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Oskarshamn site investigation

Hydrochemical logging in KLX09

Results from isotope determinations
(³H, δ²H and δ¹⁸O)

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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.

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Abstract

Hydrochemical logging, also called tube sampling, has been performed in the core drilled borehole KLX09. 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 900 m long polyamide tube divided into units of 50 m.

The water content in each tube unit constituted one sample. Every second sample, starting with the uppermost 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 ($\delta^{18}\text{O}$). Samples for isotope determinations were collected at the time of sampling and stored in a freezer (^3H in a refrigerator) for approximately eight months before they were sent to the consulting laboratories for analysis.

Sammanfattning

Hydrokemisk loggning, också kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX09. 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 900 m lång polyamidslang uppdelad i enheter om vardera 50 m.

Innehållet i en slangenhet utgör ett prov. Varannan slangenhet, med start från den översta, analyserades enligt SKB kemiklass 3 (exklusive alla tillval) i direkt anslutning till provtagningstillfället. Utförande och resultat från denna provtagning har rapporterats i en tidigare primärdatarapport /1/. Denna rapport redovisar resultaten från utförda isotopanalyser av tritium (^3H), deuterium ($\delta^2\text{H}$) och syre-18 ($\delta^{18}\text{O}$). Isotopprover togs ut i samband med provtagningen och sparades i frys eller kyl (^3H) i cirka åtta månader innan de sändes iväg för analys till de konsulterade laboratorierna.

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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/. The work was carried out in accordance with activity plan AP PS 400-05-081. 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 KLX09 /1/, which documented the performance and results from analyses of major constituents, anions, flushing 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 performance of the activity.

Activity plan	Number	Version
Hydrokemisk loggning i KLX09	AP PS 400-05-081	1.0
Method descriptions	Number	Version
Metodbeskrivning för hydrokemisk loggning	SKB MD 422.001	1.0
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 KLX09. 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 KLX09 was performed on December 15, 2005 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 KLX09 /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, δ²H and δ¹⁸O were sent for analysis to the consulting laboratories approximately eight months after the sampling occasion i.e. in the middle of August 2006. The data from the hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 10583 and 10586–10602.

Due to the lack of sample water in the uppermost tube unit, only the bottles for Uranine and major components could be filled from the uppermost section. Water intended for archive samples in the second unit were used to fill up sample bottles for the analyses mentioned above from the uppermost section (0–20 m).

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 ± 5% are considered acceptable (in surface waters ± 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.

Table 3-1. Overview of samples collected at the hydrochemical logging in KLX09. Filled cells represent collected samples. Striped (blue) fillings represent samples present in a previous report /1/, light (yellow) fillings represent samples that have been analysed and are reported here. Dashed yellow fillings represent samples stored in a freezer ($\delta^{13}\text{C}$ and ^{14}C 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	^3H	$\delta^2\text{H}$ $\delta^{18}\text{O}$	$\delta^{37}\text{Cl}$	$^{10}\text{B}/^{11}\text{B}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{34}\text{S}$	$\delta^{13}\text{C}$ ^{14}C	Filtered 2x250 mL
1	0-20	10583		ж	ж									
2	70	10586												
3	120	10587												
4	170	10588												
5	220	10589												
6	270	10590												
7	320	10591												
8	370	10592												
9	420	10593												
10	470	10594												
11	520	10595												
12	570	10596												
13	620	10597												
14	670	10598												
15	720	10599												
16	770	10600												
17	820	10601												
18	870	10602												

ж Partly filled with sample water from tube unit 2.

3.4 Nonconformities

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

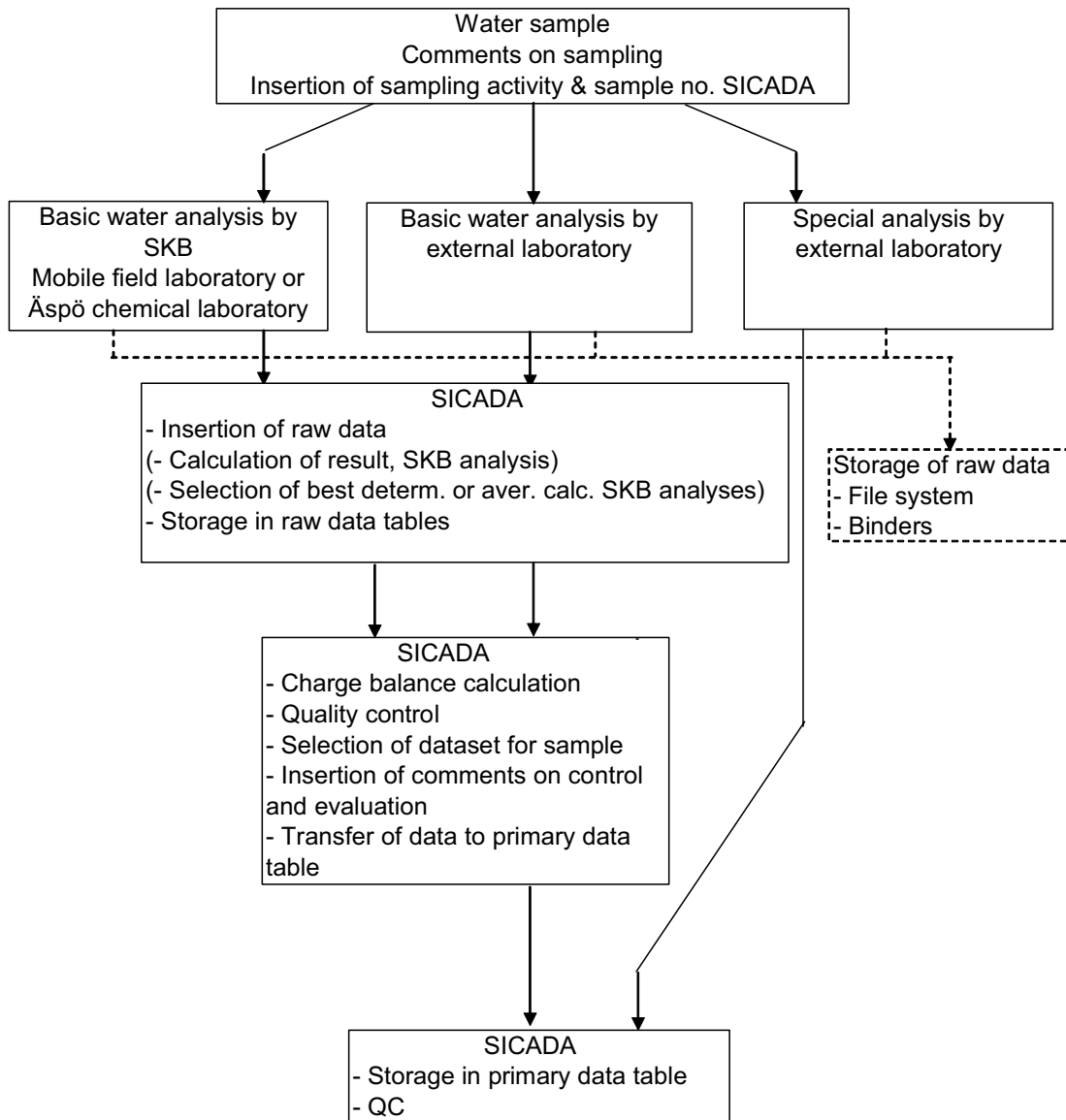


Figure 3-1. Overview of data management for hydrogeochemical data. This report only handles “Special analysis by external laboratory”. (The basic water analyses are reported in a previous report /1/.)

4 Results

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.

The original results are stored in the primary data base SICADA and it is the data in this data base that will be used for further interpretation (modelling). The data is traceable in SICADA by the Activity Plan number (AP PS 400-05-081).

Table 4-1. Hydrogen and oxygen isotope results for samples collected at the hydrochemical logging in KLX09.

Sample SKB:no	$\delta^2\text{H}$ (dev. SMOW)	^3H (TU)	$\delta^{18}\text{O}$ (dev. SMOW)
10587	-77.4	5.5	-10.8
10589	-78.4	3.1	-11.1
10591	-78.1	2.0	-11.1
10593	-78.3	2.9	-11.0
10595	-78.1	1.8	-11.0
10597	-78.1	2.3	-11.0
10599	-78.1	1.4	-10.9
10601	-79.3	2.5	-11.4

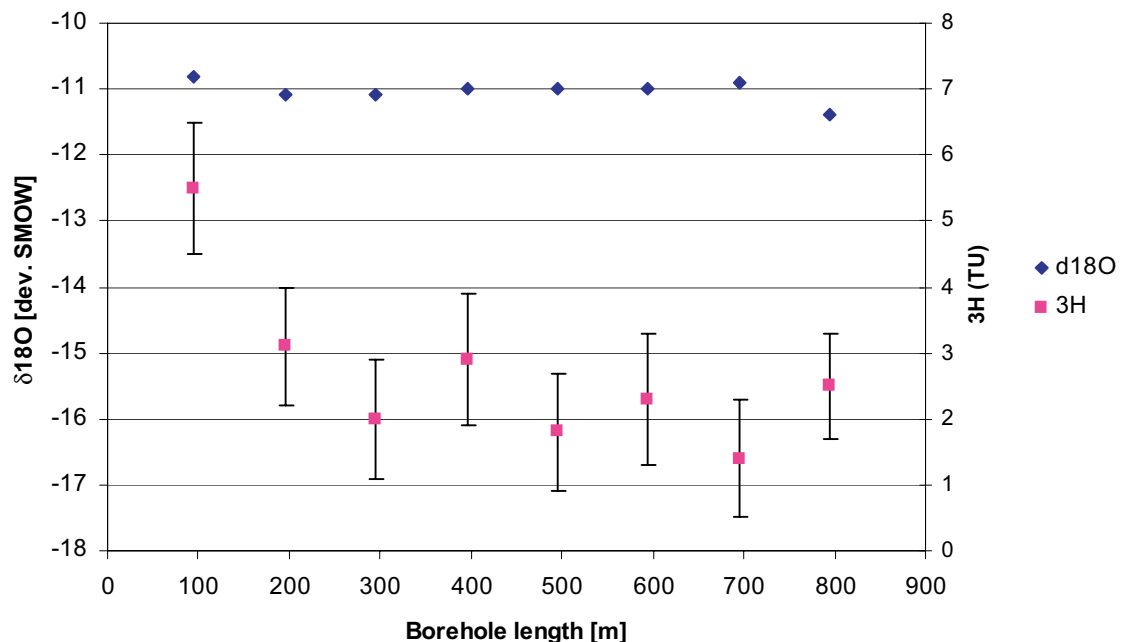


Figure 4-1. Results from analysis of $\delta^{18}\text{O}$ and ^3H in water samples obtained from the hydrochemical logging in KLX09.

5 References

- /1/ **Berg C, Gustavsson E, 2005.** Oskarshamn site investigation. Hydrochemical logging in KLX09. SKB P-06-47, Svensk Kärnbränslehantering AB.
- /2/ **SKB, 2001.** Generellt genomförande program för platsundersökningar. SKB R-01-10, 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)	Filtering	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	100	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)	Glass, dark	100×2	No	–	(A)MS	A few days
Sulphur isotopes	δ ³⁴ S	Plastic	1000	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.

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	10%	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)	>20 mg C	‰ PDB ⁷	–	–
pmC (¹⁴ C)	A (MS)	>20 mg C	pmC ⁸	–	–
δ ³⁴ S	ICP MS	0.2‰	‰ CDT ⁹	0.2‰	–
⁸⁷ Sr/ ⁸⁶ Sr	TIMS	–	No unit (ratio) ¹⁰	0.000020	–
¹⁰ B/ ¹¹ B	ICP MS	–	No unit (ratio) ¹⁰	0.0020	–

1. Reporting limits at salinity ≤ 0.4% (520 mS/m) and ≤ 3.5% (3810 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:

$$\text{pmC} = 100 \times e^{((1950-y-1.03t)/8274)}$$
 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:

$$\delta\text{‰} = 1000 \times (K_{\text{sample}} - K_{\text{standard}}) / K_{\text{standard}}$$
 where K = the isotope ratio and ‰ = ²H, ¹⁸O, ³⁷Cl, ¹³C or ³⁴S etc.