  $\text{CO}_2$  in equilibrium with the water must be compared with that of air. The water could expurge slightly the  $\text{CO}_2$  by increasing slightly the pH. The oxy-hydroxydes are undersaturated or very slightly saturated (e.g. Al, Fe, Mn, Si and As) and as usual,  $\text{Fe}(\text{OH})_3$  is undersaturated, goethite is saturated and  $\text{Fe}_2\text{O}_3$  is slightly over-saturated. Finally the clay mineral saturation indices have to be evaluated.

The on-line procedure allows us to work at the well head under *in situ*  $T$  and  $P$  conditions similar to the *in situ* conditions, i.e. artefact free. This methodology avoids the generation of artefacts produced by pH changes due to  $\text{CO}_2$  exchange, yielding potential carbonate precipitation, or by  $\text{O}_2$  contaminations yielding oxidised insoluble phases.

Table 5-4 shows that for KLX17A (416.0–437.5 m) groundwater, calcite is at equilibrium (0.07) or nearby within the error margin. Quartz is oversaturated (0.32) but chalcedony is undersaturated (–0.15) and near to equilibrium. Gibbsite may be oversaturated (0.36) but the higher concentration of Al may be due to clay colloid (see for example the oversaturation of kaolinite (2.12)). The  $P(\text{CO}_2)$  is –3.14 which would allow degassing of the water in contact with air.

**Table 5-4: PHREEQ indicative results obtained for the KLX17A (416.0–437.5 m) water chemistry given in Table 5-1. Conditions: Electrical balance =  $2.516 \times 10^{-04}$  eq, error:  $100(\text{Cat}-|\text{An}|)/(\text{Cat}+|\text{An}|) = 0.67\%$  @ 12°C, Iterations = 11.**

Parameter Phase	SI	log IAP	log KT	Formula
Al (OH) 3 (a)	–2.46	9.23	11.69	Al (OH) 3 (a)
Albite	–1.46	3.75	5.22	NaAlSi <sub>3</sub> O <sub>8</sub>
Alunite	–12.94	–12.66	0.28	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Anhydrite	–4.81	–9.14	–4.33	CaSO <sub>4</sub>
Anorthite	–4.33	23.74	28.07	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
Aragonite	–0.08	–8.34	–8.26	CaCO <sub>3</sub>
Calcite	0.07	–8.34	–8.42	CaCO <sub>3</sub>
Celestite	–4.46	–11.08	–6.63	SrSO <sub>4</sub>
Chalcedony	–0.15	–3.86	–3.71	SiO <sub>2</sub>
Chlorite (14A)	–4.70	68.75	73.44	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>
Chrysotile	–4.48	29.40	33.88	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Carbon dioxide (g)	–3.14	–21.35	–18.21	CO <sub>2</sub> (g)
Dolomite	–0.54	–17.32	–16.77	CaMg (CO <sub>3</sub> ) <sub>2</sub>
Fluorite	–0.07	–10.84	–10.77	CaF <sub>2</sub>
Gibbsite	0.36	9.23	8.87	Al (OH) <sub>3</sub>
Gypsum	–4.55	–9.14	–4.59	CaSO <sub>4</sub> ·2H <sub>2</sub> O
Hausmannite	–28.24	36.15	64.39	Mn <sub>3</sub> O <sub>4</sub>
Hydroxoapatite	–2.68	–42.29	–39.60	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH
Illite	–0.12	13.18	13.30	K <sub>0.6</sub> Mg <sub>0.25</sub> Al <sub>2.3</sub> Si <sub>3.5</sub> O <sub>10</sub> (OH) <sub>2</sub>
K-feldspar	–0.88	1.60	2.48	KAlSi <sub>3</sub> O <sub>8</sub>
Kaolinite	2.12	10.74	8.61	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Pyrochroite	–5.26	9.94	15.20	Mn (OH) <sub>2</sub>
Pyrolusite	–27.29	16.26	43.56	MnO <sub>2</sub>
Quartz	0.32	–3.86	–4.18	SiO <sub>2</sub>
Rhodochrosite	–0.32	–11.40	–11.08	MnCO <sub>3</sub>
Sepiolite	–2.95	13.17	16.12	Mg <sub>2</sub> Si <sub>3</sub> O <sub>7</sub> ·5OH : 3H <sub>2</sub> O
Siderite	–0.88	–11.69	–10.81	FeCO <sub>3</sub>
Silica (a)	–1.03	–3.86	–2.82	SiO <sub>2</sub>
Strontianite	–1.00	–10.29	–9.28	SrCO <sub>3</sub>

Table 5-5 shows that for KLX15A (623.0 to 634.5 m) groundwater, calcite is slightly undersaturated (-0.29) within the error margin. Quartz is nearby equilibrium (0.08) but chalcedony is undersaturated (-0.39). Gibbsite may be oversaturated (0.34) but the higher concentration of Al may be due to clay colloids (see for example the oversaturation of kaolinite (1.60)). The  $P(\text{CO}_2)$  is -3.53 which makes the water in equilibrium with air. Fluorite is slightly over-saturated (0.53), however, this was also found, for example, for the groundwater of the Grimsel Test Site /Degueldre *et al.* 1989/.

The colloid concentration was determined  $C_{col} \sim 20\text{--}60 \mu\text{g}\times\text{l}^{-1}$  for sizes ranging from 50 to 200 nm or  $N_{col} \sim 4\times 10^{-10} \text{L}^{-1}$  for sizes larger than 50 nm. These colloids are clay. These concentrations are indicative since they concern a single filtration campaign but the results make sense. These colloid concentrations are comparable with those found in the Swiss granitic groundwater e.g. Leuggern and Zurzach /Degueldre *et al.* 1996/.

**Table 5-5: PHREEQ indicative results obtained for the KLX15A (623.0–634.5 m)water chemistry given in Table 5-2. Conditions: Electrical balance =  $-2.318\text{e}\times 10^{-04}$  eq, error:  $100(\text{Cat}-|\text{An}|)/(\text{Cat}+|\text{An}|) = -0.68\%$  @ 18°C, Iterations = 8.**

Parameter Phase	SI	log IAP	log KT	Formula
Al (OH) 3 (a)	-2.42	8.85	11.27	Al (OH) 3 (a)
Albite	-1.89	3.06	4.95	NaAlSi3O8
Alunite	-5.16	-5.67	-0.51	KAl3 (SO4) 2 (OH) 6
Anhydrite	-0.72	-5.06	-4.34	CaSO4
Anorthite	-4.27	22.63	26.91	CaAl2Si2O8
Aragonite	-0.44	-8.73	-8.29	CaCO3
Calcite	-0.29	-8.73	-8.44	CaCO3
Celestite	-4.46	-11.08	-6.63	SrSO4
Chalcedony	-0.39	-4.02	-3.63	SiO2
Chlorite (14A)	-5.61	64.44	71.05	Mg5Al2Si3O10 (OH) 8
Chrysotile	-5.85	27.24	33.09	Mg3Si2O5 (OH) 4
Carbon dioxide (g)	-3.53	-21.70	-18.17	CO2 (g)
Dolomite	-1.75	-18.67	-16.92	CaMg (CO3) 2
Fluorite	0.51	-10.17	-10.69	CaF2
Gibbsite	0.34	8.85	8.51	Al (OH) 3
Gypsum	-0.49	-5.07	-4.58	CaSO4:2H2O
Hausmannite	-26.49	36.31	62.80	Mn3O4
Illite	-1.09	11.53	12.62	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$
K-feldspar	-1.66	0.63	2.30	KAlSi3O8
Kaolinite	1.60	9.66	8.06	Al2Si2O5 (OH) 4
Pyrochroite	-5.89	9.31	15.20	Mn (OH) 2
Pyrolusite	-25.01	17.69	42.70	MnO2
Quartz	0.08	-4.02	-4.10	SiO2
Rhodochrosite	-1.30	-12.40	-11.10	MnCO3
Sepiolite	-4.53	11.45	15.98	Mg2Si3O7. 5OH : 3H2O
Siderite	-1.51	-12.35	-10.84	FeCO3
Silica (a)	-1.24	-4.02	-2.78	SiO2
Strontianite	-1.55	-10.82	-9.27	SrCO3

## 6 Summary

Samples of natural groundwater colloids were produced by micro-filtration on-line from a granitic groundwater at the well head in the *in situ*  $T$  and  $P$  conditions. This methodology avoids the generation of artefacts produced by pH changes due to  $\text{CO}_2$  exchanges, yielding potential carbonate particles, or by  $\text{O}_2$  contaminations yielding oxy-hydroxyde colloids. The on-line procedure allows us to work at the well head artefact free. Micro-filtration of the colloids is carried out after a period of regular sampling of chemical and physical parameters in the groundwater. Colloid samples were characterised by scanning electron microscopy. In the deep granitic groundwater conditions, natural colloids occur. The colloid concentration was determined  $C_{col} \sim 20\text{--}60 \mu\text{g}\times\text{l}^{-1}$  for sizes ranging from 50 to 200 nm or  $N_{col} \sim 4\times 10^{10} \text{L}^{-1}$  for sizes larger than 100 nm. The colloid concentrations were found to be  $C_{col} \sim 20 \mu\text{g}\times\text{l}^{-1}$  for KLX15A and  $C_{col} \sim 60 \mu\text{g}\times\text{l}^{-1}$  for KLX17A from 50 to 200 nm or  $N_{col} \sim 4\times 10^{10} \text{L}^{-1}$  for sizes larger than 50 nm and for both KLX15A and KLX17A. These colloids are suggested to be clay particles with an average size smaller than 200 nm. For the Na-(Ca)-Cl groundwaters KLX15A and KLX17A, with respectively pH 7.4 and 8.0, and, ionic strength  $\sim 2\times 10^{-1}$  and  $2\times 10^{-2}\text{M}$ , the colloid concentration values are comparable with values reported earlier in the literature.

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