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Oskarshamn site investigation

Hydrochemical logging in KLX11A

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

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Abstract

Hydrochemical logging, also called tube sampling, has been performed in the core drilled borehole KLX11A. 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.

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 (^{3}H), deuterium ($\delta^{2}H$) and oxygen-18 ($\delta^{18}O$). The samples were collected at the time of sampling and stored in a freezer (^{3}H in a refrigerator) for approximately four months before they were sent to the consulting laboratories for analysis.

Sammanfattning

Hydrokemisk loggning, också kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX11A. 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.

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 (^{3}H), deuterium ($\delta^{2}H$) och syre-18 ($\delta^{18}O$). Proverna togs ut i samband med provtagningen och sparades i frys (^{3}H i kylskåp) i cirka fyra månader innan de sändes iväg för analys till de konsulterade laboratorierna.

Contents

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 400-06-021. 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 KLX11A /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 database 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 KLX11A	AP PS 400-06-021	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 KLX11A. 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 ^{3}H, $\delta^{2}H$ and $\delta^{18}O$.

3 Execution

3.1 Hydrochemical logging

The hydrochemical logging in KLX11A was performed on June 8, 2006 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 KLX11A /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 (^{3}H in a refrigerator) at the time of the hydrochemical logging. Samples collected for determination of ^{3}H, δ^2H and δ^{18}O were sent for analysis to the consulting laboratories approximately four months after the sampling occasion i.e. in the middle of October 2006. The data from the hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 11119–11138.

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.

3.4 Nonconformities

The activity was performed without any deviations from the controlling documents.

Table 3-1. Overview of samples collected at the Hydrochemical logging in KLX11A. 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 ($\delta^{13}C$ 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	^{3}H	$\delta^{2}H$ $\delta^{18}O$	$\delta^{37}Cl$	$^{10}B/^{11}B$	$^{87}Sr/^{86}Sr$	$\delta^{34}S$	$\delta^{13}C$ and ^{14}C		Filtered 2×250 mL
20	0 35	11119										ж	–		–
19	85	11120													
18	135	11121													
17	185	11122													
16	235	11123													
15	285	11124													
14	335	11125													
13	385	11126													
12	435	11127													
11	485	11128													
10	535	11129													
9	585	11130													
8	635	11131													
7	685	11132													
6	735	11133													
5	785	11134													
4	835	11135													
3	885	11136													
2	935	11137													
1	985	11138													

ж Only ca 400 ml.

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

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

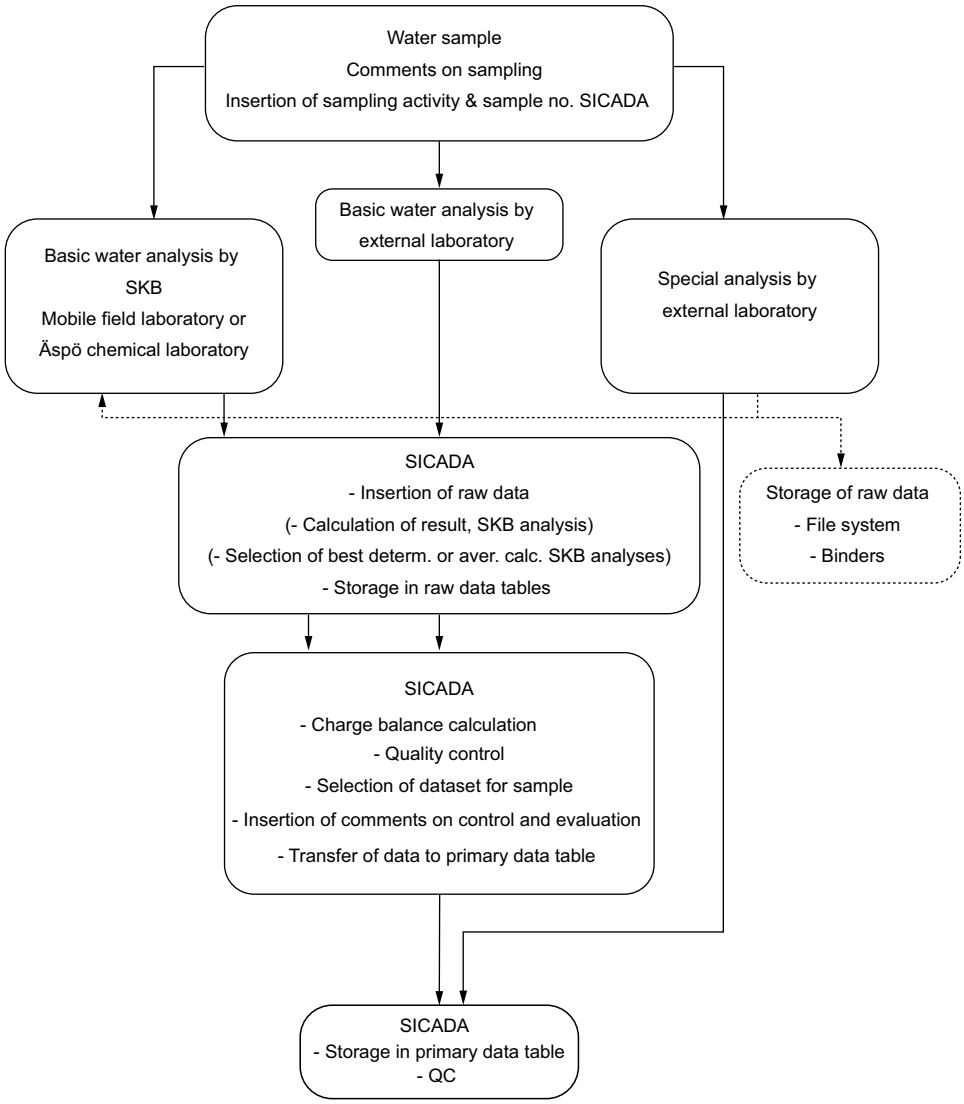

Figure 3-1. *Overview of data management for hydrogeochemical data. This report only handles "Special analysis by external laboratory". (The basic water analyses are reported in a previous report /1/.)*

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 ^{3}H and $\delta^{18}O$ 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 database SICADA and it is the data in this database that will be used for further interpretation (modelling). The data is traceable in SICADA by the Activity Plan number (AP PS 400-06-021).

Table 4-1. Hydrogen and oxygen isotope results for samples collected at the hydrochemical logging in KLX11A.

Length (m)	Sample SKB:no	$\delta^{2}H$ (dev. SMOW)	^{3}H (TU)	$\delta^{18}O$ (dev. SMOW)
35–85	11120	–73.3	5.00	–10.80
135–185	11122	–72.0	5.50	–10.80
235–285	11124	–72.5	5.40	–10.80
335–385	11126	–71.2	6.10	–10.90
435–485	11128	–73.1	5.90	–11.00
535–585	11130	–77.9	3.80	–11.70
635–685	11132	–79.7	5.00	–11.80
735–785	11134	–73.5	4.70	–11.10
835–885	11136	–74.0	4.80	–10.30
935–985	11138	–72.0	6.20	–10.80

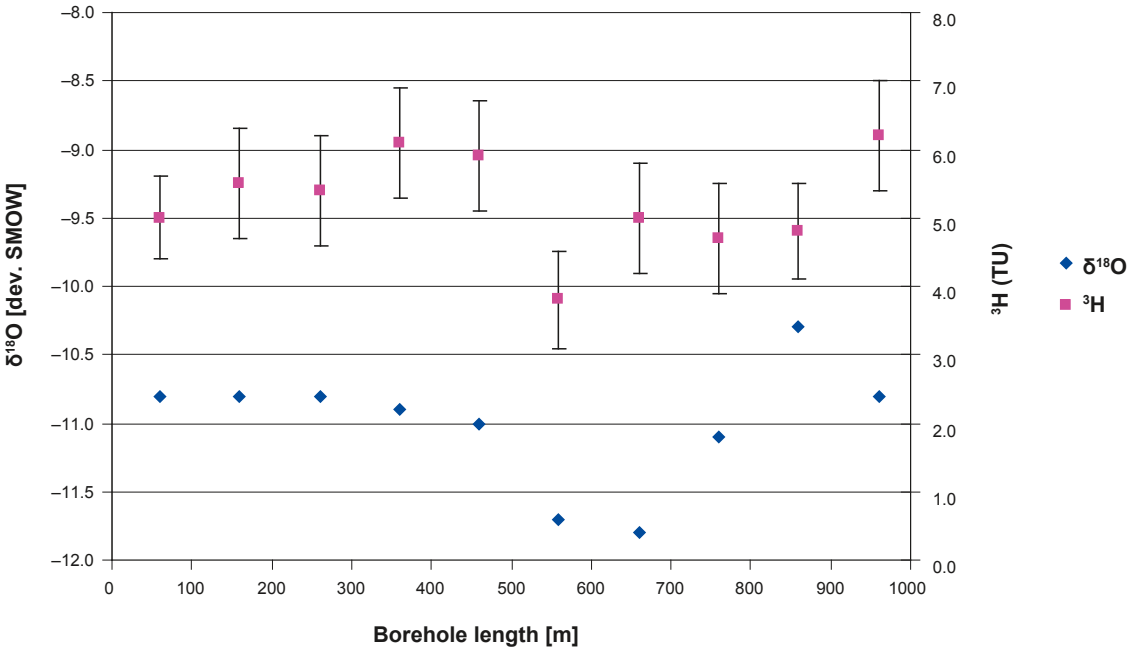

Figure 4-1. *Results from analysis of ^{3}H and $\delta^{18}O$ in water samples obtained from the hydrochemical logging in KLX11A.*

5 References

/1/ **Lindquist A, 2006.** Oskarshamn site investigation. Hydrochemical logging in KLX11A. SKB P-06-180, 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.

Appendix 1

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^2H, $\delta^{18}O$	Plastic	100	No	– –	MS	Not critical (month)
Tritium	^3H (enhanced)	Plastic (dry bottle)	500	No	–	LSC	
Chlorine-37	$\delta^{37}Cl$	Plastic	500	No	–	ICP MS	Not critical (month)
Carbon isotopes	$\delta^{13}C$, pmC (^{14}C)	Glass, dark	100×2	No	–	(A)MS	A few days
Sulphur isotopes	$\delta^{34}S$	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	250×2	Yes	No	–	Storage in freeze container

* Suprapur acid is used for conservation of samples.

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

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^2H	MS	2	‰ SMOW[4]	1‰	–
$\delta^{18}O$	MS	0.1	‰ SMOW[4]	0.2‰	–
^3H	LSC	0.8 or 0.1	TU[5]	0.8 or 0.1	Correct order of size
$\delta^{37}Cl$	ICP MS	0.2‰ (20 mg/L)	‰ SMOC[6]	–	–
$\delta^{13}C$	A (MS)	> 20 mg C	‰ PDB[7]	–	–
pmC (^{14}C)	A (MS)	> 20 mg C	pmC[8]	–	–
$\delta^{34}S$	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	–

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

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 deviation[13] 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 deviation[13] from SMOC (Standard Mean Oceanic Chloride).
7. Per mille deviation[13] from PDB (the standard PeeDee Belemnite).
8. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: $pmC = 100 \times e^{((1950-y-1.03t)/8274)}$ where y = the year of the C-14 measurement and t = C-14 age.
9. Per mille deviation[13] 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: $\delta^y I = 1{,}000 \times (K_{sample} - K_{standard})/K_{standard}$, where K= the isotope ratio and $^yI = ^2H$, ^{18}O, ^{37}Cl, ^{13}C or ^{34}S etc.