

Oskarshamn site investigation

Hydrochemical logging in KLX12A

Results from isotope determinations (^3H , $\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$)

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(³H, δ²H, δ¹⁸O, ⁸⁷Sr/⁸⁶Sr and δ³⁴S)

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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 KLX12A. 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 600 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 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 ($\delta^2\text{H}$), oxygen-18 ($\delta^{18}\text{O}$), strontium-87/strontium-86 ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) and sulphur-34 ($\delta^{34}\text{S}$). Samples for isotope determinations were collected at the time of sampling and stored in a freezer (^3H in a refrigerator) for approximately two months before they were sent to the consulting laboratories for analysis.

Sammanfattning

Hydrokemisk loggning, också kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX12A. 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 600 m lång polyamidslang uppdelad i enheter om vardera 50 m.

Innehållet i en slangenhet utgör ett prov. Varannan slangenhet, 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 primärdatarapport /1/. Denna rapport redovisar resultaten från utförda isotopanalyser av tritium (^3H), deuterium ($\delta^2\text{H}$), syre-18 ($\delta^{18}\text{O}$), kvoten strontium-87/strontium-86 ($^{87}\text{Sr}/^{86}\text{Sr}$) och svavel-34 ($\delta^{34}\text{S}$). Isotopprover togs ut i samband med provtagningen och sparades i frys eller kyl (^3H) i cirka två månader innan de sändes iväg för analys till de konsulterade laboratorerna.

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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 400-06-022. 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 KLX12A /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 the performance of the activity.

Activity plan	Number	Version
Hydrokemisk loggning i KLX12A	AP PS 400-06-022	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 KLX12A. 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 , $\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$.

3 Execution

3.1 Hydrochemical logging

The hydrochemical logging in KLX12A was performed on April 11, 2006 according to the activity plan AP PS 400-06-022 and in compliance with the method description SKB MD 422.001 (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 KLX12A. /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 (tritium and carbon isotopes in a refrigerator) at the time of the hydrochemical logging. Samples collected for determination of ^3H , $\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ were sent for analysis to the consulting laboratories approximately two months after the sampling occasion i.e. at the end of June 2006. The data from the hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 10968-10978.

Due to the lack of sample water in the uppermost tube unit, the volume of archive samples from the uppermost tube unit was reduced.

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).

Table 3-1. Overview of samples collected at the hydrochemical logging in KLX12A. Filled cells represent collected samples. Striped (blue) filling represent samples reported in a previous report /1/, light (yellow) filling represent samples that have been analysed. Dashed yellow filling 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}B	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{34}\text{S}$	$\delta^{13}\text{C}$ ^{14}C	Filtered 2x250 mL
12	0	10967												✖
	45													
11		10968												
	95													
10		10969												
	145													
9		10970												
	195													
8		10971												
	245													
7		10972												
	295													
6		10973												
	345													
5		10974												
	395													
4		10975												
	445													
3		10976												
	495													
2		10977												
	545													
1		10978												
	595													

✖ Only ca 200 ml.

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.

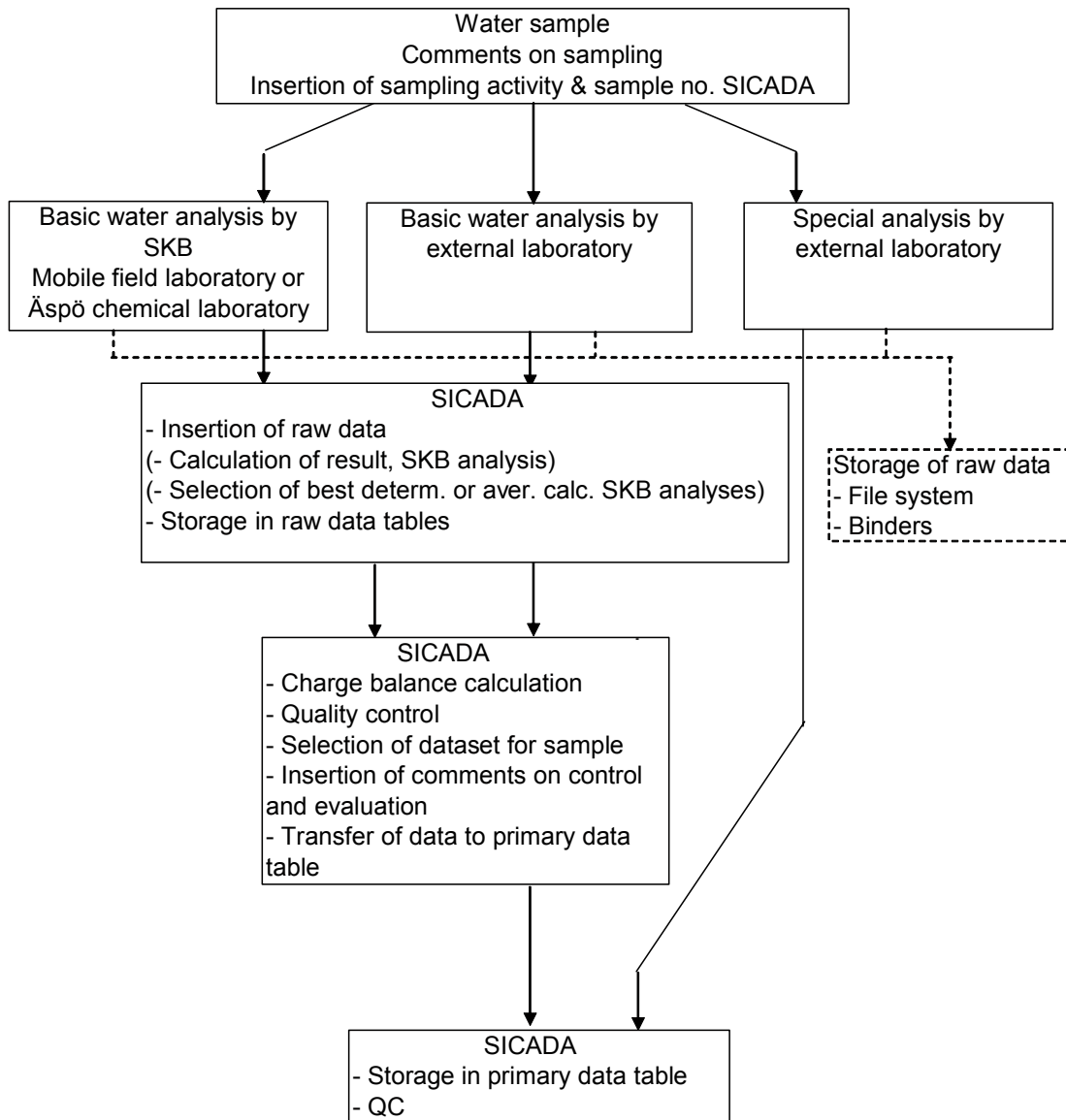


Figure 3-1. Overview of data management for hydrogeochemical data. This report only handles “Special analysis by external laboratory”. (The basic water analyses are reported in a previous report /1/.)

3.4 Nonconformities

Samples for determination of Sr- and S-isotopes were sent for analysis. However, the activity was performed without deviations from the controlling documents that can affect the quality of data.

4 Results

The results from the conducted isotope determinations are presented in Appendix 2. The samples intended for Sr- and S-isotope analyses were sent to the consulting laboratories although this was not the objective. Results from the $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ 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 ^3H result from sample number 10968 (tube unit 0–45 m) is lacking due to its damaging of the enrichment cell at the consulting laboratory.

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 400-06-022).

Table 4-1. $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ results for samples collected at the hydrochemical logging in KLX12A.

Sample SKB:no	$\delta^2\text{H}$ (dev. SMOW)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{34}\text{S}$ (‰ CTD)
10967			21.5
10968	-79.5	0.715465	
10969			22.8
10970	-80.2	0.715325	
10971			23.2
10972	-80.0	0.715128	
10973			20.4
10974	-86.9	0.715003	
10975			19.4
10976	-90.2	0.714946	
10977			16.6
10978	-87.5	0.715134	

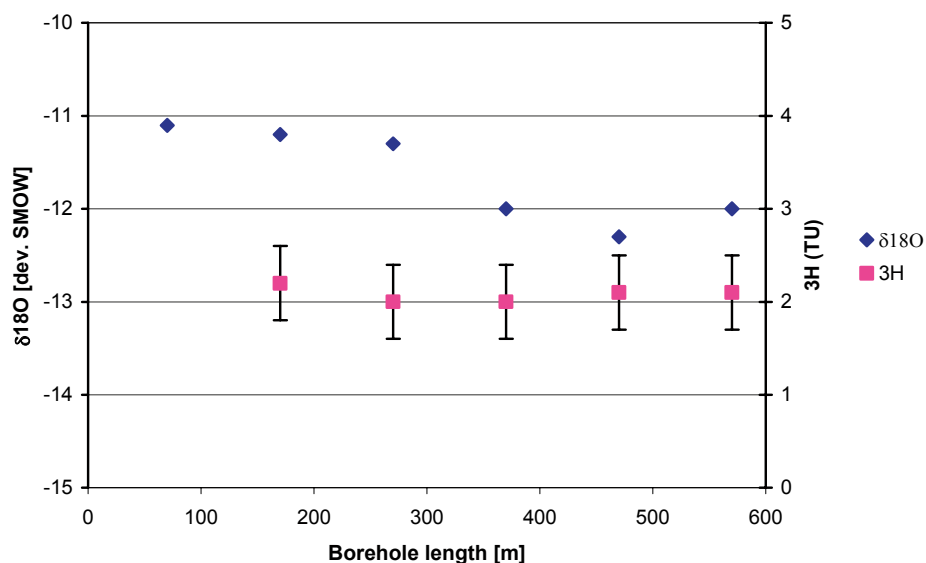


Figure 4-1. Results from analysis of ^3H and $\delta^{18}\text{O}$ in water samples obtained from the hydrochemical logging in KLX12A.

5 References

- /1/ **Nilsson K, 2006.** Oskarshamn site investigation. Hydrochemical logging in KLX12A. SKB P-06-142. 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)	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	100x2	No	–	(A)MS	A few days
Sulphur isotopes	δ ³⁴ S	Plastic	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	250x2	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% (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: pmC = 100 × e^{((1.950 - y - 1.031)/8.274)} 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: δ‰ = 1,000 × (K_{sample} - K_{standard}) / K_{standard}, where K = the isotope ratio and ‰ = ²H, ¹⁸O, ³⁷Cl, ¹³C or ³⁴S etc.

Compilation of isotope data

Water composition.

Idcode	Secup m	Seclow m	Sample no.	$\delta^2\text{H}$ dev SMOW	$\delta^{18}\text{O}$ dev SMOW	^3H TU	$\delta^{37}\text{Cl}$ dev SMOC	$^{10}\text{B}/^{11}\text{B}$ no unit	$^{87}\text{Sr}/^{86}\text{Sr}$ no unit	$\delta^{34}\text{S}$ dev CDT	$\delta^{13}\text{C}$ dev PDB	^{14}C pmC
KLX12A	0	45	10967	-	-	-	-	-	-	21.5	xxx	xxx
KLX12A	45	95	10968	-79.5	-11.1	xx	xxx	xxx	0.715465	-	-	-
KLX12A	95	145	10969	-	-	-	-	-	-	22.8	xxx	xxx
KLX12A	145	195	10970	-80.2	-11.2	2.2	xxx	xxx	0.715325	-	-	-
KLX12A	195	245	10971	-	-	-	-	-	-	23.2	xxx	xxx
KLX12A	245	295	10972	-80.0	-11.3	2.0	xxx	xxx	0.715128	-	-	-
KLX12A	295	345	10973	-	-	-	-	-	-	20.4	xxx	xxx
KLX12A	345	395	10974	-86.9	-12.0	2.0	xxx	xxx	0.715003	-	-	-
KLX12A	395	445	10975	-	-	-	-	-	-	19.4	xxx	xxx
KLX12A	445	495	10976	-90.2	-12.3	2.1	xxx	xxx	0.714946	-	-	-
KLX12A	495	545	10977	-	-	-	-	-	-	16.6	xxx	xxx
KLX12A	545	595	10978	-87.5	-12.0	2.1	xxx	xxx	0.715134	-	-	-