

Oskarshamn site investigation

Hydrochemical logging in KLX21B

Results from isotope determinations (^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$)

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November 2007

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author and do not necessarily coincide with those of the client.

Data in SKB's database can be changed for different reasons. Minor changes in SKB's database will not necessarily result in a revised report. Data revisions may also be presented as supplements, available at www.skb.se.

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Abstract

Hydrochemical logging, also called tube sampling, has been performed in the core drilled borehole KLX21B. The method is a fast and simple sampling technique for obtaining information about the chemical composition of the water along an open borehole. The equipment consists of an approximately 1,000 m long polyamide tube divided into units of 50 m. An appropriate number of tube units can be used to suit the actual borehole length, in this case c. 850 m.

The water content in each tube unit constituted one sample. Every second sample, starting with the lowest tube unit, was analysed according to SKB chemistry class 3 (isotope options excluded) at the sampling occasion. The performance and results from this sampling has been reported in a previous report /1/. This report gives the results from the performed isotope determinations of tritium (^3H), deuterium ($\delta^2\text{H}$) and oxygen-18 ($\delta^{18}\text{O}$). The samples with SKB sample number 11627 and 11629 intended for isotope determination were not analysed due to high drill water content /1/. The samples were collected at the time of sampling and stored in a freezer (^3H in a refrigerator) for approximately three months before they were sent to the consulting laboratories for analysis.

Sammanfattning

Hydrokemisk loggning, också kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX21B. Metoden är snabb och enkel att använda för att erhålla information om den kemiska sammansättningen hos grundvattnet längs ett öppet borrhål. Utrustningen består av en cirka 1 000 m lång polyamidslang uppdelad i enheter om vardera 50 m. Lämpligt antal slangenheter kan användas för att anpassa längden till det aktuella borrhålets längd, i detta fall ca 850 m.

Innehållet i en slangenheter utgör ett prov. Varannan slangenheter, med start från den nedersta, analyserades enligt SKB kemiklass 3 (exklusive alla tillval) i direkt anslutning till provtagningstillfället. Utförande och resultat från denna provtagning har rapporterats i en tidigare primär-datarapport /1/. Denna rapport redovisar resultaten från utförda isotopanalyser av tritium (^3H), deuterium ($\delta^2\text{H}$) och syre-18 ($\delta^{18}\text{O}$). Proverna med SKB provnummer 11627 och 11629 avsedda för isotopanalyser, skickades inte in för analys på grund av att halten kvarvarande spolvatten efter borrning var för hög /1/. Proverna togs ut i samband med provtagningen och sparades i frys (^3H i kylskåp) i cirka tre månader innan de sändes iväg för analys till de konsulterade laboratorier.

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1 Introduction

This document reports the results of isotope analyses gained by the Hydrochemical logging, which is one of the activities performed within the site investigation at Oskarshamn /2, 3/. The work was carried out in accordance with activity plan AP PS 400-06-155. In Table 1-1 controlling documents for performing this activity are listed. Both the activity plan and the method descriptions are SKB's internal controlling documents.

This report is a complement to the previous report regarding the Hydrochemical logging in KLX21B /1/, which documented the performance and results from analyses of major constituents, anions, drill water content, electric conductivity and pH. The original results are stored in the primary data base SICADA where they are traceable by the activity plan number.

Table 1-1. Controlling documents for the performance of the activity.

Activity plan	Number	Version
Hydrokemisk loggning i KLX21B	AP PS 400-06-155	1.0
Method descriptions	Number	Version
Metodbeskrivning för hydrokemisk loggning	SKB MD 422.001	2.0
Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning	SKB MD 600.004	1.0

2 Objective and scope

Hydrochemical logging was performed in order to obtain an overview of the chemical composition of the water along the open core drilled borehole KLX21B. The technique used for sampling is fast and simple, also for boreholes of considerable lengths.

The analysis program has previously been carried out according to SKB chemistry class 3 except for optional isotopes and was published in a previous report /1/. The conducted isotope determinations include ^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

3 Execution

3.1 Hydrochemical logging

The Hydrochemical logging in KLX21B was performed on January 9, 2007 according to the activity plan and in compliance with the method description (cf. Table 1-1).

The execution of field work and the equipment used have been described in a previous report regarding the Hydrochemical logging in KLX21B /1/.

3.2 Sample treatment and chemical analysis

An overview of sample treatment and analysis routines of the activity is given in Appendix 1.

An overview showing the samples obtained at the logging occasion is given in Table 3-1. The sample portions for isotope analyses were stored in a freezer at SKB (^3H in a refrigerator) at the time of the Hydrochemical logging. Samples collected for determination of ^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were sent for analysis to the consulting laboratories approximately three months after the sampling occasion i.e. in April 2007. The data from the Hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 11613–11629. Since the drill water content was high in some of the samples, only sample numbers 11613–11625 (uneven numbers) were sent for isotope determination.

Table 3-1. Overview of samples collected at the Hydrochemical logging in KLX21B. Filled cells represent collected samples. Striped (blue) fillings represent samples reported in a previous report /1/, light (yellow) fillings represent samples that have been analyzed. Dashed yellow fillings represent samples collected and stored in a freezer (³H in a refrigerator) and dashed (purple) cells represent archive samples.

Sample information			Collected sample portions											Archive
Tube unit	Length [m]	SKB no.	Cond., pH, alk.	Major Comp.	Ura-nine	An-ions	³ H	δ ² H δ ¹⁸ O	δ ³⁷ Cl	¹⁰ B/ ¹¹ B*	⁸⁷ Sr/ ⁸⁶ Sr	δ ³⁴ S	δ ¹³ C and ¹⁴ C	Filtered 2x250 mL
20	0 40	11613					α	α	α	-	-			
16	90	11614												-
15	140	11615									ω			
14	190	11616												
13	240	11617												
12	290	11618												
11	340	11619												
10	390	11620												
9	440	11621												
8	490	11622												
7	540	11623												
6	590	11624												
5	640	11625												
4	690	11626												
3	740	11627												
2	790	11628												
1	840	11629												

- No sample due to lack of water in tube unit.

α Filled with sample water from tube unit number 16.

ω Filled with sample water from tube unit number 14.

* The B-isotope ratio is given as ¹⁰B/¹¹B (the result reported from the consulting laboratory). The notation according to international standard for environmental isotopes is ¹¹B/¹⁰B, i.e. 1/(¹⁰B/¹¹B).

3.3 Data handling

The following routines for quality control and data management are generally applied for hydrogeochemical analysis data, irrespectively of sampling method or sampling object.

All analytical results were stored in the SICADA database. The applied hierarchy path “Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database” contains two types of tables, raw data tables and primary data tables (final data tables).

Data from **basic water analyses** are inserted into raw data Tables for further evaluation. The evaluation results in a final data set for each sample. These data sets are compiled in a primary data Table named “water_composition”. The evaluation is based on:

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10%).
- Calculation of charge balance errors. Relative errors within $\pm 5\%$ are considered acceptable (in surface waters $\pm 10\%$).

$$\text{Relative error (\%)} = 100 \times \frac{\sum \text{cations(equivalents)} - \sum \text{anions(equivalents)}}{\sum \text{cations(equivalents)} + \sum \text{anions(equivalents)}}$$

- General judgement of plausibility based on earlier results and experiences.

All results from **special analyses of trace metals and isotopes** are inserted directly into primary data Tables. In cases where the analyses are repeated or performed by more than one laboratory, a “best choice” notation will indicate the results considered most reliable.

An overview of the data management is given in Figure 3-1.

3.4 Nonconformities

The activity was performed without any deviations from the controlling documents for the activity that can affect the quality of data.

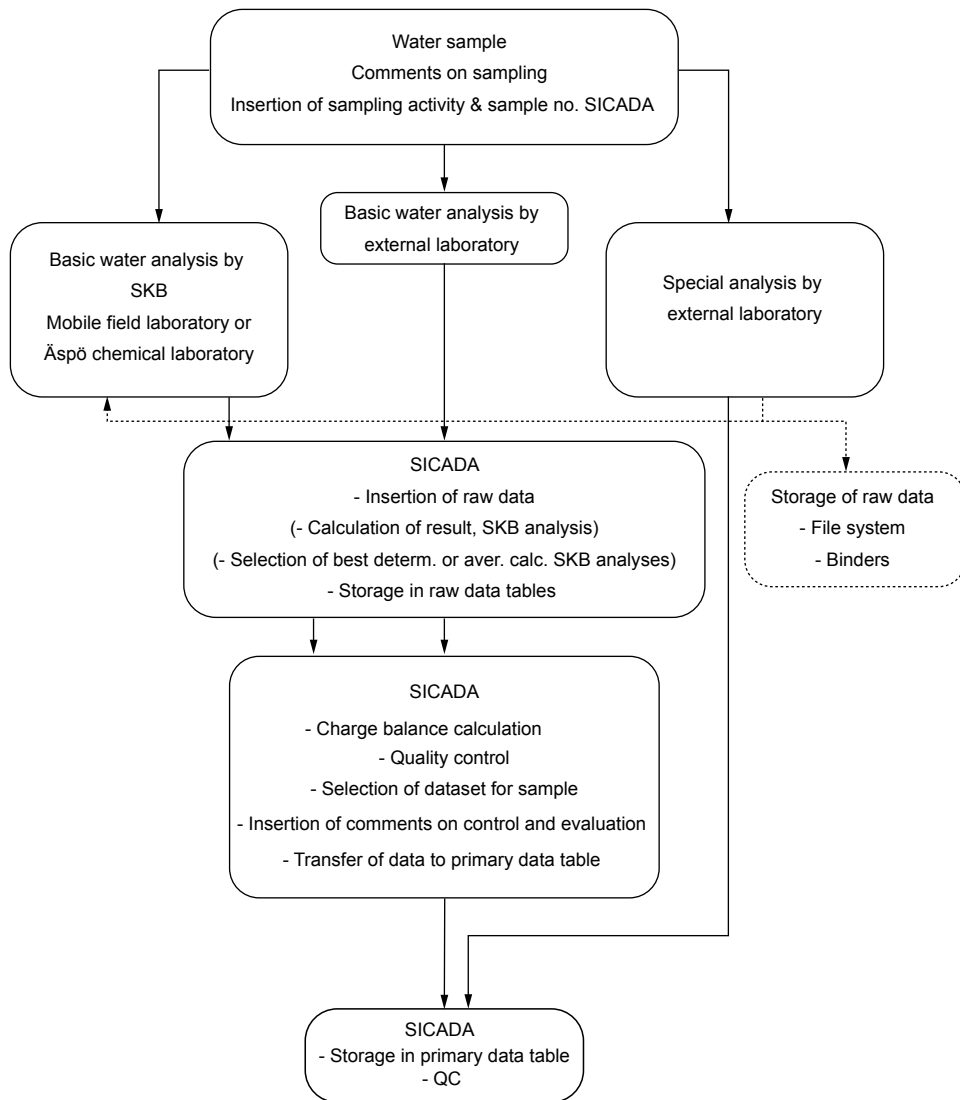


Figure 3-1. Overview of data management for hydrogeochemical data. This report only handles “Special analysis by external laboratory”. (The basic water analyses are reported in a previous report /1/.)

4 Results

Original data from the reported activity are stored in the primary database Sicada. Data are traceable in Sicada by the Activity Plan number (AP PS 400-06-155). Only data in databases are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the databases may be revised, if needed. However, such revision of the database will not necessarily result in a revision of this report, although the normal procedure is that major data revisions entail a revision of P-reports. Minor data revisions are normally presented as supplements, available at www.skb.se.

Results from the hydrogen and oxygen isotope determinations received from the Hydrochemical logging are shown in Table 4-1. A diagram showing the ^3H and $\delta^{18}\text{O}$ values along the borehole, at the time of the Hydrochemical logging, is presented in Figure 4-1. The results are plotted for the mid-length of each tube unit.

Table 4-1. Hydrogen and oxygen isotope results for samples collected at the Hydrochemical logging in KLX21B.

Length (m)	Sample SKB no	$\delta^2\text{H}$ (dev. SMOW)	^3H (TU)	$\delta^{18}\text{O}$ (dev. SMOW)
0–40	11613	–78.6	4.4	–11.1
90–140	11615	–79.6	4.1	–11.1
190–240	11617	–85.5	4.5	–11.1
290–340	11619	–89.3	3.4	–11.1
390–440	11621	–88.8	2.6	–11.1
490–540	11623	–89.7	3.2	–11.1
590–640	11625	–89.3	3.1	–11.0

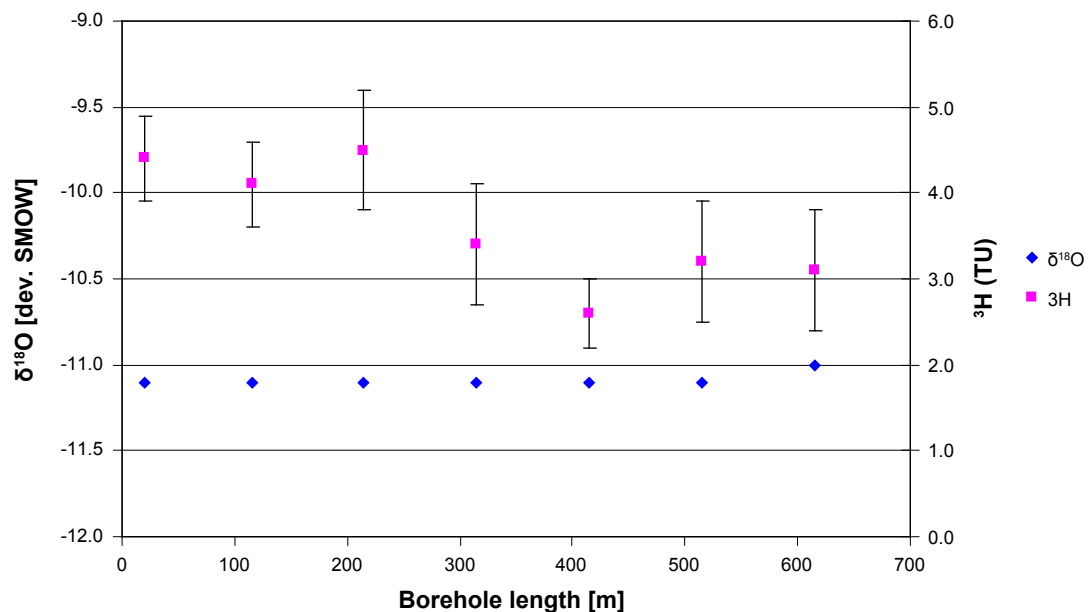


Figure 4-1. Results from analysis of ^3H and $\delta^{18}\text{O}$ in water samples obtained from the Hydrochemical logging in KLX21B.

5 References

- /1/ **Lindquist A, 2007.** Oskarshamn site investigation. Hydrochemical logging in KLX21B. SKB P-07-73, Svensk Kärnbränslehantering AB.
- /2/ **SKB, 2001.** Generellt genomförande program för platsundersökningar. SKB R-01-10, Svensk Kärnbränslehantering AB.
- /3/ **SKB, 2005.** Platsundersökning Oskarshamn. Program för fortsatta undersökningar av berggrund, mark, vatten och miljö inom delområde Laxemar. SKB R-05-37, Svensk Kärnbränslehantering AB.

Sampling and analytical methods

Table A1-1. Sample handling routines and analytical methods.

Component group	Component/element	Sample container (material)	Volume (mL)	Filtrating	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab.
Anions 1	HCO ₃ ⁻ pH (lab) cond (lab)	Plastic	250	No	No	Titration Pot. meas, Cond. meas	The same day – maximum 24 hours
Anions 2	Cl ⁻ , SO ₄ ²⁻ , Br ⁻ , F ⁻	Plastic	250	Yes (in connection with analysis)	No	Titration (Cl ⁻) IC (Cl ⁻ , SO ₄ ²⁻ , Br ⁻ , F ⁻) ISE (F ⁻)	Not critical (month)
Cations, Si and S according to SKB class 3	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (at low conc. acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO ₃)	ICP-AES ICP-MS	Not critical (month)
Environmental isotopes	δ ² H, δ ¹⁸ O	Plastic	100	No	–	MS	Not critical (month)
Tritium	³ H (enhanced.)	Plastic (dry bottle)	500	No	–	LSC	
Chlorine-37	δ ³⁷ Cl	Plastic	500	No	–	ICP MS	Not critical (month)
Carbon isotopes	δ ¹³ C, pmC (¹⁴ C)	Plastic (fluorated)	100×2	No	–	(A)MS	A few days
Sulphur isotopes	δ ³⁴ S	Plastic	500–1,000	No	–	Combustion, ICP MS	No limit
Strontium-isotopes	⁸⁷ Sr/ ⁸⁶ Sr	Plastic	100	No	–	TIMS	Days or Week
Boron isotopes	¹⁰ B/ ¹¹ B **	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP – MS	No limit
Archive samples without acid	–	Plastic	250×2	Yes	No	–	Storage in freeze container

* Suprapur acid is used for conservation of samples.

** The B-isotope ratio is given as ¹⁰B/¹¹B (the result reported from the consulting laboratory). The notation according to international standard for environmental isotopes is ¹¹B/¹⁰B, i.e. 1/(¹⁰B/¹¹B).

Abbreviations and definitions:

IC	Ion Chromatograph
ISE	Ion Selective Electrode
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MS	Mass Spectrometry
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometer

Table A1-2. Reporting limits and measurement uncertainties.

Component	Method	Reporting limits or range	Unit	Measurement uncertainty ²	“Total” uncertainty ³
HCO ₃ ⁻	Alkalinity titration	1	mg/L	4%	< 10%
pH	Pot. meas.	–	–	5%	–
Cond.	Cond. meas.	0.02	mS/m	4%	–
Cl ⁻	Mohr- titration	> 70	mg/L	5%	< 10%
Cl ⁻	IC	1–100		6%	10%
SO ₄ ²⁻	IC	1	mg/L	10%	15%
Br ⁻	IC	0.2	mg/L	9%	20%
F ⁻	IC	0.1	mg/L	10%	20%
F ⁻	ISE	–		–	
Na	ICP	0.1	mg/L	4%	10%
K	ICP	0.4	mg/L	6%	15%
Ca	ICP	0.1	mg/L	4%	10%
Mg	ICP	0.09	mg/L	4%	10%
S(tot)	ICP	0.160	mg/L	21%	15%
Si(tot)	ICP	0.03	mg/L	4%	15%
Sr	ICP	0.002	mg/L	4%	15%
Li	ICP	0.2 ¹ 2	mg/L	10%	20%
δ ² H	MS	2	‰ SMOW ⁴	1‰	–
δ ¹⁸ O	MS	0.1	‰ SMOW ⁴	0.2‰	–
³ H	LSC	0.8 or 0.1	TU ⁵	0.8 or 0.1	Correct order of size
δ ³⁷ Cl	ICP MS	0.2‰ (20 mg/L)	‰ SMOC ⁶	–	–
δ ¹³ C	A (MS)	–	‰ PDB ⁷	–	–
pmC (¹⁴ C)	A (MS)	–	pmC ⁸	–	–
δ ³⁴ S	ICP MS	0.2‰	‰ CDT ⁹	0.3‰	–
⁸⁷ Sr/ ⁸⁶ Sr	TIMS	–	No unit (ratio) ¹⁰	–	–
¹⁰ B/ ¹¹ B **	ICP MS	–	No unit (ratio) ¹⁰	–	–

** The B-isotope ratio is given as ¹⁰B/¹¹B (the result reported from the consulting laboratory). The notation according to international standard for environmental isotopes is ¹¹B/¹⁰B, i.e. 1/(¹⁰B/¹¹B).

1. Reporting limits at salinity ≤ 0.4% (520 mS/m) and ≤ 3.5% (3,810 mS/m) respectively.
2. Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.
3. Estimated total uncertainty by experience (includes effects of sampling and sample handling).
4. Per mille deviation¹³ from SMOW (Standard Mean Oceanic Water).
5. TU =Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10⁻¹⁸ (1 Bq/L Tritium = 8.45 TU).
6. Per mille deviation¹³ from SMOC (Standard Mean Oceanic Chloride).
7. Per mille deviation¹³ from PDB (the standard PeeDee Belemnite).
8. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age:

$$\text{pmC} = 100 \times e^{((1950-y-1.031)/8274)}$$
 where y = the year of the C-14 measurement and t = C-14 age.
9. Per mille deviation¹³ from CDT (the standard Canyon Diablo Troilite).
10. Isotope ratio without unit.

Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:

$$\delta\text{‰} = 1,000 \times (K_{\text{sample}} - K_{\text{standard}}) / K_{\text{standard}}$$
 where K = the isotope ratio and ‰ = ²H, ¹⁸O, ³⁷Cl, ¹³C or ³⁴S etc.