



Öppen

Minutes of meeting

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## Minutes of Gechemistry Meeting 2007-02-20

### SKI-SSI-SKB Meeting of Geochemistry Experts

SKB Office 9th Floor, Tuesday 20 February 2007

#### 1. Participants

Adrian Bath, IntelliSci, UK  
Anders Winberg, Conterra AB  
Ann-Chatrin Nilsson, Geosigma AB  
Bill Wallin, Geockema AB  
Bo Stromberg, SKI  
Eva-Lena Tullborg, Terralogica AB  
Hans-Peter Hermansson, Studsvik AB  
Ignasi Puigdomenech, SKB  
Isabel Hedkvist, Studsvik AB  
Jisong Liu, SSI  
John Smellie, Conterra AB  
Kristina Skagius, Kemakta AB  
Marcus Laaksoharju, Geopoint AB

Attended part of the meeting:

Anders Ström, SKB  
Björn Söderbeck, SKB  
Peter Wikberg, SKB

#### 2. Presentations and discussions

All presentations are attached at the end of this document as reduced images. Original files have been distributed to the meeting participants by e-mail.

## **2.1 Uncertainties in thermodynamic data and key hydrochemical parameters for the SKB sites**

As a prelude to the review of the hydrochemical data for the SKB sites, H.-P. Hermansson presented an assessment of possible uncertainties in Eh and pH data. The main results are: a) uncertainties in pH are estimated to be in the range 0.2 to 0.4 units; b) most measured pH-Eh data are close to the calculated Eh values for the sulphate-sulphide couple; c) the uncertainty in Eh values is estimated to be  $\pm 100$  mV. The presentation was followed by a short discussion on redox reactions, redox kinetics and electrode processes.

## **2.2 Compilation and review of hydrochemistry data**

A. Bath presented his views on the meeting objectives, namely the discussion of the hydrochemical data for the SKB sites. On behalf of SKI, hydrochemical data has been compiled into an Excel table. General aspects of data collection from SKB's database Sicada were discussed. It was confirmed that the procedure to follow is to request the data in "Chemnet format", and that all data collected before the latest data freeze and published as P-reports is made available to the authorities.

## **2.3 Data acquisition & compilation up to 2.1; plans for 2.2 - 2.3**

Following the introduction by A. Bath, M. Laaksoharju presented the working procedures for ChemNet, the group analysing the site hydrochemical data at SKB. The plans and schedules for version 2.2 and 2.3 were summarised. For each data freeze all Sicada data is retrieved and quality controlled from the beginning, and it was proposed that date flags, which have lately been introduced in Sicada, could be used to make this effort less time-consuming.

## **2.4 Quality control and representativity**

J. Smellie discussed the procedures and criteria used for quality control of the data. The selection of Eh values was reviewed. It was stressed by the meeting participants that this procedure must be well documented as it involves "expert judgement". The presentation ended by noting that for Forsmark there are at present 10 representative samples at 400-700 m depth, while for the Laxemar sub-area only 3 samples are available for this depth range.

This presentation was followed by a short discussion on specific Eh data that were brought up to attention by A. Bath:

- a) KFM07A at 925 m: Eh = +9mV. It was noted during the meeting that it is mentioned in section 3.2 of the report P-05-170 that due to a tight time schedule injection tests were allowed to precede the chemical investigation in KFM07A. These injection tests are described in P-05-133, where it is stated that in addition to standard injection tests along the whole borehole, a single packer injection test was performed between 850m and the bottom of the borehole, where later chemical sampling and Eh measurements were performed.
- b) Several disagreements between the Eh data reported in Simpevarp 1.2, Laxemar 1.2 and 2.1. For example, for KAS02, sample 1560, Eh = -150mV which was listed in the POM data compilation in S1.2 as representative is not reported in L2.1. Similarly, for KLX02, sample 3719 with Eh = -125mV (measured 2002) is reported in L1.2 (Table 3-3

in R-06-12), but again, absent in L2.1. Sample 1516 in KLX01 is reported in L2.1 as Group 2 with  $E_h = -265\text{mV}$ , but previously only samples 1502 and 1517 from the same interval in KLX01 were reported in S1.2 with  $E_h = -275$  &  $-280\text{mV}$  respectively, both being marked as doubtful in the POM data; sample 1502 was also used to satisfy suitability in L1.2 (Table 3-3 in R-06-12). It was agreed during the meeting that these data discrepancies would be checked and that an explanation would be reported to the meeting participants.

## **2.5 Tritium in KLX08**

B. Wallin explained that the high tritium contents of the samples collected from borehole KLX08 in May and June 2006 were in fact artefacts. A leakage in the pumping equipment resulted in dilution of the samples by de-ionised water used to drive the hydraulic down-hole pump. This was seen in the sampling flow logging as well as in the chloride contents of the samples. For some reason the de-ionised water, delivered by the Oskarshamn nuclear power plant, was contaminated by tritium. P. Wikberg explained by a drawing how this leaking water could not disperse in the borehole, but was pumped directly to the surface.

## **2.6 Status of reporting**

M. Laaksoharju explained that the 2.1 report for the Laxemar site would be a full model report, while for Forsmark the 2.1 report would be a collection of issues. The issues raised by SR-Can and by the INSITE and SIERG groups will be included in the 2.3 modelling and they were reviewed. It was also mentioned that a special issue of the journal "Applied Geochemistry" will contain 12 papers on the ChemNet methodology.

## **2.7 Final discussion**

The meeting ended by a short review of pending questions (section 2.4 above). It was noted that the meeting had been useful in resolving issues that would not need to be discussed through INSITE questions, which in this way could concentrate in modelling aspects rather than on data inconsistencies.

No date for a future meeting was set, but it was agreed that when the need arises the group would convene again.

## Presentation by H.-P. Hermansson

### **Brief presentation 2007-02-20**

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#### Variability and Uncertainties of Key Hydrochemical Parameters for SKB Sites

Adrian Bath

Hans-Peter Hermansson

SKI report in print

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### **Geochemical Modelling of Redox**

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- Thermodata review
- Redox couples modelling with MEDUSA and PHREEQC
- A couple of conclusions

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## Thermodata review

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- A good and generally accepted database is needed for good redox modelling.
- Coming with PHREEQCI are llnl.dat, wateq4f.dat and phreeqc.dat.
- The llnl.dat is the largest.
- Coming with MEDUSA is HYDRA.
- There are also the PSI/NAGRA databases.

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## Thermodata review

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- log K data for selected, essential complexes and solids were compared.
- The HYDRA database was used as a reference together with the PSI/NAGRA.
- The deviations from HYDRA could be roughly ranked as Minteqv4 (Mv4) > llnl > Minteq > phreeqc database
- As the total number of observations is small the statistics should be viewed with caution.
- In general, there is a large degree of comparability between the databases, as would be expected because many of the thermodata are from the same original sources.

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## Thermodata review

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- There are several causes of differences and those are not elucidated here.
- However, sign errors and the status of a participating species and solid phase are examples of such causes.
- As databases differ it is important to clarify which database has been used when reporting specific results.
- The interpretation of redox equilibria is clearly dependent on identifying the relevant solid phases and being able to characterise them thermodynamically.

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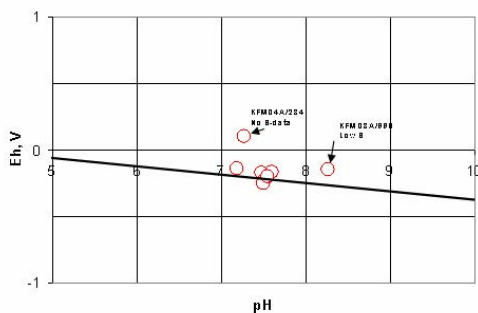
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## pH/Redox modelling

- This case: Modelling of pH/Redox in Forsmark
- MEDUSA was used.
- SKB approved pH and Eh data were used
- The pH data had been adjusted by modelling CO<sub>2</sub> loss using the saturation index method.

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## pH/Redox modelling



Compilation of pH/Eh data points from the selected set of groundwater data.  
The line represents the equilibrium of the couple HS-/SO<sub>4</sub><sup>2-</sup> when pH > 7.

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## MEDUSA pH/Redox modelling

- Most measured pH/E<sub>h</sub> points are located close to the HS-/SO<sub>4</sub><sup>2-</sup> line, also as a function of pH. This would be expected if the couple HS-/SO<sub>4</sub><sup>2-</sup> determines E<sub>h</sub>.
- Some exceptions exist with special reasons like data shortage or very low HS-/SO<sub>4</sub><sup>2-</sup> concentrations.
- It thus seems as if the HS-/SO<sub>4</sub><sup>2-</sup> couple determines E<sub>h</sub> at 'normal' concentrations.
- If extreme data are excluded, the spread in E<sub>h</sub> ~ 150 mV and in pH ~ 0.5 units.
- Thus measured values fall within acceptable limits?
- If extremes are included the spread is larger. Such values, however, seem to be a result of deviating/extreme conditions and not necessarily a result of bad sampling/analysis/data handling.

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### PHREEQCI pH and Redox in Forsmark and Simpevarp

PHREEQCI modelling was used for two purposes:

- To adjust pH to compensate for CO<sub>2</sub> outgassing
- To evaluate the hypothetical E<sub>h</sub> on the basis of assumed control by Fe<sup>3+</sup>/Fe<sup>2+</sup>, Fe(OH)<sub>3</sub>/Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>/HS<sup>-</sup> redox couples.
- The majority of samples turn out to be under-saturated, thus CO<sub>2</sub> outgassing might have occurred.
- Thus rising pH and over-saturation with respect to calcite.
- The resulting 'adjusted' pH values are typically 0.2 to 0.4 pH units lower than the measured values.

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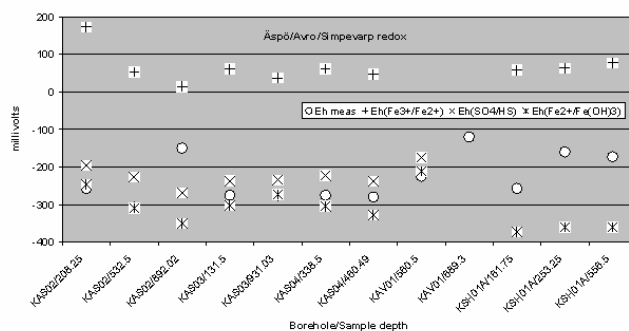
### PHREEQCI pH and Redox in Forsmark and Simpevarp

- Calculating Fe<sup>3+</sup> values as the very small difference between two much bigger generally results in invalid Fe<sup>3+</sup> values.
- There are various accepted reasons why there might be small differences between model and SKB results.
- Differences of ±10 mV in calculated E<sub>h</sub> are not surprising and only illustrate one aspect of uncertainties.
- It is evident in following Figures that E<sub>h</sub> calculated from the couples SO<sub>4</sub><sup>2-</sup>/HS<sup>-</sup> and Fe(OH)<sub>3</sub>/Fe<sup>2+</sup> are rather close to the measured E<sub>h</sub> in most cases.

In contrast, the E<sub>h</sub> calculated from the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple is oxidising, i.e. a positive E<sub>h</sub>, which is confidently the result of erroneous calculated Fe<sup>3+</sup> values.

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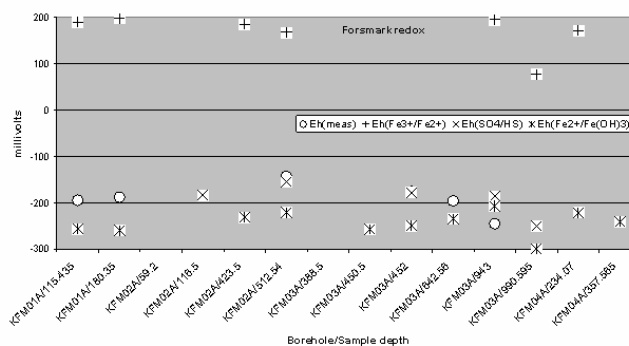
### PHREEQCI pH and Redox in Forsmark and Simpevarp



Compilation of calculated and measured Eh data points from the selected set of hydrochemical data from Äspö, Ävrö and Simpevarp.

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### PHREEQC pH and Redox in Forsmark and Simpevarp



Compilation of calculated and measured Eh data points from the selected set of hydrochemical data from Forsmark.

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### Estimated ranges of uncertainties

- The overall uncertainty in pH is estimated as typically 0.2 to 0.4 pH units.
- The lower range end is represented by the lab pH measurement or the modelled pH (depending on whether lab or Chemmac pH measurement has been adjusted).
- The higher end of the range is represented by the Chemmac (downhole and/or surface) measurement.
- There are typical differences of -30 to -50 mV and +50 mV between measured  $E_h$  and  $E_{hSO_4/HS}$  and  $E_{hFe(OH)_3/Fe^{2+}}$  respectively.
- Therefore  $\pm 100$  mV would be a conservatively pessimistic assumption for the uncertainty in these cases.

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### Estimated ranges of uncertainties

- The  $SO_4^{2-}/HS^-$  and  $Fe(OH)_3/Fe^{2+}$  redox equilibria are pH-dependent.
- Therefore changes in pH are correlated with changes in  $E_h$  at equilibrium.
- For example, a deviation of about -50 mV in  $E_h$  from the expected position in the  $E_h$ -pH diagram would be attributable to an error in pH of about +0.7.
- If such a correction could be justified and applied, the pessimistic range of uncertainty could be decreased.
- However insufficient is known about the sources of uncertainties to take such measures.

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## Presentation by A. Bath

### Compilation and review of hydrochemistry data

Adrian Bath  
Intellisci, for SKI



#### Aims

- Agree a compilation of hydrochemical data from Forsmark & Laxemar with graded reliability, for SR-Can (DF 2.1) and DFs 2.1-2.2;
- Understand the sources of data and the steps used to assess representativeness;
- Establish the basis for SKI's ongoing assessments of SKB's site interpretations in SR-Can and beyond.....

### **SKI's hydrochemistry spreadsheet ..... a user-friendly reference**

- Summary of the main data and supporting information (with comment boxes);
- Compiled from SDM spreadsheets plus P & R reports, also sources of old data;
- Reliability grades according to SKB's assessments;
- Deep groundwater data:
  - Forsmark: 14 representative (+4 with caution);
  - Laxemar: 5 representative (+15 KLX01-02 + 20 KLX03-08);
- Please correct errors! Some data have probably been missed!

### **Specific and general issues**

- Eh and DO data for KFM are OK except for 07A/925 (+9 mV)
- KLX01&02 data re-evaluated after Simp 1.2 and again after Lax 1.2 & 2.1? Also KAS data. Data sources?
- Supporting P reports for KLX03 etc data? Any Chemmac measurements at Laxemar?
- Patchy Fe, HS and U data
- Data accessibility as a general problem
- Interpretation for EBS modelling and glacial cycle scenario

### **Outcomes**

#### **Data spreadsheet**

- Errors corrected, missing data added, supporting information added, criteria understood
- Updated for SDMs 2.2, 2.3.....

#### **Interpretations for SR-Can and beyond**

- Chemical conditions and controlling reactions at repository depth and in EBS
- Palaeohydrogeology model calibration
- Modelling of future scenarios (esp glacial & permafrost)
- Chemistry along radionuclide transport paths

## **Presentations by M. Laaksoharju**

SKI meeting 20:th February 2007

Marcus Laaksoharju



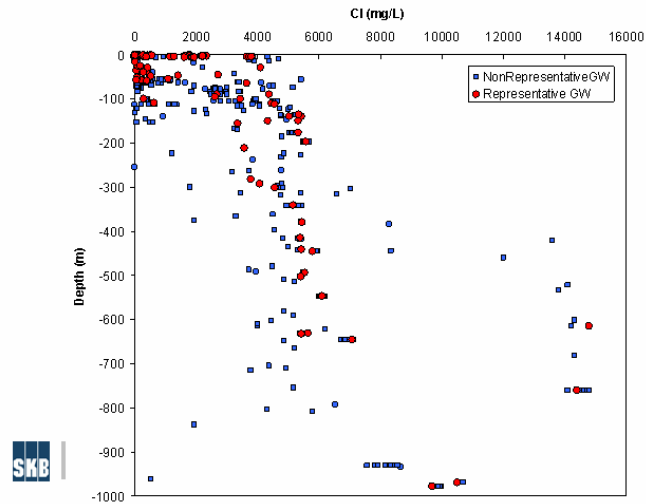
Data acquisition and compilation up to 2.1  
and plans for 2.2 and 2.3 - Introduction

Marcus Laaksoharju, John Smellie and Bill Wallin

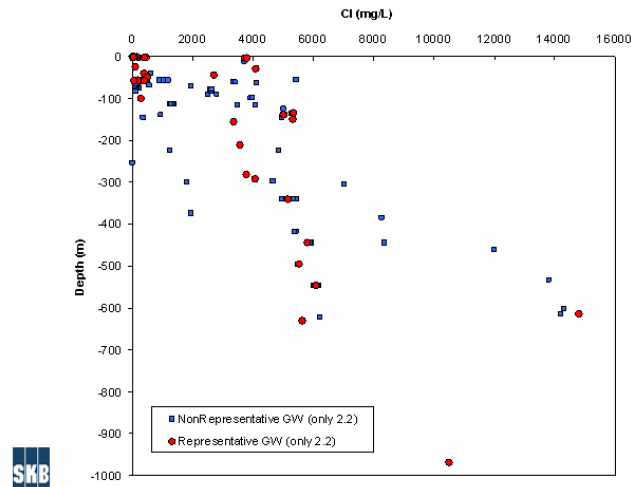




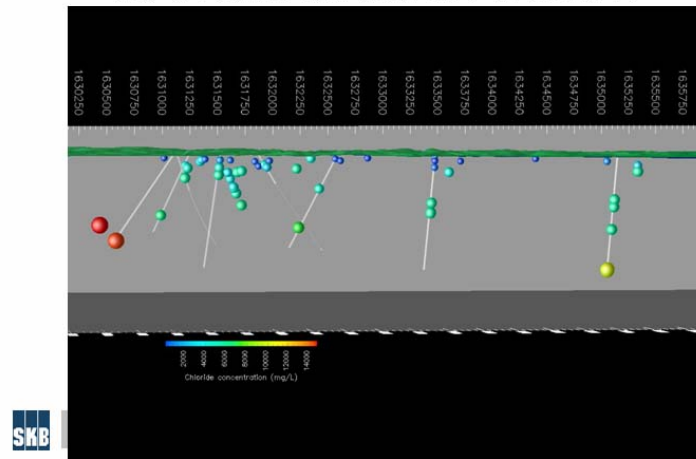
## Cl/depth for all the samples in F2.2

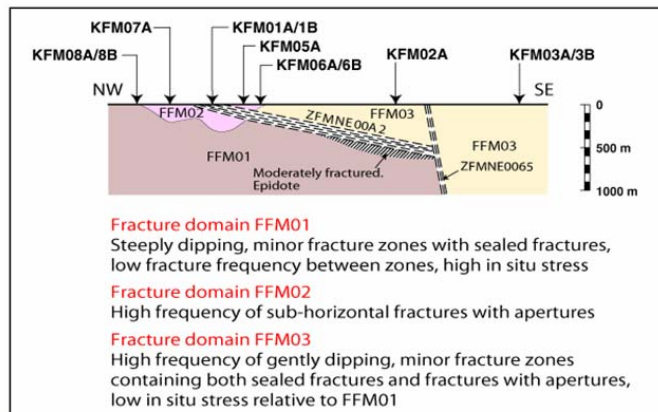


## Cl/depth, new samples in F2.2

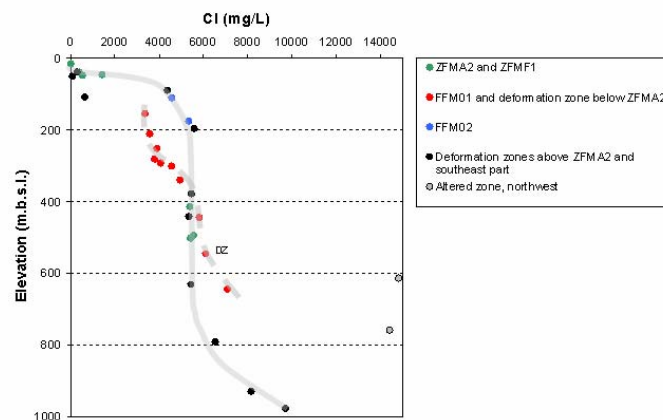


## 3D Cl distribution in Forsmark



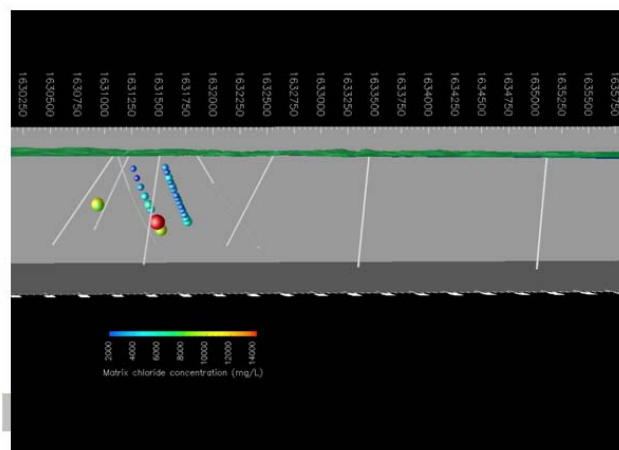


SKB



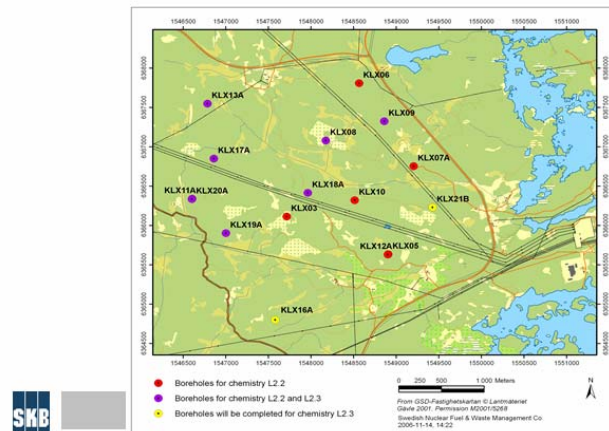
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## Pore water samples in Forsmark



SKB

## Sampled core boreholes for L2.2 and 2.3

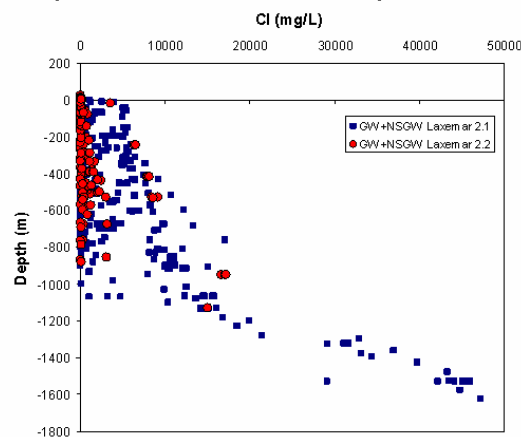


## L2.2 and L2.3 Borehole sections for CCC

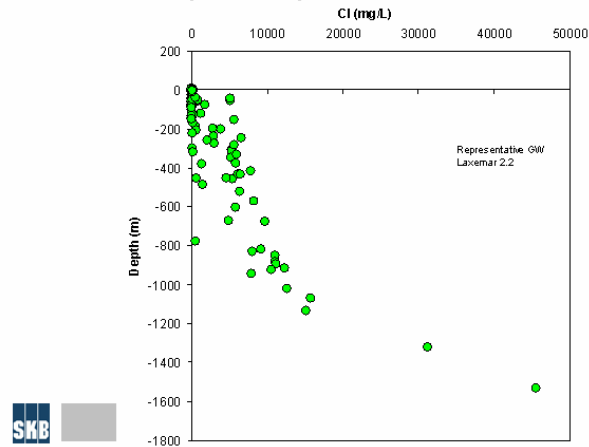
DF 2.2	KLX03	KLX08
	195m, 410m, 740m, 969m	197m, 396m, 476m, 610m
DF 2.3	KLX13	KLX17
	432m, 499m	313m, 416m, 642m



## Cl/depth for all the samples in L2.2



### Cl/Depth representative samples



### Reporting, checking and compilation: status of 2.1 and plans for 2.2 and 2.3

Marcus Laaksoharju



### Status for the reports 2.1, 2.2 and 2.3

- **L2.1:** Hydrogeochemical evaluation, Preliminary site description, Laxemar subarea - version 2.1 (SKB R-06-70), printed in February 2007
- **F2.1:** Hydrogeochemical evaluation of the Forsmark site, modelling stage 2.1 - issue report (SKB R-06-69), Draft ready, internal review ongoing to be printed in March 2007
- **F2.3:** Hydrogeochemical evaluation, Preliminary site description, Forsmark - version 2.3 (SKB R-07-XX), printed in November 2007
- **L2.3:** Hydrogeochemical evaluation, Preliminary site description, Laxemar subarea - version 2.3 (SKB R-08-XX), printed in June 2008





## Issues in the F2.1 report

### Explorative analysis issues

- Groundwater origin and evolution (App#1)
- Interaction of surface/deep groundwater systems (App#1; App#5)
- Redox front considerations (App#1, App#2)
- High Uranium content (App#1, App#2, App#3, App#6, App#7)
- High manganese values - manganese reducing bacteria (App#2, App#3)
- Microbes (App#2)
- Gases (App#2)
- Colloids (App#2)



## Issues in the F2.1 report cont.

### Mathematical modelling issues

- Redox conditions (App#2, App#3)
- Uncertainties analysis of mixing proportions and mass balance deviations (App#3)
- Integration of hydrochemical data with mineralogical and microbial data (App#3)
- Revision of conceptual model the role of monosulphides (App#3)
- Investigation of the recharge end-member and its effect on the mixing models and the site understanding and the proper use of tritium (App#4)
- Test of models including all elements and isotopes versus models with conservative constituents such as D, O18, Tr (App#4)
- Comparison of different models and the number of observations they can describe (App#4)
- Evaluation of suitable data from SICADA and DMS to perform Drilling Impact Study (DIS) calculations (App#4)
- Evaluation of the Electric Conductivity for K boreholes and its use for understanding/validate the GW spatial variability (App#4).

### Conceptual modelling issues

- Conceptual modelling in 2D and 3D (App#1, App#5)
- Better integration with hydrogeology (App#5).



## Issues for 2.2 + 2.3 modelling

### Feedback issues from SR-Can

- "A-1) Modelling of the existence of a relatively shallow "process zone" capable of buffering the meteoric water with respect to redox and cation exchange"
- "A-2) At present repository conditions redox and alkalinity buffering capacity including discussion on the effects from potassium, sulphide and iron(II) on buffer and the canister"
- "A-3) Indications of penetration depths of rain water and glacial water with oxygen intrusion in the bedrock, modelling and description based on observations"
- A-4) High U content in Forsmark

### INSITE/SIERG issues

"B) Alternative models, uncertainties and data bias (CRI-1, see INSITE document)."

"B-1) Descriptions of models based on reactions, alternative models based on reactions only"

"B-2) Alternative end-member selection, and uncertainties in selection of end-member groundwater chemistries, add/remove meteoric water show the effect at repository depth on Cl, pH and Eh"

B-3) Analytical uncertainties and how these affect the modelling results

"B-4) Introduction of bias into the interpretation from drilling, sampling, analyses, alternative end-members, adding removing meteoric water (show e.g. an interpolation of Cl data or coupled modelling affected by these uncertainties)"

B-5) Reactive transport modelling CORE 2D and PHAST

"B-6) Improved DIS (Drilling Impact Studies) characterisation of boreholes, correct groundwater compositions for drill water contamination (DIS)"



## Issues for 2.2 + 2.3 modelling cont.

### "C) Confirming models of the site-scale groundwater flow system (CRI-7, see INSITE document)"

- "C-1) Hydrogeochemical signatures of deep discharge to the shallow hydrological system"
- C-2) Hydrochemistry in large transmissive fractures versus low transmissive
- C-3) Mixing processes during sampling of water bodies

### "D) Groundwater compositions at repository depth (CRI-8, see INSITE document)"

- "D-1) 3D variability of redox, pH and other SKB suitability criteria and buffer capacity at repository depth under current conditions (use SR-Can results)"



## Issues for 2.2 + 2.3 modelling cont.

### "E) Spatial variability of hydrochemical data (CRI-9, see INSITE document)"

- "E-1) a) at repository rock volumes, permeable deformation zones, fractures and rock matrix, b) at site boundaries, c) at shallow depths to detect recharge and discharge pathways, and d) in potential radionuclide pathways"

- "E-2) Dilution/concentration of repository groundwater to establish the level of variability allowed before SKB suitability criteria are affected"

### "F) Geochemical and isotopic data for palaeohydrogeology and groundwater evolution (CRI-10, see INSITE document)"

- "F-1) Indications of glacial versus Littorina sea in the bedrock, establish the Littorina (perhaps also the Brine in Forsmark) end-member composition"

- "F-2) High concentrations of helium in GW's suggests that the waters have been in contact with uranium and/or thorium bearing minerals for a (very) long time. To be used for residence time indication."

- "F-3) Geochemical and isotopic data for groundwater and minerals are used to interpret the groundwater evolution over time"

### "G) Mineralogical and petrographical characterisation of fracture and matrix minerals (CRI-11, see INSITE document)"

- "G-1) Modelling of redox and pH buffering and water-rock reactions at repository depth"



## Issues for 2.2 + 2.3 modelling cont.

### "H) Characterisation of colloidal, organic, microbial and gaseous species in groundwaters (CRI-12, see INSITE document)"

- "H-1) Describe the limitations of microbial reactions and include the condition when there are sufficient reactants (e.g. sulphate and methane)"

- H-2) Better characterisation and modelling of colloids and organics

- "H-3) The gases in deep groundwater such as CH<sub>4</sub>, He and H<sub>2</sub> and how they can be used to indicate origin and transport"

### "I) Data from pre-existing boreholes in and near the sites (CRI-14, see INSITE document)."

- "I-1) Can groundwater data from Äspö-HRL, old boreholes in Laxemar and CLAB be used more efficiently and appropriately when describing Laxemar?"

- "I-2) Can groundwater data from Finnsjön and SFR be used more efficiently and appropriately when describing Forsmark?"

### "J) Geochemical analogues of radionuclide (CRI-15, see INSITE document)."

- "J-1) Trace constituents used as analogues of radionuclide (e.g. Cs, trace metals, rare earth elements, U and some isotopes such as U/Th/Ra/Rn)"



The ChemNet data used for 2.1, 2.2 and 2.3  
is stored in the SKB model database  
SIMON which is located on the Project  
Place



ChemNet is preparing a special issue (12  
papers) for Applied Geochemistry. This  
issue will focus on the hydrogeochemical  
methodology used in site investigation. Will  
be printed in early 2008



### Authors for the special issue in AG

- Auqué, L., Gimeno, M.J., Gómez, J. and Nilsson A-C. (2007) Potentiometrically Measured Eh in Groundwaters from the Scandinavian Shield (Paper#4, this issue).
- Drake, H., Tullborg, E-L and Annersten, H. (2007) Red-Staining of the Wall Rock and Its Influence on the Reducing Capacity around Water Conducting Fractures (Paper#7a, this issue).
- Gómez, J.B., Auqué, L.F. and Gimeno, M.J. (2007) Sensitivity and Uncertainty Analysis of Mixing and Mass Balance Calculations with Standard and PCA-Based Geochemical Codes. (Paper#9, this issue).
- Hallbeck, L. and Pedersen, K. (2007) Conceptual Modelling of Microorganisms as Posing Agents of the Oxidation-Reduction Potential in Groundwater over a Depth Range Suggested for a Geological Repository for Nuclear Waste (Paper#3, this issue).
- Hunter, F.M.I., Hartley, L.J., Hoch, A., Jackson, C.P., McCarthy, R., Marsic, N. and Gylling, B. (2007) Calibration of Regional Palaeohydrology and Sensitivity Analysis Using Hydrochemistry Data in Site Investigations (Paper#11, this issue).
- Laaksoharju, M., Gascoyne, M. and Gurban, I. (2007) Understanding Groundwater Chemistry Using Mixing Models (Paper#8, this issue).
- Laaksoharju, M., Pitkanen, P., Follin, S. and Koskinen, L. (2007) Hydrogeochemical-Hydrogeological Modelling in Fractured Crystalline Rock – Principles Used and Examples of Experiences Made in the Swedish and Finnish Programmes for Nuclear Waste Disposal (Paper#12, this issue).
- Laaksoharju, M., Smellie, J., Tullborg, E-L, Gimeno, M., Molinero, J., Gurban, I. and Hallbeck, L. (2007) Hydrogeochemical Evaluation and Modelling Performed within the Site Investigation Programme (Paper#2, this issue).
- Molinero, J., Raposo, J.R., Galindez, J.M., Arcos, D. and Guimerá, J. (2007) Coupled Hydrogeological and Reactive Transport Modelling of the Simpevarp Area (Sweden) (Paper#10, this issue).
- Rönneback, P., Åström, M. and Gustafsson, J-P. (2007) Comparison of the Behaviour of Rare Earth Elements in Surface Waters, Overburden Groundwaters and Bedrock Groundwaters in two Granitoidic Settings, Eastern Sweden (Paper#6, this issue).
- Ström, A., Andersson, J., Skagius, K., and Winberg A. (2007) Site Descriptive Modelling During Characterization for a Geological Repository for Nuclear Waste in Sweden (Paper#1, this issue).
- Tullborg, E-L, Drake, H. and Sandström, B. (2007) Palaeohydrogeology: A Methodology Based on Fracture Mineral Studies (Paper#7, this issue).
- Waber, H.N. and Smellie, J.A.T. (2007) Characterisation of Pore Water in Crystalline Rocks (Paper#5, this issue).



## Presentation by J. Smellie

SKI meeting 20:th february 2007

Quality control evaluation of L.2.2 and F.2.2  
hydrochemical data

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### Cored Borehole Quality Control

**Orange** = Representative or suitable.

The final selection of data which best represents the sampled borehole section is based on identifying as near as possible:

- charge balance of  $\pm 5\%$ ;
- close to 0-1% drilling water;
- complete set of major ion data;
- complete set of isotope data (particularly tritium,  $^{18}\text{O}$  and deuterium plus carbon isotopes when available).

(Result of detailed understanding of the borehole site).



## Cored Borehole Quality Control

**Green** = Less representative or of limited suitability and should be used with caution:

- charge balance of  $\pm 5\%$ ;
- close to 1-5% drilling water;
- fairly complete major ion data (e.g. missing Br, Fe data;)
- isotope data (particularly tritium,  $^{18}\text{O}$  and deuterium);
- lack of time-series data;
- long sections sampled (e.g. during drilling)



## Percussion Borehole Quality Control

**Orange:** In addition to the cored borehole criteria:

- borehole sections < 50 m long where the groundwater data can be related approximately (or precisely – to a few metres) to a more constrained bedrock level, i.e. dominant water-conducting fracture using flow logging data (not available for all boreholes).



## Percussion Borehole Quality Control

**Green:**

- total borehole lengths can vary from 100 m to approx. 250 m depth;
- these boreholes mostly represent homogenised mixed groundwaters from different sources;
- important to know the chemistry of this groundwater mixture, e.g. when used as a source of flushing water during drilling of the deep cored boreholes.



## Soil Pipe Quality Assurance Control

### Green:

- satisfactory charge balance ( $\pm 5\%$ );
- good coverage of major elements  $\pm$  trace elements;
- tritium,  $^{18}\text{O}$  and deuterium;
- many samples have more complete data, e.g.  $^{14}\text{C}$  and REEs;
- samples with more complete analytical data could have been highlighted in orange, but because of the complex nature of this near-surface environment, all samples have been highlighted in green until greater understanding suggest otherwise.



## Quality Control - Colour Code 'White'

White (uncoloured) samples: These represent various conditions:

- a) When one orange or green sample is chosen from a borehole section with good time-series information, the remaining samples are left unmarked, i.e. white, even though some or all of them may be equally as representative as the one chosen. On the other hand, if a representative sample has been selected when the groundwater has stabilised in composition following an initial increase (or decrease) in salinity, these initial samples are certainly not representative, but all of the later stabilised samples may be. Great care has to be taken when using 'White' sample data.
- b) No charge balance because of inadequate data, or no isotopes, makes it impossible to judge.
- c) Tube samples or long sections result in mixing problems, i.e. problem to ascertain the depth of origin etc.
- d) Sections in general which contain considerable excess drilling fluid ( $> 10\%$ ) or unacceptable charge balance values.



## Quality Control - Colour Code 'Grey'

### Grey samples:

- samples with little or no data - often restricted to electrical conductivity  $\pm$  pH  $\pm$  drilling water;
- many of this type are of an exploratory nature, i.e. mostly taken to see if there is adequate water volume and to check strategic indicators such as drilling water content, salinity (EI conductivity)  $\pm$  pH  $\pm$  major ions ( $\text{Cl}$ ,  $\text{Br}$ ,  $\text{SO}_4$ ,  $\text{HCO}_3$ );
- future updating of the database (and/or resampling) may allocate some of these sections to an 'orange' or 'green' category etc.



## Quality Control - Additional Support Information

- Communication with field personnel and the responsible site chemist is very important to resolve field difficulties in sampling, contamination problems, and laboratory problems etc.
- Referring to borehole data recorded in SICADA, but with no published information or results, it is essential to obtain quickly: a) Differential Flow Logs, b) Boremap Protocols, c) results from pump-tests, and d) single-hole geological information.
- Use is made of all published reports/papers/articles, together with personal contact with involved field and laboratory personnel. This involves also KAV and KOV data from Oskarshamn, old data from Finnsjön and SFR, and also the old KBS-3 sites.



## Quality Control - Groundwater Redox Measurements

- With the onset of downhole measurements using the Chemmac system, a more rigorous methodology to select the most representative Eh data has evolved.
- The first stage was to re-analyse all the available continuous logging information (derived from the SICADA database) for the Laxemar and Forsmark sites and also for some other Swedish sites.
- The objective was to select a high-quality Eh (pH, temperature, etc) values to create a database as complete as possible to be used for geochemical modelling.
- After revision, the selected and rejected values were compared with the data published in the original reports. With only some exceptions, the degree of concordance generally was very good.



## Quality Control - Groundwater Redox Measurements

### Methodology

- *The selection of an Eh value for a borehole section must be based on a very careful analysis of the results obtained with the different electrodes at depth and at the surface, namely the logging time, the pH, the conductivity, and the dissolved oxygen values.*
- *The basic requirement is that the measured potential corresponds to the equilibrium potential and this fact can only be demonstrated when the different electrodes give coincident results.*
- *Ideally, the Eh values selected as representative should only be those obtained simultaneously and within a small Eh range ( $\pm 50$  mV) by the six electrodes over a long period of time. However this criterion seems excessively restrictive. There can be undesirable effects selectively affecting one electrode or the other, or technical problems affecting one of the two measurement cells (downhole or at the surface).*



## Quality Control – Groundwater Redox Measurements

*Taking into account all these issues, the following selection criteria were applied:*

- logs longer than 3 days (usually longer than a week);
- logs with stable and coincident readings (in a range smaller than  $\pm 50$  mV) by several electrodes in the long term; and
- logs with simultaneous and stabilised pH logging (in order to minimise the uncertainty associated with the pH).



## Quality Control – Groundwater Redox Measurements

*The sets of Eh logs that fulfilled these criteria were then checked for the quality of the redox values. Two groups of representative Eh values were defined depending on the number of electrodes giving coincident readings:*

- Group 1 Eh values: stable and coincident readings in, at least, three electrodes, two of them at depth. *More trustworthy values.*
- Group 2 Eh values: stable and coincident readings in two electrodes, at depth or at the surface. *Less reliable values.*



Chemmac measurements in KFM06A, section 353.5–360.6 m

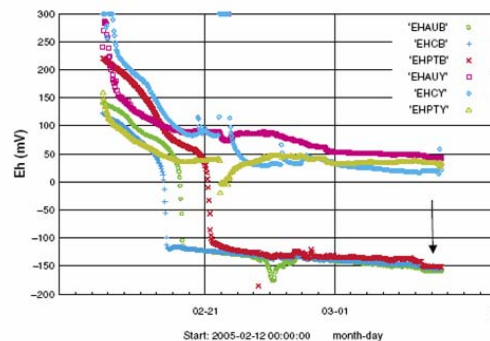


Figure A6-1. Redox potential measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCU). The arrow shows the chosen representative Eh values for the borehole section.





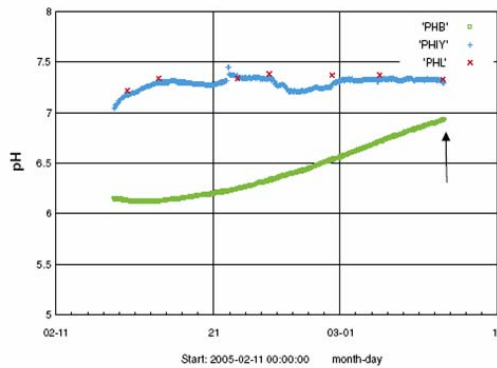


Figure A6-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIY) and two glass electrodes at the surface (PHIY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.



### Quality Control - Factors considered when borehole samples are taken at different times

- a) Knowledge of borehole fracture geometry and borehole flow character is essential.
- b) Adequate time-series data is essential at all sampling occasions.
- c) The initial hydrochemical conditions are the most important to establish following drilling since these will represent the reference data to compare later data with. For example, depending on the hydrodynamics of the borehole and its surroundings, later sampling may show a decrease in salinity with time, which means that the earlier samples taken could be more representative (i.e. likely to be expected at Laxemar), whilst in other areas there may be an increase in salinity (i.e. likely at Forsmark and Simpevarp). If these initial conditions are missed, as is the case in several of the Laxemar boreholes (especially 0-800 m in KLX02), then, based on knowledge of the hydrogeological system at Laxemar, an increase in less saline water with time, represents an increase in hydrochemical uncertainty for that sample.



### Quality Control - Factors considered when borehole samples are taken at different times

- d) It is also obvious but important that the long-term monitoring installations should correspond accurately with those levels initially sampled and characterised. It is easy to miss or only partially include an important fracture or fracture zone during installation (e.g. KLX03: compare sampled level at 735.50-748.03 m with the monitored section at 729.00-751.00 m). In other cases the monitoring positions have sometimes represented borehole sections which were not initially sampled (e.g. KLX04: 870-897 m).
- e) Analytical methods and precision need to be compared. For example, old (pre-2002) tritium data have a detection limit of 4.2 TU and 8TU, compared with present levels of precision at 0.8 TU.
- f) Radioactive decay of tritium must be taken into account.
- g) Improved sampling methods must also be taken into consideration.



## Quality Control - Number of Representative Samples (Laxemar 2.2 dataset)

### Simpevarp Area

Site	Orange	Green	Total	Rep. Depth (400-700m)
Äspö	0	26	26	5
Ävrö	0	6	6	1
Laxemar	2	40	42	3
Simpevarp	2	7	9	3
<b>TOTAL</b>	<b>4</b>	<b>79</b>	<b>83</b>	<b>12</b>



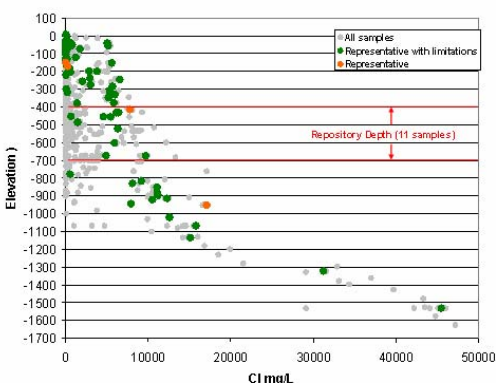
## Quality Control - Number of Representative Samples (Forsmark 2.2 dataset)

### Forsmark Area

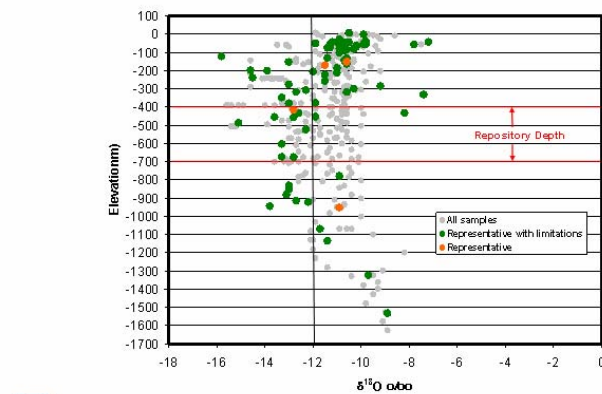
	Orange	Green	Total	Rep. Depth (400-700 m)
<b>TOTAL</b>	<b>12</b>	<b>41</b>	<b>53</b>	<b>10</b>



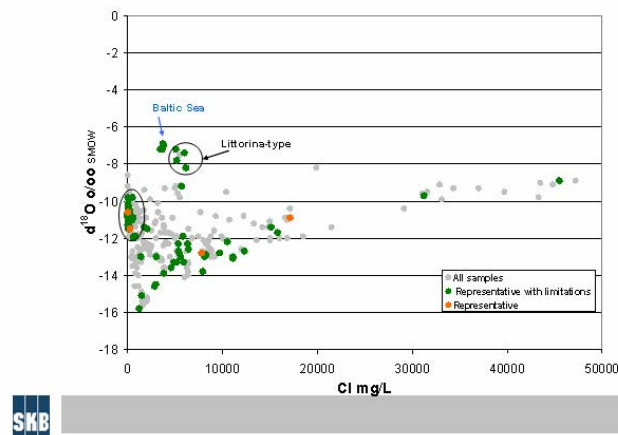
## Quality Control - Simpevarp Area



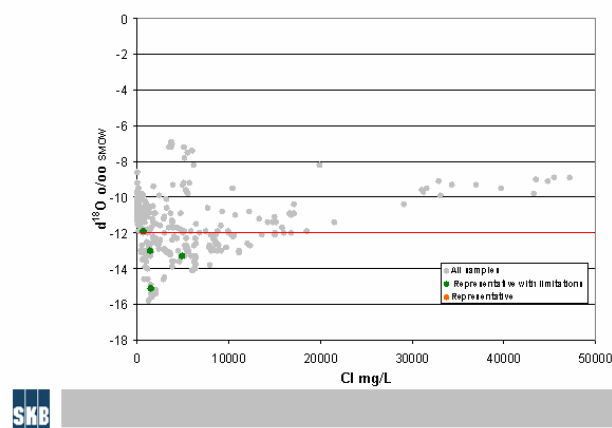
### Quality Control - Simpevarp Area



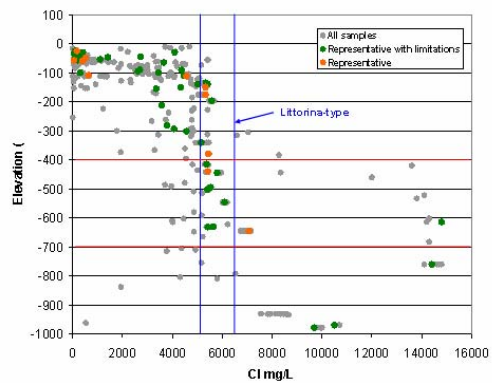
### Quality Control - Simpevarp Area



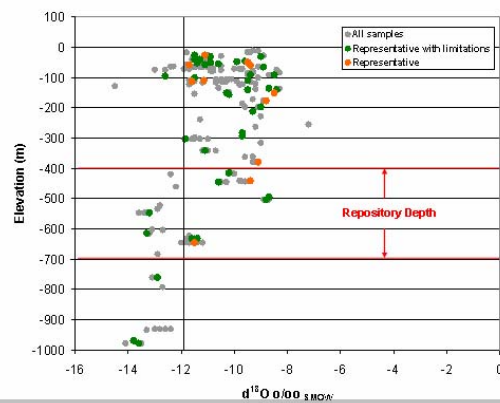
### Quality Control - Repository Depth Laxemar Site



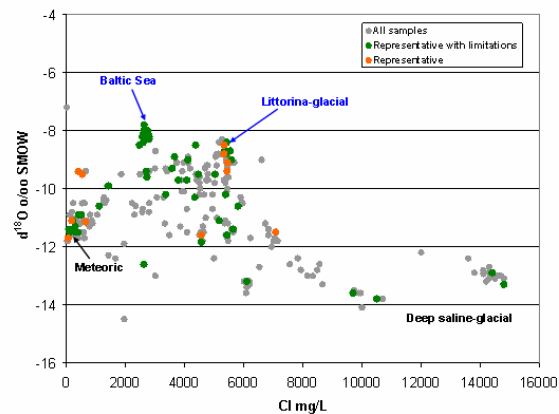
## Quality Control - Forsmark Area

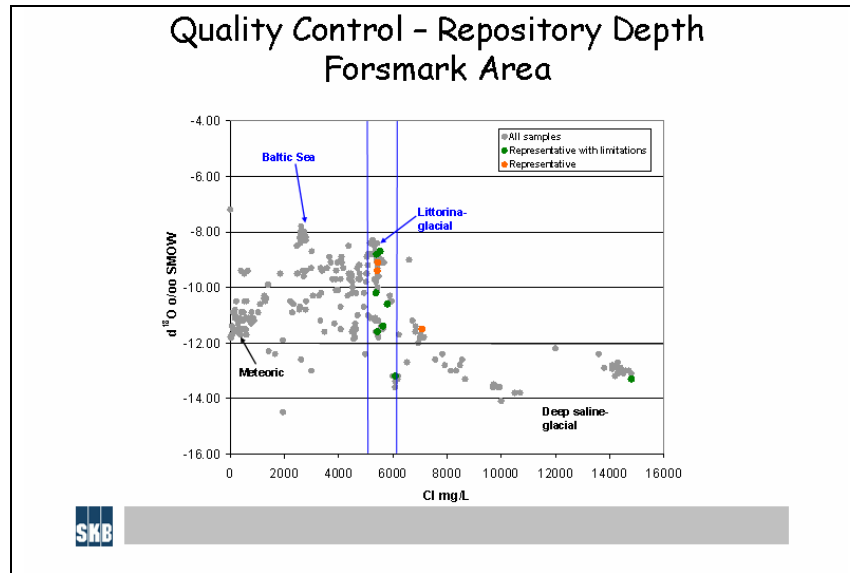


## Quality Control - Forsmark Area



## Quality Control - Forsmark Area





## Presentation by B. Wallin

### Tritium ( $^3\text{H}$ ) in KLX08 and its consequences

Bill Wallin



### Background on sampling in KLX08A at 476 m

- Drilling completed in 2005-06-13
- Pumping for the chemical sampling started in April (2006-04-12)
- Pumping stop for one week – cleaning
- Pumping continues (2006-04-19) – Minor stops
- Pumping and sampling during the period 2006-05-22 to 2006-06-26 (a few pump stops)



### Analytical results by mid-November

Section		SKB nr	Date	Waterloo Laboratory	Class	$^3\text{H}$ (TU)
476.00	485.62	10959	2006-05-22	2006-05-30	4	95.2
476.00	485.62	11087	2006-05-24	2006-05-30	5	756.6
476.00	485.62	11094	2006-05-30	2006-05-30	5	2.9
476.00	485.62	11088	2006-06-01	2006-06-07	4	2.2
476.00	485.62	11115	2006-06-07	2006-06-07	5	111.4
476.00	485.62	11118	2006-06-09	2006-06-12	4	52.3
476.00	485.62	11143	2006-06-12	2006-06-12	5	38.9
476.00	485.62	11158	2006-06-15	2006-06-26	4	2.2
476.00	485.62	11159	2006-06-19	2006-06-19	5	2.1
476.00	485.62	11183	2006-06-26	2006-06-26	5	2.1



### Archive sample sent to laboratory for a second measurement

Results: (Lab report dated 2006-12-10)

High value confirmed

710 TU (sample at 476 m)



### Third analyses made by a new laboratory

- University of Krakow contacted for 3<sup>rd</sup> analyses (2006-12-22)
- Last archive sample from high tritium reading sent on 2006-12-27
- Preliminary results 2007-01-04 (High readings, counting continue)
- Final result 770  $\pm$ 50 TU (2007-01-08)



## Additional analyses with distillation

- Additional analyses of  $^3\text{H}$  by distillation is made at University of Krakow to ensure that tritium is incorporated in the water (2007-01-17)
- Result:  $756 \text{ TU} \pm 20$  - high precision

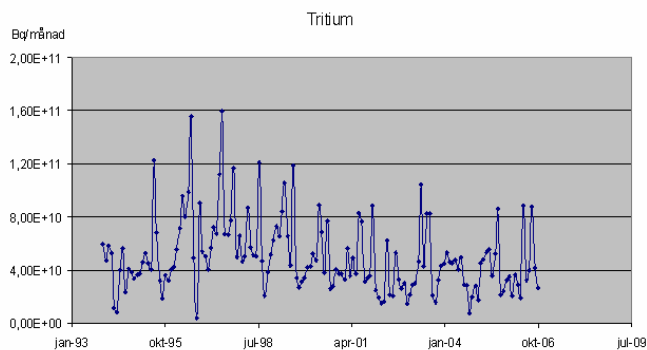


## Possible sources of tritium

- Release of tritium in air/water from OKG
- True Block scale experiments at Äspö
- Bomb test tritium
- Contamination of equipment/sampling
- Contamination from storage of samples



## Possible sources - OKG



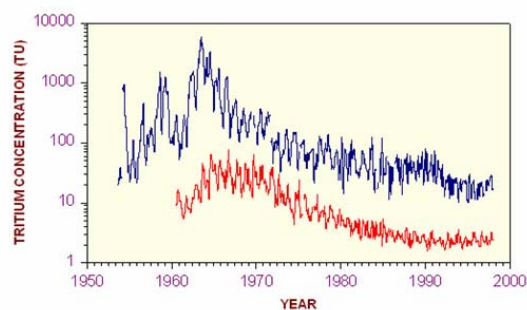


## Possible sources – True Block Scale experiments at Äspö

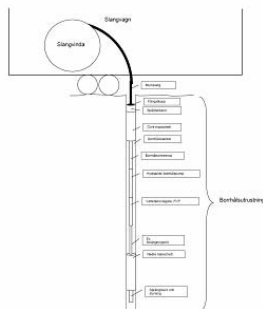
- Injected amount:  $240 \times 10^6$  Bq
- $C_{\max}$  injection in drillhole:  $20 \times 10^6$  Bq / kg ( $170 \times 10^6$  TU)
- After experiment:  $< 37$  Bq/kg ( $< 310$  TU)
- Max recovered during experiment 2400 Bq/kg (20 000 TU)



### Bomb test tritium



## Contamination of the equipment/sampling



## Collection of background data - SICADA

- Drilling information
- Sampling routines
- Sample equipment
- Sample handling
- Sample storage
- Sample shipment
- Laboratory routines
- Etc.



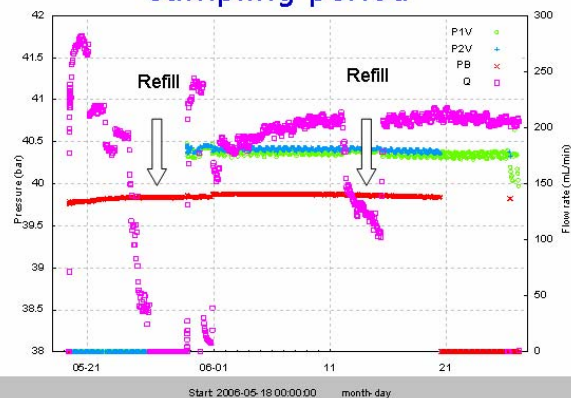
## Task Force Meeting (2007-01-31)

Output from meeting: Focus on sampling and sample treatment as a possible contaminant

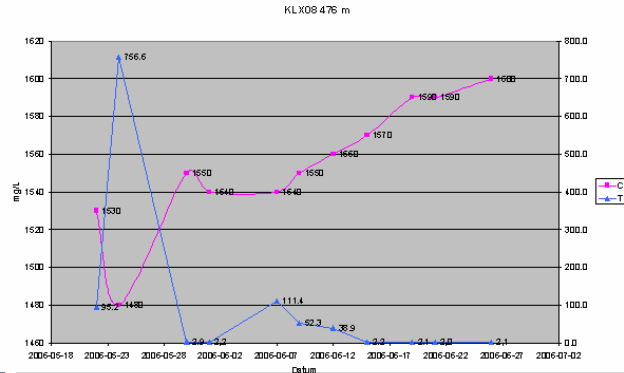
- Equipment problems/maintenance
- Sampling procedures
- Sample storage
- Addressing questions to people involved in the sampling



## Pressure/flow rate in KLX08A during sampling period



## Chloride versus $^3\text{H}$ during sampling – dilution?



SKB

## Changes of the equipment

- New pump installed in sample equipment
- Pump host de-ionized water collected at from OKG in May (2006-05-18)
- Leakage of the washer

SKB

## Sampling equipment



← Borehole pump



Washer

SKB

## Confirmed high $^3\text{H}$ in water from OKG

- Analyses of the de-ionized water in the so called "hydrofor" in sample equipment hold 3100 TU - Geosigma
- OKG report  $^3\text{H}$  concentration of 450 Bq/l (3800 TU) in the 733-water at pumpstation CSV



## Conclusion - Leakage of pump in sample equipment

Mixing of sample water and pump water in the sampling equipment during sampling



## Impact and consequences

- This is the first observed problem/leakage of the pump in the sampling equipment.
- No other high reading have been reported from earlier sampling with the equipment at Laxemar.
- The dilution of the samples is between 0,6 - 3,8 % for all samples except for the sample with high tritium reading (750 TU) which has a dilution of 8 % based on Cl concentration. No de-ionized water flow into the borhole section.
- Tritium free samples are available from this depth
- Chemical parameters from 476 m level have been checked and will be used in the modelling

