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Oskarshamn site investigation

Hydrochemical logging in KLX20A

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

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December 2006

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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 KLX20A. 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 450 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 three months before they were sent to the consulting laboratories for analysis.

Sammanfattning

Hydrokemisk loggning, också kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX20A. 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 450 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 tre 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 400-06-064. 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 KLX20A /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 KLX20A | AP PS 400-06-064 | 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 KLX20A. 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 KLX20A was performed on June 14, 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 KLX20A /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 three months after the sampling occasion i.e. in the beginning of September 2006. The data from the hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 11161–11169.

Due to the lack of sample water in the uppermost tube unit, not all of the bottles could be filled from the uppermost section. Water intended for archive samples in the second unit (50–100 m) were used to fill up sample bottles for analysis of δ²H and δ¹⁸O, from the uppermost section (0–50 m).

Table 3-1. Overview of samples collected at the hydrochemical logging in KLX20A. 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 (δ¹³C and ¹⁴C in a refrigerator) and dashed (purple) cells represent archive samples.

| Sample information | | | Collected sample portions | | | | | | | | | | | Archive Filtered 2x250 mL |
|--------------------|------------|---------|---------------------------|-------------|----------|---------|----------------|------------------------------------|--------------------|----------------------------------|------------------------------------|-------------------|-----------------------------------|---------------------------|
| 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/ ⁸⁷ Sr | δ ³⁴ S | δ ¹³ C ¹⁴ C | |
| 9 | 0-50 | 11161 | Striped | | | Striped | | ω | | ω | ω | | | |
| 8 | 100 | 11162 | | | | | | | | | | Light | | |
| 7 | 150 | 11163 | Striped | | | Striped | | Light | | Light | Light | | | |
| 6 | 200 | 11164 | | | | | | | | | | Light | | Light |
| 5 | 250 | 11165 | Striped | | | Striped | | Light | | Light | Light | | | |
| 4 | 300 | 11166 | | | | | | | | | | Light | | Light |
| 3 | 350 | 11167 | Striped | | | Striped | | Light | | Light | Light | | | |
| 2 | 400 | 11168 | | | | | | | | | | Light | | Light |
| 1 | 450 | 11169 | Striped | | | Striped | | Light | | Light | Light | | | |

ω Filled with sample water from tube unit 8.

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 results. Due to problems with lack of water in the uppermost sampling tube number nine (0–50 m), the bottles intended for archive samples from tube number eight were instead used to fill sample bottles for analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the uppermost tube unit.

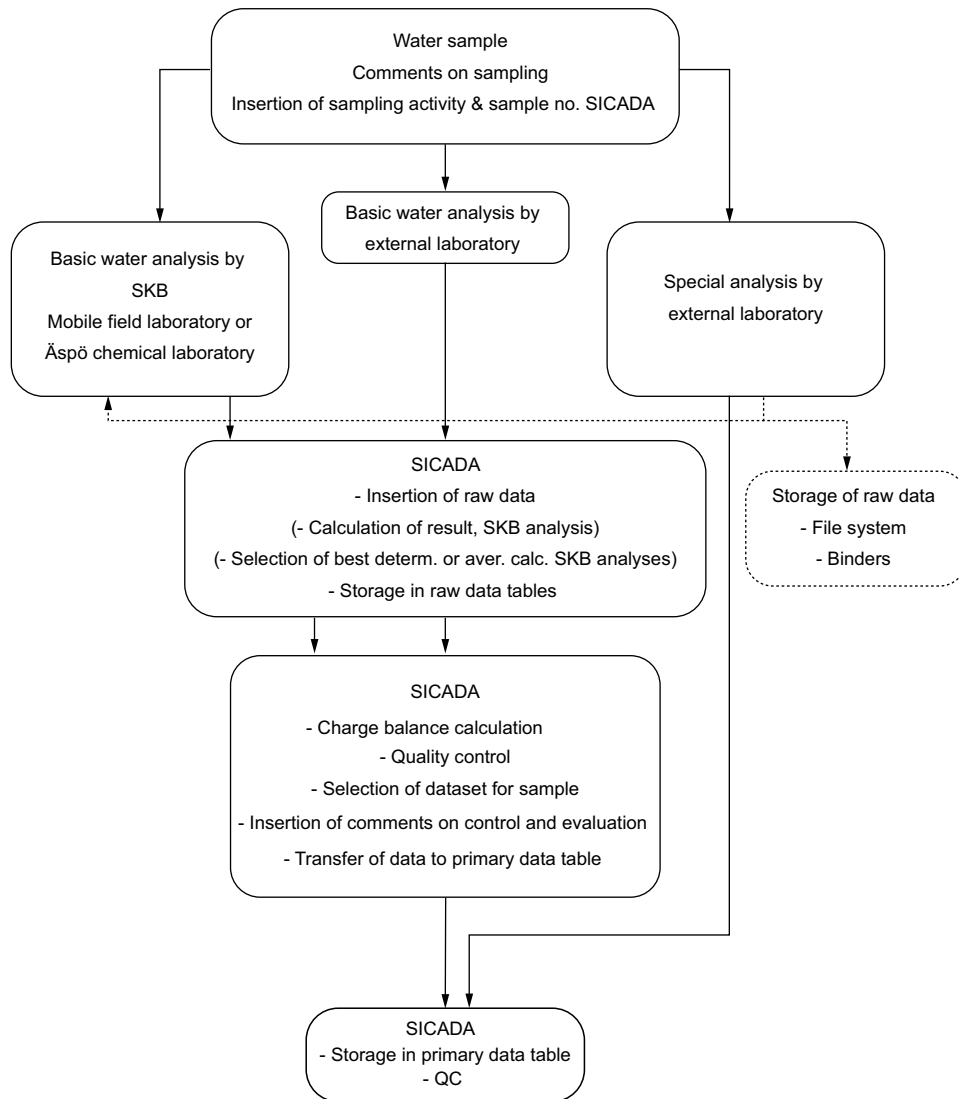


Figure 3-1. Overview of data management for hydrogeochemical data. This report only handles “Special analysis by external laboratory”. (The basic water analyses are reported in a previous report /1/.)

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 400-06-064).

Table 4-1. Hydrogen and oxygen isotope results for samples collected at the hydrochemical logging in KLX20A.

| Sample SKB no | $\delta^2\text{H}$ (dev. SMOW) | ^3H (TU) | $\delta^{18}\text{O}$ (dev. SMOW) |
|---------------|--------------------------------|-------------------|-----------------------------------|
| 11161 | -79.7 | 2.5 | -11.9 |
| 11163 | -89.9 | 1.2 | -13.0 |
| 11165 | -104.3 | < 0.8 | -14.6 |
| 11167 | -102.9 | 1.8 | -14.6 |
| 11169 | -103.8 | < 0.8 | -14.6 |

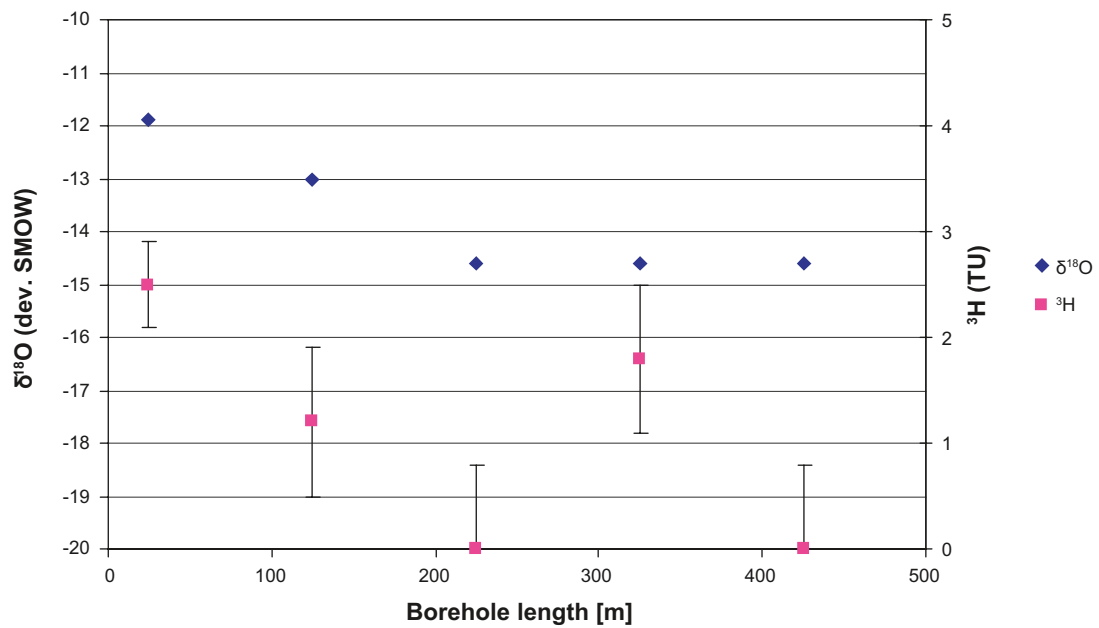


Figure 4-1. Results from analysis of $\delta^{18}\text{O}$ and ^3H in water samples obtained from the hydrochemical logging in KLX20A.

5 References

- /1/ **Nilsson K, 2006.** Oskarshamn site investigation. Hydrochemical logging in KLX20A. SKB P-06-181, 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 | 100 × 2 | 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 | 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: pmC = 100 × 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: δ‰ = 1,000 × (K_{sample} - K_{standard}) / K_{standard}, where K = the isotope ratio and ‰ = ²H, ¹⁸O, ³⁷Cl, ¹³C or ³⁴S etc.