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Research

Variability and Uncertainties of Key Hydrochemical Parameters for SKB Sites

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SKI-perspective

Background

An important part of the site investigations conducted by the Swedish Nuclear Fuel and Waste Management Company (SKB) is the characterisation of groundwater chemical conditions in the deep bedrock environment where a final repository for spent nuclear fuel is planned to be located. This work is currently in its final stages at the two candidate sites, Forsmark and Laxemar, and should be completed by the summer of 2007. It is essential that the information which is gathered is of high quality and representative of conditions in the environment of consideration. Parameters of particular interest are those that are related to SKB´s suitability criteria such as E_h, pH and salinity, but a range of other geochemical parameters are also needed to establish a sufficient site understanding. The process of extracting the required information has been more problematic than expected during the early stages of the site investigations, and it is therefore of key interest to evaluate this part of the site investigation programme in more detail.

Purpose of the project

This project includes an assessment of geochemical information (available at the time) related to the E_h and pH in the deep bedrock environment. The purpose is to evaluate the uncertainties in these parameters and the level of understanding of the fundamental processes that control them.

Results

The result of this study is an identification and evaluation of sources that contribute to uncertainty and spatial variability in key geochemical parameters. Uncertainty limits are discussed based on geochemical modelling of redox controlling chemical reactions.

Future work

There is a need to follow up SKB’s groundwater sampling and characterisation after the completion of the ongoing site investigations. There is also a need to follow up the use of the conceptual understanding of geochemical processes in safety assessment. In safety assessment it is not sufficient to understand the present day conditions, possible future perturbations to groundwater conditions must also be assessed.

Project Information

SKI Project Manager: Bo Strömberg

Project Identification Numbers:
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Research

Variability and Uncertainties of Key Hydrochemical Parameters for SKB Sites

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December 2006

Summary

The work described in this report is a development of SKI's capability for the review and evaluation of data that will constitute part of SKB's case for selection of a suitable site and application to construct a geological repository for spent nuclear fuel. The aim has been to integrate a number of different approaches to interpreting and evaluating hydrochemical data, especially with respect to the parameters that matter most in assessing the suitability of a site and in understanding the geochemistry and groundwater conditions at a site. It has been focused on taking an independent view of overall uncertainties in reported data, taking account of analytical, sampling and other random and systematic sources of error. The insights and principles that are discussed here should be applicable for evaluating key hydrochemical parameters for SKB's target sites at Forsmark and Laxemar.

This evaluation was carried out initially with a compilation and general inspection of data from the Simpevarp, Forsmark and Laxemar sites plus data from older 'historical' boreholes in the Äspö area. That was followed by a more specific interpretation by means of geochemical calculations which test the robustness of certain parameters, namely pH and redox/E_h (which is a proxy for dissolved oxygen). Geochemical model calculations have been carried out with widely available computer software.

Data sources and their handling were also considered, especially access to SKB's SICADA database. Direct access to SICADA has not been established in the way that was originally intended. Instead, extracts from SICADA provided by SKB as well as data from SKB's P- and R-reports have been used for the present work.

In preparation for the use of geochemical modelling programs and to establish comparability of model results with those reported by SKB, the underlying thermodynamic databases were compared with each other and with other generally accepted databases. Comparisons of log K data for selected solid phases and solution complexes from the different thermodynamic databases were made. In general, there is a large degree of comparability between the databases, but there are some significant, and in a few cases large, differences. The present situation is however adequate for present purposes. The interpretation of redox equilibria is dependent on identifying the relevant solid phases and being able to characterise them thermodynamically.

Geochemical modelling with the MEDUSA program and the HYDRA thermodynamic database was used to construct a set of E_h/pH diagrams for the iron and sulphur system in Forsmark groundwaters.

Geochemical modelling with the PHREEQCI program was used for two purposes connected with uncertainties in key hydrochemical parameters: (i) to adjust pH to compensate for CO_2 outgassing on the basis of an assumption that in situ groundwater should be at equilibrium with calcite, and (ii) to evaluate the hypothetical E_h on the basis of assumed control by Fe^{3+}/Fe^{2+}, $Fe(OH)_3/Fe^{2+}$ and SO_4^{2-}/HS^- redox couples so as to assess evidence for control and buffering of redox and for reactivity of other redox-sensitive parameters. These calculations were carried out with reported groundwater data from Forsmark and Simpevarp sites and also from the Äspö HRL. No data were

yet reported from new boreholes at the Laxemar site at the time of carrying out this geochemical modelling.

It is emphasised that the purpose of these calculations is to explore and illustrate the theoretical basis of geochemical interpretations, and to understand what are the assumptions, simplifications and uncertainties in interpreting hydrochemical data especially redox and pH. Though the aim is not just to make a repeat calculation of redox values with similar modelling as those reported in SKB's site descriptive model reports, the agreement from doing this is reassuring in terms of basic model consistency. Deviations of ±10 mV are attributable to minor differences in thermodynamic data and other model inputs. This work has been concerned with uncertainties in a broader context than just that of geochemical modelling uncertainties.

Some of the conclusions from geochemical modelling are:
(i) pH data, when adjusted to compensate for CO_2 outgassing, are typically 0.2 to 0.4 pH units lower than the measured values, which suggests one aspect of uncertainty in measured pH values.
(ii) Most measured pH/E_h points for Forsmark are located close to the HS^-/SO_4^{2-} line in an E_h/pH diagram, suggesting that the couple HS^-/SO_4^{2-} controls E_h at normal SO_4^{2-} concentrations (above about 0.5 mM and around 5 mM).
(iii) E_h calculated from the couples SO_4^{2-}/HS^- and $Fe(OH)_3/Fe^{2+}$ are rather close to the measured E_h in most cases. In contrast, the E_h calculated from the Fe^{3+}/Fe^{2+} couple is oxidising, i.e. a positive E_h, which is the result of erroneous Fe^{3+} values obtained by subtraction of Fe^{2+} from Fe_{total}.
(iv) There are high uncertainties in $E_{hSO4/HS}$ for Forsmark samples because HS^- data are near or at the analytical detection limit. pH is an important factor in modelled E_h values and in the cumulative uncertainty about redox interpretation. A potential difference of about -50 mV could for example be explained by an error in pH of about 0.7.
(iv) There are typical differences of -30 to -50 mV and +50 mV between measured E_h and $E_{hSO4/HS}$ and $E_{hFe(OH)3/Fe2+}$ respectively. Therefore ±100 mV is a cautious assumption for the uncertainty on redox estimations from E_h measurements and from redox modelling.

Some other general conclusions are:
(i) Uncertainty in all hydrochemical data arises from the effect of mixing with flushing or other extraneous water. The perturbations of pH and redox by such mixing are non-linear and not reliably estimated or predicted and are thus included in the overall uncertainty estimate.
(ii) Salinity and the underlying measurements, namely electrical conductivity, TDS and chloride, are less prone to significant uncertainties than pH and redox. The estimated maximum overall uncertainty quoted by SKB is ±10% and this seems to be reasonable but is valid only for samples which comply with SKB's acceptability criterion of <1% flushing water (or perhaps up to <5%).
(iii) Raw data for chloride and TDS could be corrected for dilution by flushing water, using the simple tracer data and/or results from the drilling impact (DIS) study method; SKB have done this only for one set of water samples from Simpevarp.
(iv) There have not been sufficient data reported so far for DOC, colloids, microbes and other parameters that relate to SKB's 'suitability criteria' or other important aspects of site geochemistry to make an independent assessment of the uncertainties.

Sammanfattning

Det arbete som redovisas i denna rapport är en del av SKIs kompetensutveckling inför granskning och utvärdering av data som kommer att ingå i SKBs underlag för platsval och ansökan om att bygga ett slutförvar för använt kärnbränsle. Målsättningen har varit att sammanföra ett antal olika sätt att tolka och utvärdera vattenkemiska data, speciellt vad gäller de parametrar som betyder mest för att avgöra lämpligheten i ett platsval och för att förstå geokemin och grundvattnets egenskaper på en vald plats. Arbetet har fokuserats på att göra en fristående värdering av osäkerheter i rapporterade data och att därvid ta hänsyn till fel i provtagnings- och analysförfaranden ävensom tillfälliga och systematiska felkällor. De insikter och principer som redovisas och diskuteras här bör kunna användas för att utvärdera vattenkemiska nyckelparametrar hos SKBs kandidatplatser i Forsmark och Laxemar.

Utvärderingen påbörjades med en sammanställning och allmän granskning av data från Simpevarp, Forsmark och Laxemar, samt från äldre “historiska” borrhål i Äspö området. Detta arbete följdes av mer specifika tolkningar genom geokemiska beräkningar för att pröva kvalitén hos huvudparametrarna pH och redox/E_h (som markör för löst syre). De geokemiska modellberäkningarna har utförts med allmänt tillgängliga datorprogram.

Datakällor och deras handhavande har också värderats. Speciellt gäller detta tillgång till SKBs databas ”SICADA”. Direkt access till SICADA har inte kunnat upprättas så som ursprungligen var meningen. Istället har utdrag ur SICADA använts i den form de erhållits från SKB, såväl som data från SKBs P- och R- rapporter.

För att uppnå kompatibilitet mellan våra modelleringsresultat och SKBs data krävs naturligtvis rättvisande användning av de geokemiska modelleringsprogrammen. Därför var det en viktig startåtgärd att kontrollera underliggande termodynamiska databaser gentemot varandra och mot andra allmänt accepterade databaser. Log K data för utvalda fasta faser och lösliga komplex från de olika databaserna jämfördes. Allmänt sett är kompatibiliteten stor, men det finns några signifikanta och i ett fåtal fall stora avvikelser. Den nuvarande situationen har dock bedömts som adekvat för detta arbete. Tolkningen av redox jämvikter beror bl.a. av att relevanta fasta faser säkert identifieras och att det är möjligt att karakterisera dem termodynamiskt.

Programmet MEDUSA och databasen HYDRA har använts för att beräkna och rita ett antal E_h/pH diagram för järn och svavel systemen gällande grundvatten i Forsmark.

Geokemisk modellering med PHREEQCI programmet gjordes av två anledningar som hade samband med osäkerheten hos de hydrokemiska nyckelparametrarna: (i) för att justera pH med avseende på CO_2 förluster vid provtagning under antagande av att in-situ grundvatten bör vara i jämvikt med kalcit, och (ii) för att utvärdera hypotetiska E_h med antagande av att E_h bestäms av redoxparen Fe^{3+}/Fe^{2+}, $Fe(OH)_3/Fe^{2+}$ respektive SO_4^{2-}/HS^-. Detta för att kunna värdera indikationer på hur kontroll och buffring av redox sker, samt för att uppskatta inverkan av andra redox känsliga parametrar. Beräkningarna utfördes på rapporterade grundvattendata från Forsmark och Simpevarp, samt också på data från Äspö HRL. Inga data hade ännu rapporterats från nya borrhål i Laxemar vid tiden för denna geokemiska modellering.

Det skall framhållas att syftet med beräkningarna är att utforska och illustrera den teoretiska bakgrunden till de geokemiska tolkningarna och att förstå vilka antaganden, förenklingar och osäkerheter som förekommer när vattenkemiska data, speciellt redox och pH, tolkas. Även om syftet inte enbart är att upprepa beräkningar av redox värden med liknande beräkningsmetoder som beskrivs i SKBs platsbeskrivningsrapporter, kan den överensstämmelse som erhålls genom att göra detta skapa tillförsikt. Detta gäller både grundläggande överensstämmelse mellan beräkningssätten och slutsatsen att resultatavvikelser på ±10 mV kan hänföras till mindre skillnader i termodynamiska data och andra beräkningsunderlag.

Några av slutsatserna från den genomförda geokemiska modelleringen är:
(i) pH data som kompenserats för CO_2 förlust ligger typiskt 0.2 till 0.4 pH enheter lägre än uppmätta värden. Detta implicerar en osäkerhetsaspekt hos uppmätta pH-värden.
(ii) De flesta uppmätta pH/E_h par för Forsmark ligger nära HS^-/SO_4^{2-} linjen i ett E_h/pH diagram. Detta implicerar att redox paret HS^-/SO_4^{2-} kontrollerar E_h vid normala SO_4^{2-} koncentrationer (över ca. 0.5 mM och omkring 5 mM).
(iii) E_h beräknat från paren SO_4^{2}/HS^- och $Fe(OH)_3/Fe^{2+}$ ligger ganska nära de uppmätta E_h värdena i de flesta fall. Som kontrast skall nämnas att E_h beräknat från redox paret Fe^{3+}/Fe^{2+} blir oxiderande, dvs. positivt, om de felaktiga Fe^{3+} värden används som erhålles om Fe^{2+} subtraheras från Fe_{total}.
(iv) Osäkerheten i $E_{hSO4/HS}$ för Forsmark prover är hög eftersom HS^- data ligger nära eller på den analytiska detektionsgränsen. pH är en viktig faktor för enskilda beräknade E_h värden och dessutom för den ackumulerade osäkerheten vid tolkningar av redoxdata. Exempelvis kan en potentialdifferens på ca. -50 mV förklaras av ett fel i pH på ca. 0.7 pH enheter.
(iv) Typiska avvikelser mellan uppmätta E_h och beräknade $E_{hSO4/HS}$ respektive $E_{hFe(OH)3/Fe2+}$ ligger på -30 to -50 mV respektive +50 mV. Därför torde ±100 mV vara en försiktig angivelse av osäkerheten mellan redox uppskattningar från E_h mätningar och motsvarande redox beräkningar.

Ytterligare allmänna slutsatser är:
(i) Provkontamination med spolvatten och annat främmande vatten påverkar alltid alla vattenkemiska data. Störningarna i pH och redox genom sådan vattentillblandning är icke-linjära och kan inte uppskattas eller förutses på ett säkert sätt. De inräknas därför i den övergripande uppskattningen av osäkerheten.
(ii) Salinitet och den bakomliggande mätningen, nämligen av elektrisk konduktivitet, TDS och klorid, är mindre utsatta för signifikanta osäkerheter än pH och redox. Den uppskattade maximala totala osäkerheten som anges av SKB är ±10% och denna verkar vara rimlig. Dock gäller den endast för prover som överensstämmer med SKB's acceptanskriterium på <1% spolvatten (eller möjligen upp till <5%).
(iii) Rådata för klorid och TDS kan korrigeras för utspädning med spolvatten. För korrektion används enkla tracer data och/eller resultat som erhållits med "drilling impact" (DIS) metoden; SKB har genomfört denna korrektion enbart för en uppsättning av provvatten från Simpevarp.
(iv) Ännu så länge har tillräckliga data ej rapporterats för DOC, kolloider, mikrober och andra parametrar som relaterar till SKB's 'suitability criteria' eller andra viktiga aspekter av platsgeokemin för att kunna göra en fristående värdering av osäkerheterna i dessa parametrar.

Contents

1 Introduction

1.1 General Background

The work described in this report is a development of SKI's capability for the review and evaluation of data that will constitute part of SKB's case for selection of a suitable site and application to construct a geological repository for spent nuclear fuel. It has been carried out by Studsvik Nuclear AB and Intellisci Ltd in collaboration on separate orders from SKI.

The collaborative work between the authors was started as a planning meeting at Studsvik on November 18, 2004. The objectives of this meeting were to establish a working contact between the participants and to define literature entries, computer programs and databases to be used in this work. Working meetings between the authors were held at Studsvik on January 17-18, 2006 and at Intellisci on April 3-4, 2006.

One of the categories of site-specific data which is being acquired by SKB for its candidate siting areas at Forsmark and Laxemar is chemical compositions of groundwaters. Some of these hydrochemical parameters have a direct significance to the performance of the engineered barrier system (EBS) and have therefore been included in a list of 'suitability indicators' that SKB identified for evaluation in site investigations [1]. Among these suitability indicators are pH, dissolved oxygen and salinity. A broader set of geochemical parameters that are obtained from site investigations are of indirect importance for site characterisation and 'site understanding'.

The geoscientific background for SKI's requirements with respect to the suitability indicators and other geochemical data has been discussed in a previous report in which issues relating to sampling, analyses and interpretation were covered [2]. SKI put large emphasis in the evaluation of these criteria and to understand and to help this work the intention is to have modelling work going on. This is done in order to assure the robustness of the SKB's conclusions and via consultants to judge the quality and comprehensiveness of the flow of SKB data and criteria and to develop a reference tool for the judgment of various safety critical processes.

The aim of the present report is to illustrate a method for evaluating key hydrochemical parameters for the SKB sites Forsmark and Laxemar. This evaluation is carried out initially with a compilation and general inspection of data and then a more specific interpretation by means of geochemical calculations which test the robustness of certain parameters, namely pH and redox/E_h (which is a proxy for dissolved oxygen). Geochemical model calculations have been carried out with widely available computer software. The work is a continuation of that reported in [3] for which the focus was on planning of subsequent work, on the review and selection of a computer program and thermodynamic database, and on preliminary geochemical model calculations. The present report accounts for work performed.

Preparatory tasks in the preliminary phase of the project (before the present report) included agreeing approaches for the selection and basic checking of data, for reviewing and selecting thermodynamic databases, and for calculating chemical equilibria. In particular, the method for calculating redox/E_h as represented by Fe, S and other redox-sensitive geochemical parameters was examined so as to assess evidence for control and buffering of redox and for reactivity of other redox-sensitive parameters.

Data sources and their handling were also considered, especially access to SKB's SICADA database. However, direct access to SICADA has not been established in the way that was originally intended. Instead, extracts from SICADA provided by SKB as well as data from SKB's P-reports have been used in the present work.

1.2 Detailed Objectives and Scope of Work

Summary of objectives

- To have a compilation of the relevant site-specific hydrochemical parameters from SKB's sites and of the data commentaries provided by SKB in SICADA and P-reports;
- To add independent comments on data suitability for use in site assessment;
- To test the internal consistency of hydrochemical data with general geochemical concepts as an additional way of assessing uncertainties;
- To be able to advise SKI about the robustness and significance of SKB's data and the resulting conclusions about site suitability on the basis of understanding the uncertainties in data due to the practicalities of sampling and measurement and due to the geochemical context of measurements.

Scope of work to reach the objectives

- Compilation of relevant data from SKB's spreadsheets published with the hydrochemistry R-series reports supporting Site Descriptive Models (SDMs) and from raw data in the site investigation P-reports, plus recommendations and comments from field staff and/or interpretation team on data representativity and other aspects of data quality (e.g. drilling water contents, instrument calibration and malfunction).
- Check for data completeness – understand reasons for data "gaps" by reference to SICADA, SKB reports, and by enquiry to SKB; examine field and analytical data for redox species: E_h, Fe(total), Fe^{2+}, SO_4^{2-}, HS^-, CH_4, U_{tot} and Mn for anomalous values and raise queries with SKB if necessary; consider reliability of redox-sensitive species especially Fe and S data.
- Assessment of geochemical modelling software; the most widely used of the geochemical modelling codes, PHREEQCI v.12 [4] was selected; KTH's MEDUSA/HYDRA code [5] was also used.

- Comparison of thermodynamic databases supplied with PHREEQCI v.12 and used in other projects for equilibrium modelling of geosphere species, reactions and minerals.

- Evaluation of reported data for key geochemical parameters that are of primary significance for performance assessment.

- Observation of the practicalities of field data acquisition, instrument calibration and data processing in a visit to the Forsmark site (in conjunction with a Field Technical Review, FTR, for SKI/INSITE).

- Examination of pH data for evidence of shift due to CO_2 loss or other perturbations; use of geochemical speciation and equilibrium software to adjust pH on basis of in-titration of CO_2 to calcite equilibrium, noting sensitivity to perturbation.

- Interpretation of the chemical equilibria that are expected to be involved in controlling pH and redox in the system using geochemical equilibrium modelling of redox couples: Fe_{tot} or $Fe^{2+}/Fe(OH)_3$, HS^-/SO_4^{2-}, CH_4/CO_2, U_{tot}/UO_2 using reported and adjusted pH values; assessment of uncertainty range for redox couples corresponding to uncertainty range of pH; assessment of overall uncertainty in reported redox and estimate range of reliability.

- Use of Pourbaix-type diagrams to examine where the reported data plot relative to the species predominance boundaries for expected equilibria in pH-E_h space.

- Assessment of the overall reliability and adequacy of presently-available data for suitability indicators, especially pH, E_h, salinity, DOC, etc.

- Comment on the spatial distribution of data (areal distribution, depth distribution especially with respect to repository depth, correlation with geological units, major structural features, etc).

- Review of geochemical equilibria and ongoing mineral alterations in the groundwater system to understand the water-mineral reactions that reach equilibrium in the undisturbed groundwaters, and also those reactions that have varying degrees of kinetic controls. *(Phase 2 task)*

- Review of SKB's geochemical model for the buffering of redox conditions at repository depth and for the attenuation of dissolved oxygen in an oxygenated infiltration scenario; assessment of SKB's mineralogical database for this model. *(Phase 2 task)*

- Assessment of the effects of future changes in groundwater salinities on the speciation of ligands and radionuclides. *(Phase 2 task)*

1.3 Contents of Report

Chapter 2 describes the information and data that SKB produces and that have been the basis for the preparation of this report. Methods Documents (MDs) are the main source of information about sampling, analytical and data processing procedures. SKB's series of P reports, publishing raw data and preliminary discussions of site investigation tasks, and R reports, publishing the site descriptive models (SDMs), plus the SICADA database are the data sources.

Chapter 3 contains the main body of this report, which is the discussion of various aspects of uncertainties in the groundwater composition data that are reported from SKB's sites. Reported data for the key parameters are compiled into a temporary database that serves the purposes of this report. Causes of uncertainty in hydrochemical data are discussed, including sampling artefacts such as flushing water mixing and outgassing. Geochemical modelling is used to examine two specific aspects: effect of CO_2 outgassing on pH, and consistency between redox data from E_h measurements and redox-sensitive solutes. Ranges of overall uncertainty in pH and redox are estimated.

Chapter 4 makes some general comments about the role of data uncertainty in understanding spatial variability of geochemical conditions.

Chapter 5 contains a summary of this work and presents a bullet point list of the main conclusions and other comments.

Appendix 1 lists the MDs that are relevant to data acquisition.

Appendix 2 lists SKB's P reports which describe acquisition of data referred to in this report.

Appendix 3 contains the temporary spreadsheet of hydrochemical data and geochemical modelling results.

Appendix 4 is a tabulation of log K data for selected solution complexes and solid phases, extracted from various thermodynamic databases.

Appendix 5 contains a selection of Pourbaix E_h-pH diagrams for the Fe-S system.

2 Data Acquisition Methods and Reporting

This section describes SKB’s documentation of methods for acquiring hydrochemical data and the report and database sources from which we have compiled data for the key hydrochemical parameters, i.e. parameters that relate to pH and redox and therefore have a direct influence on site suitability and safety performance. It also summarises SKB’s comments concerning data reliability and quantification of uncertainties in the data.

The methods by which water samples are taken, processed and analysed are described by SKB in their ‘Methods Documents’ (MDs). The list of relevant MDs is tabulated here and their topics are summarised. Activities where methods documentation seems to be missing are identified. It would be useful to know whether these are available but not seen by us, or if SKB has yet to complete them.

The main sources from which the data in this report have been compiled are SKB’s printouts from the SICADA database (usually provided as spreadsheets and tabulations in Site Descriptive Model ‘R’ reports) and raw data tables and descriptions in ‘P’ reports which contain raw site investigation data and field observations that relate to data reliability.

A list of available P reports is compiled. There are only a few ‘orphan’ data which have been referred to by SKB in interpretation reports but for which there are no supporting P reports with details of data acquisition.

The original intention was to use direct electronic access to SICADA as the primary means of obtaining data and supporting quality information so as to be independent of SKB’s data extraction routes. The procedure for this turned out to be very difficult and cumbersome, so in actuality SKB’s most recent data extracts from SICADA were used along with the opportunity to raise questions with SKB about specific data issues.

2.1 Method Documents (MDs)

The set of Method Documents or MDs accounted in Appendix 1 describes the handling equipment, procedures, analytical methods, data reduction and reporting employed as SKB performs and reports analyses on groundwater samples taken from boreholes in the candidate sites. The set is a selection of those MDs that are considered to be necessary to fully understand the procedures and to be able to make well-based judgements of the quality and applicability of produced data. There are also other MDs available but those have been omitted as being less important for the purpose intended here.

The MDs that are available to us at the time of reporting are indicated in the fourth column.

One of the most important of those is considered to be SKB MD 430.017-01 (Nov 2001). The translated title is ‘Description of method for complete chemical characterization using a mobile field laboratory’. This MD describes the hydrochemical characterization using mobile sampling and field analysis equipment of which SKB has two identical complete units in operation (usually one unit based at Forsmark and one at Laxemar). Each comprises two trailers: one trailer is a mobile laboratory for limited field analyses and processing of water samples for analyses at external laboratories. The other trailer contains equipment to operate the 'Chemmac' sampling system which includes 'surface Chemmac' and 'borehole Chemmac' units for monitoring and sampling respectively of water pumped to the surface from a borehole interval isolated by inflatable packers and of water downhole in the isolated interval. Both Chemmac units monitor the fundamental parameters pH, E_h and temperature. Dissolved oxygen and electrical conductivity (EC) are also monitored by the surface Chemmac.

MD 430.017-01 contains a good discussion of accuracy of results. Most statements and comments can be supported without qualification and do not require any additional justifications or insights. There are, however, a few statements about criteria for data quality for which the justifications need further explanation or that raise additional questions:

- Why is the addition of flushing water limited to a maximum of 1% of the sampled water? Is this a practical limit?
- It is stated that some chemical parameters, namely Fe(II), alkalinity, HCO_3^- and HS^-, require analysis within the first day after sampling. This is true, but the motivations for the accepted delay time should be given.
- Have all steps of the procedures employed when using external laboratories been evaluated (certification)?

Analyses of ionic solutes are performed in accordance with SKB MD 450.001. Well proven methods of analysis are used. In addition to limited analyses at the internal SKB laboratory, external laboratories are used which, in the first instance, are accredited. Detection limits and analytical uncertainties may vary but seem to be reasonable for both internal and external laboratories.

In relation to other MDs, there are a few additional questions that are noted in the right hand column of Appendix 1:

- MDs 422.001-02 and 451.013-03, etc. How exactly is 'treatment, selection and QC of SICADA data' done?
- MD 434.006-01. How is the electrochemical connection between reference and working electrodes arranged?

2.2 Reporting of Data Acquisition

SKB's 'P' series of reports are the preliminary route for reporting data and supporting information from the site investigations. They are produced by site investigation staff to report outputs from individual tasks (as indicated on the corresponding Activity Plans). In the hydrochemistry part of the investigation, the tasks are for example sampling of water from percussion boreholes, hydrochemical logging with the tube sampling system, and full hydrochemical characterisation. P reports that include activity reports on hydrochemistry tasks and contain some hydrochemical data (even though much of the data have too low quality and are not used in interpretations) are listed for Simpevarp, Forsmark and Laxemar in Appendix 2.

SKB's formal route for reporting and interpreting 'approved' data is the Site Descriptive Model (SDM) reports. These are published in the R report series [6-10]. Data from the v1.2 updates of the SDMs for Forsmark and Laxemar were used in this work [9, 10].

There are only a few data that have been used in Site Descriptive Model reports for which the provenance has not been reported in P reports. These are:

Forsmark
HFM05 (0-200.1m) (only lab pH and major element data reported in R-05-17 [9])
PFM000001/7/8/9/10/39 (Private wells) (pH values in SDM report)

Laxemar
HLX18/22/24 (referred to in R-06-12 [10] but no complete data set available)
KLX01 (272-277m) (Chemmac pH, Fe & S species, U isotope values in SDM report)
KLX01 (456-461m) (ditto)
KLX01 (680-702.1m) (ditto but only lab pH, plus E_h value)
KLX01 (830-841m) (ditto but only lab pH)
KLX01 (910-921m) (ditto but only lab pH and no U isotope values)
KLX01 (999-1078m) (ditto but only lab pH)
KLX02 (798-802m) (ditto but only lab pH and no U isotope values) (2002 sampling)
KLX02 (1155-1165m) (ditto but only lab pH) (1999 sampling)
KLX02 (1345-1355m) (ditto but only lab pH) (1999 sampling)
KLX02 (1385-1392m) (ditto but only lab pH) (1999 sampling)
KLX04 (104-109m) (referred to in R-06-10 but no data available)
KLX04 (510-515m) (referred to in R-06-10 but no data available)
KLX04 (971-976m) (referred to in R-06-10 but no data available)

Simpevarp
KSH02 (422.3-423.3m) (referred to in R-06-12 [10] but no complete data set available).

From this comparison of data used in Site Descriptive Models with what has been reported so far in P reports, it is evident that many data from KLX01 and KLX02 have not been subject to the same level of detailed reporting as has been the case for data from the boreholes in the present site investigations. KLX01 and KLX02 were drilled in 1988 and 1993 respectively. KLX02 has been retested and resampled at various times (i.e. in 1997, 1999, 2002) since the initial post-drilling testing. The data referred to above for which there is insufficient supporting information are for samples taken between 1988 and 1990 for KLX01 and in 1999 and 2002 for KLX02.

Downhole Chemmac measurements of E_h in KLX02 during 1993-4 that were reported in SKB report TR-95-05 [11] have apparently been discounted (i.e. they have not been used in the SDMs for Laxemar), although the reasons for this are not fully explained in the SDMs or in TR-95-05. E_h values for KLX01 (680-702m, tested 1988) and KLX02

(798-802m, tested 2002) have been used in the Laxemar SDM v1.2 (R-06-12, [10]) although the origin and reliability of these data are not adequately explained.

2.3 Data Processing and Storage

As noted above, the reported uncertainties in analyses seem to be reasonable for both internal and external laboratories. A high quality of analytical data is of course necessary as the basis for data entries into the SICADA database. Various data processing steps are involved from the basic raw data stage, via calibration, quality checking, and other methods of data adjustment and selection, to the final data set in the SICADA database.

Raw data for pH and E_h are processed with the program package HILDA. Values of E_h and pH are calculated from millivolt readings from the corresponding electrodes by applying known values of calibration constants. An MD for HILDA data processing, its usage of calibration constants and how these constants are derived, was not available to this study but the program was seen in use during the field technical review visit in June 2006 (see below).

In general, the collected body of MDs covers most tasks in hydrochemical data acquisition and reporting from the in situ water sample, via downhole and surface monitoring, sampling equipment and methods, to analyses in field and remote laboratories. The methods used for data processing and calibration calculations in HILDA and SICADA appear to be valid and also to be robust against introducing inadvertent errors. However it has not been possible in this study to follow the detail in all of the data handling procedures prior to the final parameter values in SICADA. SICADA does not offer the level of transparency and easy access that would facilitate full review of the data handling procedures and database.

2.4 Field Technical Review, June 2006

The purpose of a Field Technical Review (FTR) is to provide SKI with first-hand knowledge of the methods and technologies that SKB is deploying to acquire data in their site investigations. FTRs are an opportunity for SKI’s advisers, who are involved in the review and evaluation of SKB’s outputs and interpretations of site investigation, to see field methods in ‘real world’ operation, to discuss scientific and technical details with SKB’s field staff and to clarify understanding.

An FTR visit was made to Forsmark in June 2006 and it is fully reported in [12]. Its aims were to (i) understand the procedures for making field measurements and taking samples for the key hydrochemical parameters (pH, E_h, redox-sensitive species, uranine tracer, chloride, colloids, microbes, organics, dissolved gases, etc) and (ii) discuss the procedures for calibrating and processing data and for selecting data that are representative of in situ conditions.

The scope of the FTR visit covered:

- Up-to-date Methods Documents (MDs) for the procedures and technologies involved in acquisition of hydrochemical data, plus some clarifications of details in these for our information;
- Deployment of the Chemmac tool and system for downhole and surface monitoring of unstable hydrochemical parameters and for water sampling for complete chemical characterisation, plus the issues that account for the success or failure of these operations and also the procedures involved in checking and calibrating electrodes;
- Analyses carried out in the on-site laboratory for a limited range of determinands, and clarifications of some aspects of the data provided by these analyses;
- Processing of data from the Chemmac system with the HILDA software, applying calibrations to raw data, plus the ways that processed data are selected for reporting;
- The various methods and instrumentation that SKB have been using to obtain water samples from boreholes, the experience that has limited the success rate of sampling, and the measures being attempted by SKB for future sampling to achieve an adequate distribution of reliable samples and data.

The FTR concluded that the methods, equipment, expertise of personnel, and processing and documentation of data are appropriate for the tasks, and that consistency in these and other aspects between the sites is desirable. Obtaining adequate and reliable data is perhaps turning out to be more problematic at both sites than was envisaged. Data adequacy, representativeness and overall confidence will continue to be issues of concern in SKB's site descriptive models and in the safety assessments. The two main interrelated issues of concern are (i) the performance of the Chemmac tools in achieving an adequate number, distribution and reliability of redox and pH measurements, and (ii) sampling groundwaters that are a representative distribution and that are 'contaminated' by negligible amounts of flushing water.

The key to providing assurance that E_h data are representative is the reproducibility of responses from multiple electrodes downhole and at the surface, combined with demonstration that E_h data are consistent with analyses for the redox-sensitive solutes such as Fe^{2+} and HS^- and for indicative microbial populations. SKB have taken this approach in interpretations in the hydrochemical Site Descriptive Model reports. The same criterion of reproducibility from multiple electrodes, downhole, at surface and in the laboratory, is applied to assess reliability of pH data. The internal consistency of redox couples with E_h, and the consistency of carbonate equilibria with pH, and their implications for data uncertainties are examined further in this report.

A lot of effort goes into clean-up pumping to obtain measurements and groundwater samples with the lowest achievable amounts of extraneous water. The additional procedures to quantify flushing water with uranine tracer and to calculate the overall impact with the DIS method are impressive, although so far the latter has been used in only a few cases. A more systematic estimation of the impacts, negligible or otherwise, of extraneous water on hydrochemical and isotopic parameters would further quantify the overall reliability and uncertainties in many parameters that have direct and indirect significance in the assessment and understanding of sites.

3 Data and Uncertainties in In-Situ Compositions

In the following sections, the uncertainties in key hydrochemical parameters are considered for each site. To some extent, rather different approaches are used for these evaluations for each site, with respect to geochemical calculation methods and graphical illustration, although they lead to comparable overall implications. The present intention is that these will be subsequently discussed and compared under a common heading in a final report for this project area.

Originally it was decided that the reference site for geochemical data used in the introductory and training work [1] would be Simpevarp. However, because more preparatory work had already been done on Forsmark data, for which an approved database had been published by SKB, and also because Simpevarp ceased to be a primary candidate for SKB, it was decided to focus on Forsmark data and then to add Laxemar data as they became available.

3.1 SKB's Data for Key Parameters

A compilation of hydrochemical data from SKB's site investigations is in Appendix 3. It shows sample information and the principal hydrochemical parameters. These data have been compiled from many different sources (mostly P reports) and are not a direct extract from SICADA, though many data are SICADA extracts that have been reported with the Site Descriptive Models. The compilation has been checked in reasonable detail for transcription errors between the SKB sources and this spreadsheet. Data from this spreadsheet have been used in the geochemical modelling which is reported below. It is emphasised that they have been compiled for this work only and that the overall selection of data has not been checked or approved by SKB. Nevertheless we consider it to be a useful compilation for considering issues of reliability and uncertainties.

3.2 Reported Uncertainties

SKB has reported general uncertainty ranges for analytical methods in [13]. The general uncertainty ranges suggested by SKB for the main hydrochemical parameters are in Table 1.

Uncertainty ranges on specific measurements of pH and E_h are given in the P reports and are shown in the data table in Appendix 1. For Chemmac measurements of pH and E_h, the uncertainties have been estimated by SKB from the variations between measurements with different electrodes in the multi-electrode array in the Chemmac tools (downhole and/or surface) and from the residual drift in measurements occurring at the end of the monitoring period.

Typical uncertainties for Chemmac pH data are reported as ± 0.1 to 0.2 and occasionally much higher although in these cases the Chemmac pH data are usually regarded as unreliable because the large-scale drift or electrode discrepancies would usually be associated with an unquantifiable bias. Uncertainty in laboratory measurements of pH is not reported by SKB; in addition to the measurement uncertainty, the possibility of bias due to pH drift caused by CO_2 outgassing or ingassing has to be considered. This will be investigated later on in this report. Surface Chemmac pH readings may also be slightly biased relative to downhole Chemmac readings due to CO_2 outgassing as the rising water is depressurised.

Table 1. SKB's general estimates of analytical and overall uncertainties in hydrochemical data (from P-05-198 [13])

Parameter	Measurement uncertainty	Estimated overall uncertainty[1]
Dissolved oxygen	± 0.2 mg/L	20%
Na	4%	10%
K	6%	15%
Ca	4%	10%
Mg	4%	10%
Cl (titration/IC)	5%/6%	<10%/10%
SO_4	6%	15%
HCO_3	4%	<10%
Fe(tot), Fe^{2+}	15% (>30 microg/L)	20%
Mn	8%	10%
HS^-	±0.03 mg/L (<0.2 mg/L)	
DOC	8%	30%
^3H	0.8 or 0.1 TU	

[1] Estimated overall uncertainty covers sampling and sample handling, as well as analytical uncertainty; it has been estimated by SKB's expert judgement.

Typical uncertainties for Chemmac E_h data are reported to be ± 10 to 30 mV. Uncertainties greater than this, e.g. 50 to 100 mV, are likely to be associated with continuing drift of electrode readings and/or inconsistencies between different types of electrodes, so the validity of the uncertainty estimates may be questionable. In many such cases of questionable data reliability, SKB has not attributed an E_h value. The comparability of E_h measurements from downhole and surface Chemmac sensors, and their relationship to 'in situ' chemical conditions, could be influenced by a number of factors relating to depressurisation, temperature and oxygen leakage in the rising tubing, as well by differences in performance and calibrations of electrodes in the different tools. Apart from direct comparison of Chemmac outputs, the other approach to investigating uncertainties and internal consistency of redox equilibria is to compare direct E_h measurements with E_h values calculated from redox-sensitive couples, i.e. Fe^{2+}/Fe^{3+} [or $Fe^{2+}/Fe(OH)_3$], HS^-/SO_4^{2-}, CH_4/CO_2, and U_{tot} (effectively U^{VI}/UO_2). These redox equilibria are investigated later in this report.

3.3 Sampling Artefacts, Flushing Water Effects and CO_2 Outgassing

Physical perturbation and/or chemical contamination during sampling are one of the main sources of uncertainty in hydrochemical data. Physical perturbation (e.g. temperature change, depressurisation, agitation) may cause chemical reactions and outgassing which in turn may cause changes of pH and E_h (see above) and precipitation of solids or formation of colloids. Chemical contamination and thus reduction of how representative a sample is of in situ conditions in the tested interval may occur due to in-mixing of formation waters from elsewhere in the borehole, mixing with residual drilling or flushing water, in-gassing of oxygen and other atmospheric gases, or reaction with components of the sampling set-up.

SKB's sampling equipment design and procedures implement many measures, based on many years of experience and development, to minimise perturbation and contamination of water samples. Examples of these measures are low flow rates to minimise agitation especially around electrode sensors, checking hydraulic pressures inside and outside packered intervals to test for leakage, use of local shallow groundwater as drilling water, and dosing of drilling water with uranine tracer.

Nevertheless to a greater or lesser extent these artefacts and effects influence all water samples taken from deep boreholes and are likely to enlarge the overall uncertainties in their representativeness. The problem is exacerbated in cases where the sampled interval has low transmissivity, which has been the case so far for most of the boreholes at both Forsmark and Laxemar.

Uncertainties introduced due to physical perturbations of pressure and temperature are likely to affect pH, redox, alkalinity and dissolved gases primarily. Reduction of pressure as borehole water is pumped or lifted from a deep interval causes outgassing. The additional uncertainty introduced into data is difficult to quantify except possibly for the case of CO_2 loss which can be modelled geochemically (see below). Reduction of temperature from formation conditions to the surface is a maximum of about 15°C (i.e. maximum formation temperature of about 20°C and minimum handling temperature of about 5°C). Although solubilities of most solids decrease with decreasing temperature, the opposite is the case for calcite so precipitation should not be caused by slight cooling and thus should not affect uncertainty in pH and alkalinity. Physical agitation and general effects of transferring water samples (including filtering) could cause iron oxyhydroxide to precipitate as solid or colloid, thus introducing uncertainty into the representativeness of Fe data (and also a slight effect on pH which decreases as OH^- is removed into Fe-ox). In-line filtering of water flow from the Chemmac system and use of specified procedures for the respective samples (MD 452.001) should eliminate or minimise perturbations of Fe and pH data. If Fe-ox precipitates are observed in the samples at the time of pH measurement in the field laboratory, then this should be reported along with the pH value.

The three most general sources of chemical contamination that make a borehole sample chemically unrepresentative of the tested formation interval are mixing with drilling/flushing water, mixing with water from elsewhere in the borehole or formation, and introduction of oxygen. Drilling/flushing water is taken from a nearby shallow (100 to 200m depth) percussion-drilled borehole and is therefore likely to be less mineralised than deeper groundwaters being sampled. It is tagged with uranine tracer and is circulated once only, so progressive in-mixing of formation water does not occur. It is also flushed with nitrogen gas to remove dissolved oxygen. Most likely contamination is with solutes that are characteristic of shallow fresh groundwater, e.g. NO_3^-, ^3H, higher HCO_3^- with higher ^{14}C. NO_3^- is not a primary parameter for interpretation so is not of high significance.

^3H is interpreted as a tracer of young (<50 years old since recharge) groundwater and thus of relatively rapid downflow as it is detected at depth. Maximum ^3H levels in recently-recharged shallow groundwaters in these regions are around 35 TU and values are more usually 10-15 TU. The detection limit for ^{3}H is 0.1 or 0.8 TU depending on the analytical lab and method used. Therefore 1% of such water could introduce 0.1 to 0.3 TU and 5% could introduce 0.5 to 1.5 TU in a deep water sample. Uncertainty in interpreting ^{3}H significance should therefore be considered to be at these levels, since flushing water contents as indicated by the tracer are often accepted above 1% and up to 5% (see Appendix 3).

Changes to HCO_3^- due to mixing with flushing water are not of primary significance in hydrochemical interpretation: for example, deep brackish/saline water typically has HCO_3^- between 10-100 mg/L whereas fresh shallow groundwater typically has 200-300 mg/L. 5% in-mixing of flushing water would therefore raise alkalinity by a minor amount; there would be a corresponding effect on pH but the small change would be covered by the general uncertainty attributed to pH. A more significant uncertainty would be introduced into the interpretation of ^{14}C contents in deep groundwaters. 5% in-mixing of flushing water into a deep saline water with negligible in-situ ^{14}C could raise ^{14}C in a water sample to 10 pmC or even more. This would have a significant impact on the interpretation in terms of groundwater ages.

Given proportions of flushing water in-mixing, as indicated by the concentrations of uranine tracer, it should be possible to adjust (or ‘correct’) analytical raw data for the effect of in-mixing to obtain an improved estimate of in situ groundwater composition. Such an adjustment is only practicable for non-reactive solutes that mix linearly. It would also make the assumption that in-mixed contaminating water is all traced, i.e. is derived only from flushing water; in-mixed formation water from other intervals in the open borehole would not be traced in this way. Such a calculation has been reported by SKB only for two samples from one interval in KSH01A (see data line marked ‘calc’ in Appendix 3). Drilling water content was about 10%, so the adjusted major solute concentrations were increased proportionately by about 10-12%. pH was also adjusted resulting in an increase of about 0.4 pH units. The method for adjusting pH is not known, but possibly a geochemical modelling calculation was used, involving mixing of the two component waters and readjustment to calcite equilibrium, i.e. similar to the method used to correct for CO_2 outgassing.

3.4 Geochemical Modelling of pH and Redox

3.4.1 Geochemical Modelling Software

The main tool for the modelling work was the PHREEQCI program (v2.12.5-669) with the included thermodynamic database files llnl.dat, phreeqc.dat and wateq4f.dat [4]. The rationale is that PHREEQCI and associated databases are widely used, maintained and well established since a long time; it is also the geochemical modelling program used by SKB. Therefore, there is already a large body of directly comparable PHREEQC/PHREEQCI modelling results available for comparison with the present work. A description of PHREEQCI is given in [1] and a more detailed description can be found in [4].

The thermodynamic program package MEDUSA/HYDRA [5] was also used to construct Pourbaix diagrams for the Fe-S-Cl system as a graphical way of assessing variations of redox equilibria in E_h-pH space.

3.4.2 Review of Thermodynamic Databases

A computer program needs a good and generally accepted database. Coming with PHREEQCI are the thermodynamic databases llnl.dat, wateq4f.dat and phreeqc.dat. The llnl.dat data base is the largest of those but is not completely compatible with the program and there can be errors using it.

Comparisons of log K data for solid phases from the different thermodynamic databases mentioned above were made. Selected complexes and solid phases were compared, essentially of data that will be of significance for the objectives of this work.

Values from the PHREEQCI databases have been compared with those found in the HYDRA [5] and PSI/NAGRA databases [14]. It is important that comparisons are made for exactly the same complexes, solid phases and reactions. Because of this, some log K values are directly extracted and others are calculated from other values. The selected data and comments on the comparisons can be seen in Appendix 4. The HYDRA database is the ‘best equipped’ database, containing the largest number of values, and is used as the reference so that Appendix 4 shows deviations of log K values in other databases from those in the HYDRA database. 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. For 35% of the complexes and solid phases, Minteqv4 (Mv4) database has the largest deviation from HYDRA, whilst the llnl database has the next largest deviation in 30% of the cases. In 15% of the cases, the deviation was sufficiently large that it gives rise to doubt over validity of data on one side or the other; half of these cases involved comparison of Mv4 with HYDRA.

The databases included in the PHREEQCI package differ in extension and coverage. In many cases, there are large similarities or exact equalities between log K values from the different databases, but there are also some significant and in a few cases large differences. Identical thermodata are probably imported from the same source outside (or inside) of the PHREEQCI package. The causes of differences are not elucidated here, but could for example be sign errors when recalculating source data as well as considering/not considering chemical species in source data that can have an influence but are neglected. One example of the latter is in the case of log K for hematite: the complex ion $Fe(OH)_4^-$ is considered in the reaction in the PSI/NAGRA database, but not in others. This strongly influences the reported log K value in this case. Other causes of differences could be, when applicable, which solid phase condition was considered in the source work. Therefore it is important to clarify the status of a participating solid phase.

The PHREEQCI package is widely used in this kind of work and the included databases differ in varying degrees both in completeness/extension and in single values of log K. Therefore it is important to clarify which database has been used when reporting specific PHREEQCI results to facilitate subsequent comparisons with other results.

SKB have stated in their hydrochemical site descriptive model reports that they have used the wateq4f database, and they have justified this choice clearly and satisfactorily (Appendix B in Appendix 4 of SKB R-04-74 [8]).

The ultimate wish would be a complete review of all available thermodynamic data bases and a resulting, well motivated selection of data to formulate one trusted database to be used by PHREEQCI and other thermodynamically based modelling programs. However this is unlikely to be the case in the near future since there is so much ongoing research that revises thermodata and/or the speciations that are involved in equilibria, and each individual bit of experimental work is restricted to particular solution conditions and temperature range. The present situation is however adequate for present purposes. Errors in thermodynamic data as such are unlikely to be the major source of uncertainties in the outcomes from modelling, though the interpretation of redox equilibria is clearly dependent on identifying the relevant solid phases and being able to characterise these thermodynamically.

3.4.3 Modelling of pH and Redox in Forsmark

A set of E_h/pH diagrams for the iron, sulphur and chlorine systems were calculated with MEDUSA [5] at 25 ºC for the Forsmark data from the water samples from borehole intervals KFM01A/115, KFM01A/180, KFM02A/116, KFM02A/512, KFM03A/450, KFM03A/642 and KFM03A/990. The HYDRA database included in MEDUSA was used and the total concentrations of the iron and the sulphur systems as accounted in the Forsmark selected data set in Appendix 3 have been applied. The parameter values used in each E_h/pH diagram are listed in Appendix 5, which also shows an illustrative selection of diagrams. Some diagrams have been left out of the appendix, especially those only showing dissolved species and those with unlikely solid phases (e.g. Fe-ox-Cl solids). Details about borehole references and concentrations can be found in Appendix 3.

The specific pH and E_h data as selected and approved by SKB for modelling in the Forsmark data set (Appendix 3) were used in the present modelling work. The same pH data have been adjusted by modelling CO_2 loss using the saturation index method (see next section).

The set of diagrams in Appendix 5 show that there are, as expected, slight influences of variations in the total concentrations of the components. However, most measured pH/E_h points are located close to the HS^-/SO_4^{2-} line as also shown in Figure 1. Also solid phases like FeS_2 could be part of the E_h determining system.

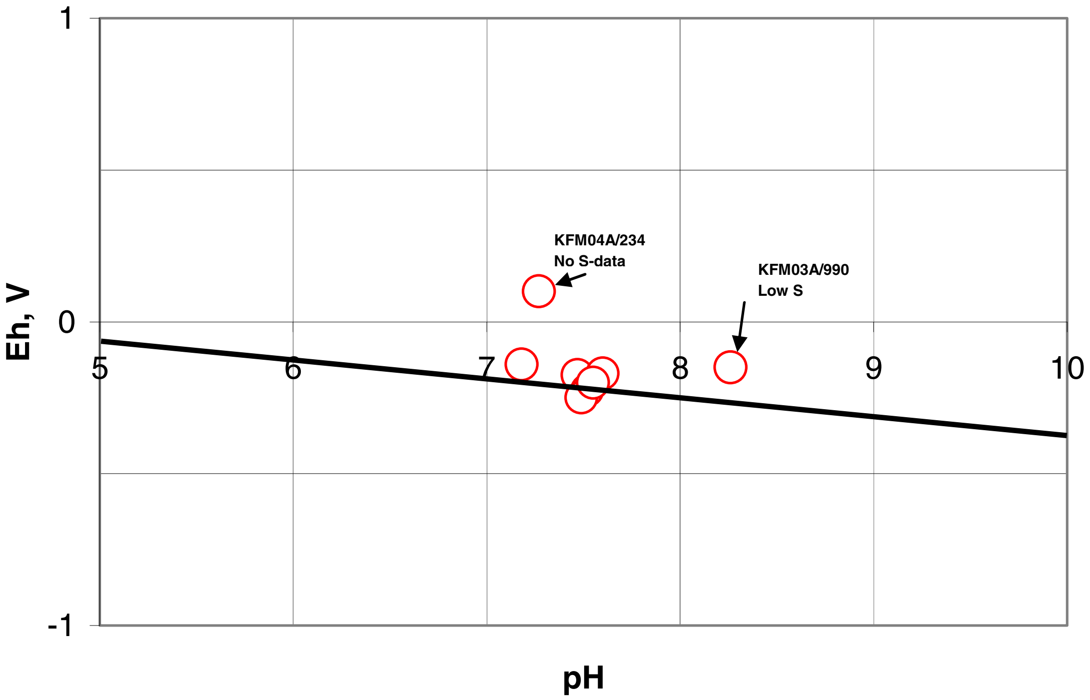

Figure 1. Compilation of pH/E_h data points from the selected set of groundwater data for Forsmark. The line represents the equilibrium of the couple HS^-/SO_4^{2-} when pH > 7.

Some comments on Figure 1:

- Most measured pH/E_h points are located close to the HS^-/SO_4^{2-} line, also as a function of pH. This would be expected if the couple HS^-/SO_4^{2-} determines E_h.
- Exceptions are for KFM04A/234, for which HS^-/SO_4^{2-} data are absent and for KFM03A/990 for which HS^-/SO_4^{2-} concentrations are very low.
- It thus seems as if the HS^-/SO_4^{2-} couple determines E_h at ‘normal’ concentrations (above about 0.5 mM and around 5 mM).
- If extreme data (KFM04A/234, KFM03A/990) are excluded, the spread in E_h would be around 150 mV. The spread in pH would be around 0.5 units.
- This spread in data would indicate that measured values fall within acceptable limits compared with what would be expected.
- If extreme values are included the spread is larger. Such values, however, seem in the selected cases to be a result of deviating/extreme conditions and not necessarily a result of bad sampling/analysis/data handling.

3.4.4 Modelling of pH and Redox in Forsmark and Simpevarp Groundwater Samples

Geochemical modelling with PHREEQCI was used for two purposes connected with uncertainties in key hydrochemical parameters: (i) to adjust pH to compensate for CO2 outgassing on the basis of an assumption that in situ groundwater should be at equilibrium with calcite, and (ii) to evaluate the hypothetical E_h on the basis of assumed control by Fe^{3+}/Fe^{2+}, $Fe(OH)_3/Fe^{2+}$ and SO_4^{2-}/HS^- redox couples.

Adjusting the reported pH to compensate for CO_2 outgassing was done by using the mixing-reaction mode of the computer program to theoretically 'titrate' CO_2 back into the water until calcite equilibrium was reached. Of course, if a solution is already saturated or over-saturated with calcite, then this exercise is not valid. However the majority of samples, in terms of their reported data, are under-saturated which supports the hypothesis that CO_2 outgassing might have occurred and would have led to rising pH and over-saturation with respect to calcite. These calculations were carried out with reported groundwater data from Forsmark and Simpevarp sites and also from the Äspö HRL. No data were yet reported from new boreholes at the Laxemar site at the time of carrying out this geochemical modelling.

The resulting 'adjusted' pH values are shown in Table 2, in the column headed 'Model pH at SI_c =0'. Adjusted pH data for Forsmark, Simpevarp and Äspö samples are typically 0.2 to 0.4 pH units lower than the measured values.

E_h was calculated according to the thermodynamics of the redox couples SO_4^{2-}/HS^-, Fe^{3+}/Fe^{2+} and $Fe(OH)_3/Fe^{2+}$. The latter calculation was done with thermodynamic data for the solubility of amorphous $Fe(OH)_3$ suggested by Grenthe et al. [15), based on a study of redox in deep groundwaters from various of SKB's early exploratory sites. Analytical data for the calculation of E_h for each of the redox couples with PHREEQCI were compiled from SKB reports (see Appendix 1), except that Fe^{3+} concentrations used here were obtained by subtraction of Fe^{2+} from Fe_{total}. In a few cases $Fe^{2+} \geq Fe_{total}$ and therefore no value can be given for Fe^{3+}. In all cases it is evident that calculating Fe^{3+} as the very small difference between two much bigger very similar values gives rise to very large uncertainty so that these calculated values for Fe^{3+} are generally invalid. SKB have not analysed Fe^{3+} directly because concentrations are so low that analyses using conventional methods would be unreliable for the purpose of redox calculation.

Measured and modelled redox values for groundwater samples from the Simpevarp/Äspö and Forsmark areas are compiled in Table 3 and are shown in Figures 2 and 3 respectively. Data are compiled from SKB's P and R reports. E_h data in parentheses are reported by SKB as unreliable and should be disregarded.

It is emphasised that the purpose of these calculations is to explore and illustrate the theoretical geochemical basis of this modelling and of the resulting inferences about redox conditions, redox indicators and redox buffering. It is also particularly to understand what are the assumptions, simplifications and uncertainties in interpreting hydrochemical data. The aim is not to compare directly calculated redox values with those calculated by similar methods and reported in SKB's site descriptive model reports. There are various understood and acceptable reasons why there might be small differences between model results here and those reported by SKB. Typically, differences of ±10 mV in calculated E_h are not surprising and have no significance for these purposes other than to illustrate one aspect of uncertainties.

Table 2. Data for pH adjustment calculations based on assumption that in situ waters are saturated with respect to calcite.

Sample	Depth, m	pH^1	pH^2	pH^3	HCO_3^- mg/L	Sat Index (calcite)	Log P_{CO2}	Model pH at SI_c=0
KFM01A/115	110.1-120.77	7.68	7.62	7.47	61	0.05	-2.92	7.41
KFM01A/180	176.8-183.9	7.41	7.41	7.60	99	0.39	-2.85	7.21
KFM02A/59	18-100.4			7.99	378	0.36	-2.52	7.61
KFM02A/116	106.5-126.5	(7.55)	7.53	7.52	353	0.37	-2.11	7.16
KFM02A/423	413.5-433.5		7.11	7.37	93	0.25	-2.64	7.12
KFM02A/512	509-516.08	6.83	6.93	7.18	125	0.13	-2.31	7.06
KFM03A/388	386-391		7.42	7.30	101	0.13	-2.53	7.17
KFM03A/450	448-453		7.58	7.49	91	0.31	-2.76	7.19
KFM03A/642	639-646.12	7.38	7.48	7.55	22	-0.04	-3.44	n/a
KFM03A/990	980-1001.19	(8)		8.26	6	0.31	-4.88	7.87
KFM04A/234	230.5-237.64		7.36	7.16	110	0.17	-2.36	7.00
KFM04A/357	354-361.13		7.33	7.27	78	0.13	-2.64	7.14
KSH01A/161	156.5-167		8.17	7.36	25	0.3	-4.0	7.79
KSH01A/253	245-261.5		8.08	7.34	17	0.2	-4.1	7.85
KSH01A/556	548-565		8.15	7.63	11	0.2	-4.5	8.00
KAS02/208	202-214.5		7.5	7.4	71	0.3	-2.9	7.20
KAS02/532	530-535		7.73	8	10	0.1	-4.3	7.88
KAS02/892	860-924.04		8.5	8.3	11	0.6	-5.0	7.77
KAS03/131	129-134		8	8	61	0.1	-3.4	7.88
KAS03/931	860-1002.06		8	8.1	11	0.3	-4.4	7.60
KAS04/338	334-343			8	69	0.6	-3.3	7.30
KAS04/460	440-480.98		8.1	8.1	21	0.4	-4.1	7.64

pH^1 = pH measured with borehole Chemmac system
pH^2 = pH measured with surface Chemmac system; these values were used as the basis for modelling the pH adjustment for KSH samples.
pH^3 = pH measured in laboratory; these values were used as the basis for modelling the pH adjustment for all samples except the KSH samples.
n/a = no adjustment of pH because Sat Index <0.

It is evident in Figures 2 and 3 that E_h calculated from the couples SO_4^{2-}/HS^- and $Fe(OH)_3/Fe^{2+}$ are rather close to the measured E_h in most cases. In contrast, the E_h calculated from the Fe^{3+}/Fe^{2+} couple is oxidising, i.e. a positive E_h, which is confidently the result of erroneous calculated Fe^{3+} values for the reason discussed above. $E_{hSO4/HS}$ is almost always less negative than $E_{hFe(OH)3/Fe2+}$. If KAS02/892 is discounted, $E_{hSO4/HS}$ is about 30 to 50 mV less negative than measured E_h in Äspö samples. It should also be noted that HS^- values from Forsmark samples are very low, at or close to the detection limit, whereas the historical values for Äspö area samples are rather higher. The reason for the difference is not evident and should be investigated, but the higher uncertainties due to near-detection limit HS^- should be propagated into the calculated $E_{hSO4/HS}$ for Forsmark samples.

$E_{hFe(OH)3/Fe2+}$ values are within +10 to -50 mV of the measured E_h in Äspö samples, but are about 100 mV more negative for the three Simpevarp samples, noting that Fe^{2+} values are higher for these samples. This raises a question about reasons for real differences in E_h at the two adjacent areas and/or sources of error in measured E_h values and analysed Fe^{2+} values. Another important factor in modelled $E_{hFe(OH)3/Fe2+}$ values and in the cumulative uncertainty about redox interpretation is pH, to which the $Fe(OH)_3$ - Fe^{2+} equilibrium is sensitive. Reported pH values for Simpevarp are lower than those for Äspö (Table 3).

Table 3. Measured E_h and redox-sensitive solutes and results from geochemical modelling of E_h for the SO_4^{2-}/HS^-, Fe^{3+}/Fe^{2+}, and $Fe(OH)_3/Fe^{2+}$ redox couples for groundwater samples from boreholes at Forsmark, Simpevarp, Äspö and Ävrö.

Sample	Depth, m	E_h^1	pH^4	SO_4^{2-} mg/L	HS^- mg/L	Fe_{tot} mg/L	Fe^{2+} mg/L	E_h SO_4/ HS	E_h^2 Fe^{3+}/ Fe^{2+}	E_h^3 $Fe(OH)_3$ /Fe^{2+}
KFM01A/115	110.1-120.77	-195	7.47	316	-0.03	1.00	0.95		190	-257
KFM01A/180	176.8-183.9	-188	7.60	547	-0.03	0.54	0.48		198	-260
KFM02A/116	106.5-126.5		7.52	90	0.01	1.35		-184		
KFM02A/423	413.5-433.5		7.37	434		0.75	0.73		185	-232
KFM02A/512	509-516.08	-143	7.18	498	0.01	1.85	1.84	-155	168	-222
KFM03A/450	448-453		7.49	472	-0.03	0.92	0.92			-257
KFM03A/452	448.5-456.6	-176	7.42	511	0.05	1.10	1.11	-178		-250
KFM03A/642	639-646.12	-196	7.55	197		0.23	0.23			-235
KFM03A/943	939.5-946.6	-245	7.78	74	0.06	0.22	0.21	-186	195	-207
KFM03A/990	980-1001.19	(-130)	8.26	47	0.03	0.03	0.03	-250	77	-300
KFM04A/234	230.5-237.64		7.16	514		2.13	2.12		172	-221
KFM04A/357	354-361.13	(100)	7.27			2.10	2.16			-241
KFM05A/717	712.6-722	(-274)								
KFM06A/357	353.5-360.6	-155	7.41	157						
KFM06A/771	768.0-775.1	(-200)	8.26	36	0.02					
KFM07A/925	848-1001.6	9	8.00	99						
KLX03/412	408-415.3	-275								
KSH01A/161	156.5-167	-257	7.36	32		1.413	1.397		58	-372
KSH01A/253	245-261.5	-160	7.34	51		1.318	1.296		63	-361
KSH01A/556	548-565	-173	7.63	230		0.523	0.511		77	-361
KAS02/208	202-214.5	-257	7.4	106	0.5	0.502	0.483	-196	172	-246
KAS02/532	530-535	-308	8	550	0.18	0.244	0.24	-227	53	-309
KAS02/892	860-924.04	-150	8.3	519	0.72	0.051	0.049	-269	14	-350
KAS03/131	129-134	-275	8	31	0.71	0.125	0.123	-237	61	-302
KAS03/931	860-1002.06	-275	8.1	709	1.28	0.078	0.077	-235	37	-274
KAS04/338	334-343	-275	8	220	0.41	0.327	0.324	-223	61	-304
KAS04/460	440-480.98	-280	8.1	407	0.6	0.259	0.256	-238	47	-328
KAV01/560	558-563	-225		220	0.81	1.02	1.02	-174		-212

E_h^1 = E_h as reported from borehole or surface Chemmac measurements and reported in P reports and/or R SDM reports; values in parentheses ( ) are reported to be unreliable measurements.

E_h^2 = modelled E_h for the Fe^{3+}/Fe^{2+} couple using a Fe^{3+} value calculated as the difference between Fe_{tot} and Fe^{2+}.

E_h^3 = modelled E_h for the $Fe(OH)_3/Fe^{2+}$ couple using the thermodynamic data for amorphous $Fe(OH)_3$ recommended by Grenthe et al. [15].

pH^4 = pH measured in the laboratory.

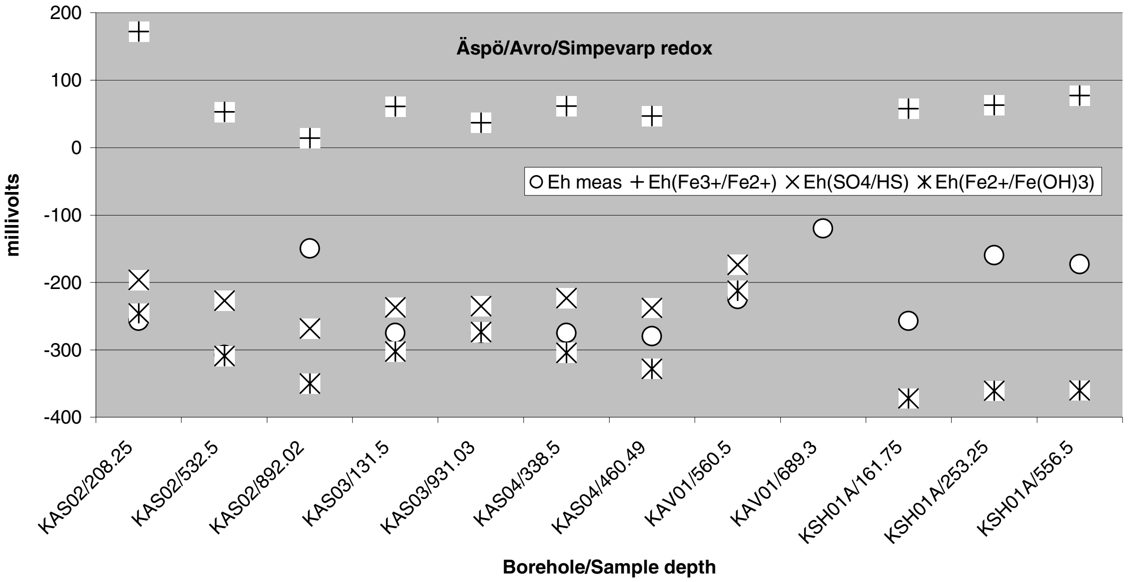

Figure 2. Compilation of calculated and measured E_h data points from the selected set of hydrochemical data from Äspö, Ävrö and Simpevarp.

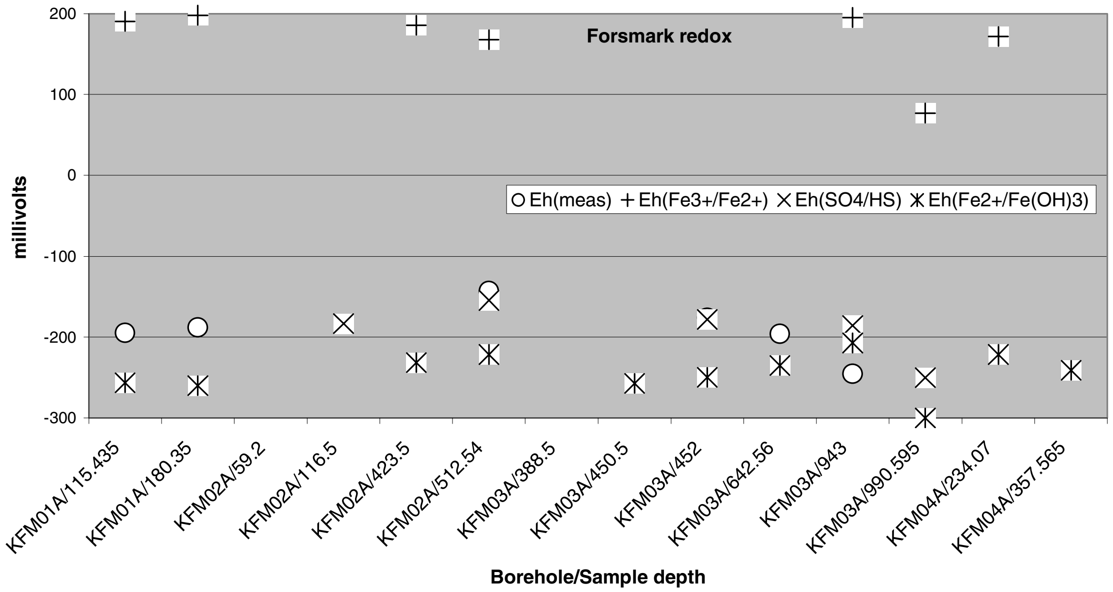

Figure 3. Compilation of calculated and measured E_h data points from the selected set of hydrochemical data from Forsmark.

3.5 Ranges of Uncertainties

3.5.1 pH

The modelled pH shown as 'Model pH at $SI_c = 0$' in Table 2, adjusted on the assumptions that CO_2 has been lost during sampling and that in situ groundwater is at equilibrium with calcite, is not necessarily the correct pH. It is one hypothesis for uncertainty in measured pH values. Evidence against this hypothesis comes from comparison of the downhole and surface Chemmac pH values with the lab pH values, as discussed above.

Downhole measurements should be the most reliable, but are higher than lab values (whereas CO_2 loss is expected to cause lab values to be higher). Accepting that the Chemmac tool and the lab pH measurements are put through well controlled calibration procedures, there are not obvious explanations for these apparent inconsistencies. Therefore there may be another source of variation or uncertainty, in addition to or instead of outgassing, which has not been recognised.

Overall uncertainty in pH is estimated, based on the data in Table 2, as typically 0.2 to 0.4 pH units. The lower end of the possible range for an in situ pH value 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.

An important consideration in discussing uncertainties in pH is the process that regulates pH. Because pH, i.e. $\log_{10} [H^+]$, represents a very low concentration of protons, it is sensitive to water-rock reactions and is susceptible to various perturbations which are then counteracted by water-rock equilibrium. The key reactions are reversible carbonate equilibria, both in solution and between solid and solution, and irreversible silicate alteration. The primary buffer of pH, in terms of reversibility and fast reaction, is the carbonate system – in simple terms, the lower the concentrations of dissolved carbonate species, the less well-buffered will be pH. Table 2 shows that most deep groundwaters have low to very low HCO_3^- concentrations which are semi-correlated with increasing salinity. pH is coupled to the evolution of the dissolved carbonate species, so in general terms a more saline groundwater, evolving towards a high-Ca, low-HCO_3, composition has a higher pH typically >8 which is more sensitive to perturbation and thus has rather higher uncertainty. This consideration has to be taken into account when considering what are reasonable and acceptable ranges of uncertainty or reliability in pH measurements when comparing reported data with suitability criteria or when using them for geochemical modelling of EBS reactions or of radionuclide speciation.

3.5.2 Redox

As seen in Figures 2 and 3 there seem to be typical differences of -30 to -50 mV and +50 mV between measured E_h and $E_{hSO4/HS}$ and $E_{hFe(OH)3/Fe2+}$ respectively. Therefore ±100 mV would be a conservatively pessimistic assumption for the uncertainty on redox estimations from E_h measurements and from Fe^{2+} and HS^- analyses as long as unreliable and near-detection limit (or near-quantification limit, which is usually about 3x the detection limit value) data for the redox-sensitive solutes are discounted and erroneous extreme measurements of E_h can be confidently detected and discarded.

However discrepant measurements of E_h (or pH also) should not be discounted simply because they are anomalous. It would be wrong in comparing in situ parameter values with suitability criteria to predetermine that any anomalies outside ‘expected’ ranges are *per se* erroneous. Evidence-based reasoning to interpret the reliability of data, which is exemplified in SKB’s P reports of site data, is required.

The comparisons of measured and calculated redox potentials and the systematic differences suggest that there is a significant amount of bias rather than random uncertainty. As explained above, this might be due to non-equilibrium or kinetic factors, or it might be due to failure to identify controlling solid phases or solute species, or error in thermodynamic data. It might be that the bias could be attributed to error in correlated parameters which could be addressed with corrective measures. The SO_4^{2-}/HS^- and $Fe(OH)_3/Fe^{2+}$ redox equilibria are pH-dependent, and 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 (see Figure 1) 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.

3.5.3 Salinity

The variability and reproducibility of salinity measurements have not been examined in the way that pH and redox measurements have been considered in the above sections. Salinity and the underlying measurements, namely electrical conductivity, TDS and chloride, are less prone to significant uncertainties than pH and redox. The estimated maximum overall uncertainty quoted by SKB is ±10% and this seems to be a reasonable and cautious general value.

The other issue to be considered for salinity is whether the raw data for chloride and TDS might be corrected for dilution by flushing water, using the simple tracer data and/or results from the drilling impact study (DIS) method [16]. Although mixing with flushing water is a similar or even greater issue for the reliability of pH and redox for in situ conditions than it is for salinity, the perturbations of pH and redox by such mixing are non-linear and not reliably estimated or predicted and are thus included in the overall uncertainty estimate. Salinity, chloride and TDS are, however, perturbed by linear mixing and so can in theory be corrected by a simple mixing calculation. However SKB have done this only for a set of water samples from one sampled interval in KSH01A (see Appendix 1).

Therefore the uncertainty estimate of ±10% is valid only for samples which comply with SKB's acceptability criterion of <1% flushing water (or perhaps up to <5%).

3.5.4 Other Parameters (DOC, colloids, microbes)

There have not been sufficient data reported so far for these and other parameters that relate to SKB's 'suitability criteria' or other important aspects of site geochemistry to make an independent assessment of the uncertainties. These issues should be examined in the future when more data and supporting raw data interpretations are available.

4 Spatial Variability

Spatial variability of geochemical properties within investigated sites is one of the main challenges for interpretation of the limited quantities of data and of the associated uncertainties.

Spatial variability of groundwater compositions is an established feature of the sites. In addition to the inherent significance of variability with respect to suitability criteria especially at repository depth in the target area, variability should also be understood in relation to the hydrogeological and palaeohydrogeological groundwater flow models, and preferably also at the scale of distinct flow pathways, i.e. transmissive deformation zones.

Heterogeneity of groundwater salinity and other compositional parameters indicates a complexity of flow field and velocities with which the groundwater model for safety assessment should be consistent, and that should be reflected in the evaluation of uncertainties and alternative models.

4.1 Limited Distribution of Data

3D spatial variability of geochemical data, especially groundwater compositions, is an important aspect of site evaluation and groundwater model testing. The quantity of geochemical data acquired so far and the associated uncertainties in values indicate that explorative interpretation and quantitative modelling (with thermodynamic and statistical models) of groundwater chemistry will be based on a sparse distribution of data. The different uses of hydrochemical data each have different requirements in terms of reliability and quantification of uncertainties.

4.2 Geochemical Conditions at Repository Depth

Homogeneity of redox and other key chemical parameters within a proposed repository location would need to be supported by a spatially-representative set of site specific redox-related data for both waters and minerals plus geochemical reasoning for the buffering capacity and the potential magnitudes of change over time in the future.

At Forsmark only three out of twelve sampled points are in repository depth range and none of those are in SKB's preferred area. It is not yet clear whether apparent redox variation at Forsmark (see Table 3 and Figure 3) is entirely attributable to data uncertainties, or at least partly reflects spatial variations in the water-rock reactions that locally control redox. On the other hand, pH variation in repository depth samples from Forsmark is so far less significant.

5 Summary and Conclusions

The work described in this report is a development of SKI's capability for the review and evaluation of data that will constitute part of SKB's case for selection of a suitable site and application to construct a geological repository for spent nuclear fuel.

The aim has been to integrate a number of different approaches to interpreting and evaluating hydrochemical data, especially with respect to the parameters that matter most in assessing the suitability of a site and in understanding the geochemistry and groundwater conditions at a site. It has been focused on taking an independent view of overall uncertainties in reported data, taking account of analytical, sampling and other random and systematic sources of error. The insights and principles that are discussed here should be applicable for evaluating key hydrochemical parameters for SKB's target sites at Forsmark and Laxemar.

This evaluation was carried out initially with a compilation and general inspection of data from the Simpevarp, Forsmark and Laxemar sites plus data from older 'historical' boreholes in the Äspö area. That was followed by a more specific interpretation by means of geochemical calculations which test the robustness of certain parameters, namely pH and redox/E_h (which is a proxy for dissolved oxygen). Geochemical model calculations have been carried out with widely available computer software. The work is a continuation of that reported in [1] for which the focus was on planning of subsequent work, on the review and selection of a computer program and thermodynamic database, and on preliminary geochemical model calculations.

Data sources and their handling were also considered, especially access to SKB's SICADA database. Direct access to SICADA has not been established in the way that was originally intended. Instead, extracts from SICADA provided by SKB as well as data from SKB's P- and R-reports have been used for the present work.

In preparation for the use of geochemical modelling programs and to establish comparability of model results with those reported by SKB, the underlying thermodynamic databases were compared with each other and with other generally accepted databases. Comparisons of log K data for selected solid phases and solution complexes from the different thermodynamic databases were made. The selected data and comments on the comparisons can be seen in Appendix 4. In general, there is a large degree of comparability between the databases, but there are some significant and in a few cases large differences. The present situation is however adequate for present purposes. Errors in thermodynamic data *per se* will not be the major source of uncertainties in the outcomes from modelling, though the interpretation of redox equilibria is clearly dependent on identifying the relevant solid phases and being able to characterise these thermodynamically.

Geochemical modelling with the MEDUSA program was used to construct a set of E_h/pH diagrams for the iron, sulphur and chlorine systems at Forsmark. The HYDRA thermodynamic database included in MEDUSA was used and the total concentrations of dissolved iron and sulphur as accounted in the Forsmark selected data set in Appendix 3 have been applied. The parameter values used in each E_h/pH diagram are listed in Appendix 5, which also shows an illustrative selection of diagrams. Some diagrams have been left out of the appendix, especially those only showing dissolved species and those with unlikely solid phases (e.g. Fe-ox-Cl solids).

Geochemical modelling with the PHREEQCI program was used for two purposes connected with uncertainties in key hydrochemical parameters: (i) to adjust pH to compensate for CO_2 outgassing on the basis of an assumption that in situ groundwater should be at equilibrium with calcite, and (ii) to evaluate the hypothetical E_h on the basis of assumed control by Fe^{3+}/Fe^{2+}, $Fe(OH)_3/Fe^{2+}$ and SO_4^{2-}/HS^- redox couples so as to assess evidence for control and buffering of redox and for reactivity of other redox-sensitive parameters.

These calculations were carried out with reported groundwater data from Forsmark and Simpevarp sites and also from the Äspö HRL (Appendix 3; Tables 2 and 3). No data were yet reported from new boreholes at the Laxemar site at the time of carrying out this geochemical modelling.

It is emphasised that the purpose of these calculations is to explore and illustrate the theoretical basis of geochemical interpretations, and to understand what are the assumptions, simplifications and uncertainties in interpreting hydrochemical data. The aim is not to compare directly calculated redox values with those calculated by similar methods and reported in SKB's site descriptive model reports.

The main conclusions from the modelling of pH and redox are:

- pH data for Forsmark, Simpevarp and Äspö samples, when adjusted to compensate for CO_2 outgassing, are typically 0.2 to 0.4 pH units lower than the measured values. However these modelled pH values are not necessarily correct. They are hypotheses for uncertainty in measured pH values, and conflicting evidence comes from comparison of the downhole and surface Chemmac pH values with the lab pH values. Therefore there may be another source of variation or uncertainty, in addition to or instead of outgassing, which has not been recognised.

- pH is sensitive to water-rock reactions and is susceptible to various perturbations which are then counteracted by carbonate equilibria and silicate alteration. Most deep groundwaters have low to very low HCO_3^- concentrations which are semi-correlated with increasing salinity, so in general terms a more saline groundwater has a higher pH typically >8 which is more sensitive to perturbation and thus has rather higher uncertainty.

- Most measured pH/E_h points are located close to the HS^-/SO_4^{2-} line in the Pourbaix E_h/pH diagram, suggesting that the couple HS^-/SO_4^{2-} controls E_h at 'normal' SO_4^{2-} concentrations (above about 0.5 mM and around 5 mM). If extreme data that are thought to be erroneous are excluded, the spread in E_h would be around 150 mV which is substantial; the geochemical significance for this needs to be understood. The spread in pH is around 0.5 units. This spread in measured E_h data indicates that measured values fall within acceptable limits but realistic or cautious estimates of uncertainties on these values, and the significance of spatial variability also need to be taken into account.

- E_h was also modelled for the redox couples SO_4^{2-}/HS^-, Fe^{3+}/Fe^{2+} and $Fe(OH)_3/Fe^{2+}$, the latter according to Grenthe et al. [15]. E_h calculated from the couples SO_4^{2}/HS^- and $Fe(OH)_3/Fe^{2+}$ are rather close to the measured E_h in most cases. In contrast, the E_h calculated from the Fe^{3+}/Fe^{2+} couple is oxidising, i.e. a positive E_h, which is the result of erroneous Fe^{3+} values which were obtained simply by subtraction of Fe^{2+} from Fe_{total}. $E_{hSO4/HS}$ is almost always less negative than $E_{hFe(OH)3/Fe2+}$. There are high uncertainties in $E_{hSO4/HS}$ for Forsmark samples because HS^- data are near or at the analytical detection limit. pH is an important factor in modelled $E_{hFe(OH)3/Fe2+}$ values and in the cumulative uncertainty about redox interpretation.

- There are typical differences of -30 to -50 mV and +50 mV between measured E_h and $E_{hSO4/HS}$ and $E_{hFe(OH)3/Fe2+}$ respectively. Therefore ±100 mV is a cautious assumption for the uncertainty on redox estimations from E_h measurements and from redox modelling as long as unreliable and near-detection limit data for Fe^{2+} and HS^- are discounted and erroneous extreme measurements of E_h can be confidently detected and discarded.

- Discrepant measurements of E_h (and pH also) should not be discounted simply because they are anomalous. Evidence-based reasoning to interpret the reliability of data, which is exemplified in SKB's P reports of site data, is required.

- Comparisons of measured and calculated redox potentials and the systematic differences suggest that there is a significant amount of bias rather than random uncertainty. This might be due to non-equilibrium or kinetic factors, or it might be due to failure to identify controlling solid phases or solute species, or error in thermodynamic data. There is also the dependence of the various redox couples on pH to be considered. A potential difference of about -50 mV could for example be explained by an error in pH of about 0.7.

- Understanding of the variability of redox and other key chemical parameters within a proposed repository location will need to be supported by spatially-representative redox data for waters and minerals plus geochemical reasoning for the buffering capacity and the potential magnitudes of change over time in the future.

- It is not yet clear whether apparent redox variation at Forsmark is attributable to data uncertainties or reflects spatial variations in the water-rock reactions that locally control redox.

The conclusions concerning other important hydrochemical parameters are:

- Uncertainty in all hydrochemical data arises from the effect of mixing with flushing or other extraneous water. The perturbations of pH and redox by such mixing are non-linear and not reliably estimated or predicted and are thus included in the overall uncertainty estimate.

- Salinity and the underlying measurements, namely electrical conductivity, TDS and chloride, are less prone to significant uncertainties than pH and redox. The estimated maximum overall uncertainty quoted by SKB is ±10% and this seems to be a reasonable and cautious general value. The uncertainty estimate of ±10% in salinity (chloride or TDS) is valid only for samples which comply with SKB's acceptability criterion of <1% flushing water (or perhaps up to <5%).

- Raw data for chloride and TDS could be corrected for dilution by flushing water, using the simple tracer data and/or results from the drilling impact (DIS) study method. However SKB have done this only for a set of water samples from one sampled interval in KSH01A (see Appendix 1).

- There have not been sufficient data reported so far for DOC, colloids, microbes and other parameters that relate to SKB's 'suitability criteria' or other important aspects of site geochemistry to make an independent assessment of the uncertainties. These issues should be examined in the future when more data and supporting raw data interpretations are available.

- Spatial variability of groundwater compositions is one of the main challenges for interpretation of the limited quantities of data and of the associated uncertainties. In addition to variability of suitability parameters at repository depth in the target area, variability should also be understood in relation to the hydrogeological and palaeohydrogeological groundwater flow models, and preferably also at the scale of distinct flow pathways. The different uses of hydrochemical data each have different requirements in terms of reliability and quantification of uncertainties.

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Appendix 1: Method Documents (MDs)

Method Documents (MDs) for hydrochemical data acquisition.

SKB MD number	Titel/Title	Version, Date	Avail -able	Short comments
422.001-02	Metodbeskrivning för hydrokemisk loggning Method description for hydrochemical logging	2.0. May 2005	Yes	What means 'treatment and QC of SICADA raw data'?
423.002-02	Metodbeskrivning för vattenprovtagning i hammarborrhål efter borrning Method description for water sampling in percussion boreholes after drilling	2.0, June 2005	Yes	OK
423.003-02	Metodbeskrivning för provtagning och analys av nederbörd Method description for sampling and analysis of precipitation	2.0, May 2005	Yes	OK
430.016-0?	Mätsystembeskrivning för mobilt fältlaboratorium Description of measurement system for the mobile field laboratory	Latest ver	No	Not available
430.017-02	Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium Method description for comprehensive chemical characterisation with the mobile field laboratory	2.0, May 2005	Yes	Very important MD. OK
430.018-02	Metodbeskrivning för vattenprovtagning och on-line mätning i borrhål Method description for water sampling and on-line measurement in bore holes	2.0, May 2005	Yes	OK
433.018-01	Mätsystembeskrivning – Mätapplikation. Beskrivning av användarinterface Method description – Measurement application. Description of user interface	1.0, March 2003	Yes	The largest part of the document is not accessible
434.004-01	Mätsystembeskrivning – Allmän del. Mobila kemienheter Measurement system description – General part. Mobile chemistry units	1.0, April 2003	Yes	OK
434.005-02	Mätsystembeskrivning – Handhavande del. Slangvagn S2 och S3 Measurement system description – Handling part. Tubewagon S2 and S3	2.0, Feb 2006	Yes	OK
434.006-01	Mätsystembeskrivning – Handhavande del. Mobila kemienheter – Borrhålsutrustning, BU2, BU3 och BU4 Measurement system description – Handling part. Mobile chemistry units – Borehole equipment, BU2, BU3 and BU4	1.0, April 2003	Yes	How is the electrochemical connection between reference and working electrodes arranged?

SKB MD number	Titel/Title	Version, Date	Avail -able	Short comments
434.007-02	Mätsystembeskrivning – Handhavande del. Mobila kemienheter – Chemmac mätsystem Measurement system description – Handling part. Mobile chemistry units – The Chemmac measurement system	2.0, Feb 2006	Yes	Reporting to SICADA?
450.001-0?	Instruktioner för provtagning och analys Instructions for sampling and analysis	Latest ver?	No	Not available
451.001-03	Ackrediteringens omfattning Accreditation scope	3.0, May 2004	Yes	Method list OK
451.002-02	Kvalitetspolicy för SKB:s vattenkemiska analysverksamhet Quality policy for SKB's water chemistry analytical operation	2.0, Nov 2001	Yes	OK
451.004-04	Beskrivning av SKBs vattenkemiska analysverksamhet Description of SKB's water chemistry analytical operation	4.0 March 2004	Yes	HS^-
451.005-04	Underleverantörer som anlitas vid SKBs vattenkemiska analyslaboratorier Subcontractors who are engaged at SKB's water chemistry analytical laboratories	4.0, April 2004	Yes	OK
451.006-03	Rapportering av data från SKB:s kemilaboratorium Reporting of data from SKB's chemistry laboratory	3.0, March 2004	Yes	OK
451.007-03	Arkivering av information från SKB:s kemilaboratorium Archiving of information from SKB's chemistry laboratory	1.0, May 2001	Yes	OK
451.008-05	Dokumentstyrning Document control	5.0 Dec 2003	Yes	OK
451.012-02	Referensmaterial som används i SKBs vattenkemiska analysverksamhet Reference materials which are used in SKB's water chemistry analytical operation	2.0, May 2002	Yes	OK
451.013-03	Rapportering av data till SICADA Reporting of data to SICADA	3.0, March 2004	Yes	How exactly is the QC and selection done?
452.001-02	Provtagning och provhantering Sampling and sample handling	2.0, Oct 2003	Yes	OK
452.002-02	Kalibreringsprogram Calibration programme	2.0, Jan 2004	Yes	OK
452.003-02	pH-analys med PHM 240 pH analysis with the PHM 240	2.0, Aug 2001	Yes	OK
452.004-03	Konduktivitetsanalys med CDM-230 Conductivity analysis with the CDM-230	3.0, May 2001	Yes	OK
452.005-02	Titrerutrustning TIM900 Autotitrator TIM900	2.0, Aug 2001	Yes	OK
452.006-02	Alkalinitet Alkalinity	2.0, Sept 2001	Yes	OK
452.007-03	Klorid Chloride	3.0, Sept 2001	Yes	OK

SKB MD number	Titel/Title	Version, Date	Avail -able	Short comments
452.009-03	Ammonium Ammonium	3.0, April 2004	Yes	OK
452.010-03	Järn Iron	3.0, April 2004	Yes	OK
452.011-03	Sulfid Sulphide	3.0, April 2004	Yes	OK
600.004-01	Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning Instruction for cleaning of bore hole equipment and some surface based equipment	1.0, Feb 2002	Yes	OK
	Missing MDs (in preparation?) without title and number:			
?	MD for pressurized sampling for gas and bacteria analyses	Latest ver?	No	Not available
?	MD for sampling of colloids (filter) and analyses of colloids	Latest ver?	No	Not available
?	MD for sampling and analyses of humic/fulvic acids	Latest ver?	No	Not available

Appendix 2: SKB's P reports

SKB's P reports which describe the acquisition of hydrochemical data.

Simpevarp

Report no	Title	Date
P-03-113	Drilling of cored borehole KSH01	Mar 2004
P-04-151	Drilling of cored borehole KSH02	Sept 2004
P-04-233	Drilling of cored borehole KSH03	Oct 2004
P-05-25	Drilling of cored borehole KAV04	Jan 2005
P-05-194	Percussion drilling of boreholes HSH04, HSH05, HSH06, HAV11, HAV12, HAV13 and HAV14.	Aug 2005
P-03-87	Hydrochemical logging in KSH01A	Apr 2003
P-03-88	Hydrochemical logging in KSH02	Oct 2003
P-04-51	Hydrochemical logging in KSH03A	Mar 2004
P-05-54	Hydrochemical logging in KSH03A – Results from isotope determinations (^{3}H, δD, δ^{18}O and δ^{37}Cl)	June 2004
P-03-89	Hydrochemical logging in KAV01	Oct 2003
P-04-220	Hydrochemical logging in KAV04A	Aug 2004
P-04-304	Hydrochemical logging in KAV04A – Results from isotope determinations (^{3}H, δ^{2}H and δ^{18}O)	Nov 2004
P-04-12	Complete hydrochemical characterisation in KSH01A – Results from four investigated sections, 156.0-167.0, 245.0-261.6, 586.0-596.7 and 548.0-565.4 m	Dec 2004
P-04-276	Total numbers and metabolic diversity of microorganisms in borehole KSH01A – Results from three investigated sections, 158.7-167 m, 245-261.6 m and section 548-565 m	Mar 2004
P-04-281	Water sampling in KSH02A – Summary of water sampling analysis in connection with Pipe String System (PSS) and Single Well Injection Withdrawal (SWIW) measurements	June 2004
P-04-249	Borehole KSH02: Characterisation of matrix pore water (Feasibility Study)	Apr 2004
P-04-13	Surface water sampling at Simpevarp 2002-2003	Feb 2004
P-06-127	Hydrochemical monitoring programme for core drilled boreholes 2005. Summary of analyses from water sampling	Sept 2006

Forsmark

Report no	Title	Date
P-03-32	Drilling of the telescopic borehole KFM01A at drilling site DS1	May 2004
P-03-52	Drilling of the telescopic borehole KFM02A at drilling site DS2	June 2004
P-03-95	Hydrochemical logging and "clean up" pumping in KFM02A	Oct 2003
P-03-96	Hydrochemical logging in KFM03A	Dec 2003
P-04-47	Hydrochemical logging of KFM04A	Mar 2004
P-05-33	Hydrochemical logging in KFM06A	Jan 2005
P-05-187	Hydrochemical logging in KFM07A	June 2005
P-05-206	Hydrochemical logging in KFM08A	Oct 2006
P-06-95	Hydrochemical logging in KFM09A	May 2006
P-06-179	Hydrochemical logging in KFM09B	Sept 2006
P-03-47	Sampling and analyses of groundwater in percussion drilled boreholes and shallow monitoring wells at drillsite DS1 – Results from the percussion boreholes HFM01, HFM02, KFM01A (borehole section 0-100 m) and the monitoring wells SFM0001, SFM0002 and SFM0003	Mar 2003
P-03-48	Sampling and analyses of groundwater in percussion drilled boreholes and shallow monitoring wells at drillsite DS2 – Results from the percussion boreholes HFM04, HFM05, KFM02A (borehole section 0-100 m) and the monitoring wells SFM0004 and SFM0005	Apr 2003

Report no	Title	Date
P-03-49	Sampling and analyses of groundwater in percussion drilled boreholes at drillsite DS3 – Results from the percussion boreholes HFM06 and HFM08	Apr 2003
P-04-92	Sampling and analyses of groundwater from percussion drilled boreholes – Results from the percussion boreholes HFM09 to HFM19 and the percussion drilled part of KFM06A	June 2004
P-05-48	Sampling and analyses of groundwater from percussion drilled boreholes – Results from percussion drilled boreholes HFM20, HFM21 and HFM22	Feb 2005
P-03-94	Complete hydrochemical characterisation in KFM01A – Results from two investigated sections, 110.1-120.8 and 176.8-183.9 metres	Dec 2003
P-04-70	Hydrochemical characterisation in KFM02A – Results from three investigated sections; 106.5-126.5, 413.5-433.5 and 509.0-516.1 m	May 2004
P-04-108	Hydrochemical characterisation in KFM03A – Results from six investigated borehole sections: 386.0-391.0 m, 448.0-453.0 m, 448.5-455.6 m, 639.0-646.1 m, 939.5-946.6 m, 980.0-1001.2 m	May 2004
P-04-109	Hydrochemical characterisation in KFM04A – Results from two investigated borehole sections, 230.5-237.6 and 354.0-361.1 metres	June 2004
P-05-178	Chemical characterisation in borehole KFM06A – Results from the investigated sections at 266.0-271.0 m, 353.5-360.6 m and 768.0-775.1 m	Oct 2005
P-05-170	Chemical characterisation in borehole KFM07A – Results from the investigated section at 848.0-1001.6 m	Sept 2005
P-06-63	Hydrochemical characterisation in Borehole KFM08A	June 2006
P-06-217	Hydrochemical characterisation in borehole KFM09A. Results from the investigated section at 785.1-792.2 m	Sept 2006
P-05-171	Sampling and analyses of near surface groundwaters – Results from sampling of shallow soil monitoring wells, BAT pipes, a natural spring and private wells May 2003-April 2005	Sept 2005
P-03-27	Sampling and analyses of surface waters – Results from sampling in the Forsmark area, March 2002-March 2003	May 2003
P-05-274	Sampling and analyses of surface waters – Results from sampling in the Forsmark area, March 2004-June 2005	Dec 2005
P-04-136	Undisturbed pore water sampling and permeability measurements with BAT filter tips – Soil sampling for pore water analyses	June 2004
P-06-57	Hydrochemical monitoring of percussion- and core drilled boreholes – Results from water sampling and analyses during 2005	Apr 2006

Laxemar

Report no	Title	Date
P-05-167	Drilling of cored borehole KLX03	July 2005
P-05-111	Drilling of cored borehole KLX04	June 2005
P-05-41	Compilation and evaluation of data from monitoring of flushing water from KLX03 and KLX04	Apr 2005
P-05-233	Drilling of cored borehole KLX05	Jan 2006
P-05-234	Drilling of cored borehole KLX06	Nov 2005
P-04-299	Hydrochemical logging in KLX03A	Nov 2004
P-05-89	Hydrochemical logging in KLX03 – Results from isotope determinations (^{3}H, δD and δ^{18}O)	June 2005
P-05-88	Hydrochemical logging in KLX04 – Results from isotope determinations (^{3}H, δD and δ^{18}O)	June 2005
P-05-195	Hydrochemical logging in KLX05	Nov 2005
P-06-17	Hydrochemical logging in KLX05 – Results from isotope determinations (^{3}H, δD and δ^{18}O)	Jan 2006
P-05-85	Hydrochemical logging in KLX06	Sep 2005

Report no	Title	Date
P-05-244	Hydrochemical logging in KLX06 – Results from isotope determinations (^{3}H, δD and δ^{18}O)	Dec 2005
P-05-226	Hydrochemical logging in KLX07A	Nov 2005
P-06-16	Hydrochemical logging in KLX07A – Results from isotope determinations (^{3}H, δD and δ^{18}O)	Feb 2006
P-05-230	Hydrochemical logging in KLX08	Sept 2005
P-06-47	Hydrochemical logging in KLX09	Feb 2006
P-06-142	Hydrochemical logging in KLX12A	Aug 2006
P-05-271	Water sampling in KLX04 and KLX06. Summary of analyses from water sampling during pumping with the Pipe String System	June 2006
P-05-177	Numbers and metabolic diversity of microorganisms in boreholes KFM06A and KFM07A – Results from sections 353.5-360.6 and 768-775 in KFM06A and section 848-1001.6 m in KFM07A	June 2005
P-06-12	Borehole KLX03: Characterisation of pore water. Part 1: Methodology and analytical data	Jan 2006
P-06-77	Borehole KLX03: Characterisation of pore water – Part 2: Rock properties and diffusion experiments	Apr 2006

Appendix 3: Temporary spreadsheet

Temporary spreadsheet of key hydrochemical parameters from SKB’s site investigation reports

Dark grey shading indicates higher status (i.e. ‘recommended’) in SKB’s SDM reports, light grey shading indicates lower status (i.e. ‘use with caution’), and no shading indicates status unknown.

(Note: This data compilation is for the purposes of this report only. Data in it are compiled from various SKB reports and may not be identical to data approved by SKB for use in final site descriptive models)

Sample	SKB No	Type*	Depth range	Date	Drill water	pH Chemmac	+/-	pH surf Chem	+/-	pH lab	pH for model	Temp Chem-mac	Diss O_2	Eh Chemmac	+/-	Eh Fe^{3+}/ Fe^{2+}	Eh SO_4^{2-}/ S^{2-}	Eh $Fe(OH)_3$ /Fe^{2+}	Na	K	Ca	Mg	Cl	SO_4	HCO_3	Charge bal
			m bgl		%							°C	mg/L	mV					mg/L							%
FORSMARK																										
KFM01A/115	4538	Chem	110.1-120.77	2003-02-24	0.76	7.68	0.22	7.62	0.06	7.47	7.47	6.90	<0.2	-195	32	190		-257	1740	25.6	874	142	4563	316	61	-1.6
KFM01A/180	4724	Chem	176.0-183.9	2003-03-31	4.00	7.41	0.18	7.41	0.25	7.60	7.60	7.57	<0.1	-100	16	190		-260	2000	29.2	934	204	5330	547	99	-3.0
KFM02A/59	4398	HTHB	18-100.4	2002-11-28						7.99	7.99								168	6.5	34	8	84	54	378	0.6
KFM02A/118	8100	PTest	106.5-126.5	2003-11-18	0.40	(7.55)		7.53	0.09	7.52	7.52			(-200, -250)			-184		386	9.7	139	31	642	90	353	-0.1
KFM02A/423	8272	PTest	413.5-433.5	2004-02-23	2.10			7.11	0.10	7.37	7.37					185		-232	1820	21.4	1140	198	5300	434	93	-2.9
KFM02A/512	8016	Chem	509-516.08	2003-10-20	6.77	6.83	0.15	6.93	0.24	7.18	7.18	11.35	<0.01	-143	30	168	-155	-222	2040	34.2	934	226	5410	498	125	-3.1
KFM03A/388	8012	PTest	386-391	2003-10-06	0.55			7.42	0.12	7.30	7.30								2110	47.6	925	223	5450	495	101	-2.5
KFM03A/450	8017	PTest	448-453	2003-10-24	0.25			7.50	0.12	7.49	7.49	10.70	<0.01					-257	2070	26.0	985	202	5430	472	91	-2.4
KFM03A/452	8284	Chem	448.5-455.6	2004-04-27	0.40	7.29	0.14	7.27	0.42	7.42				-176	10				2180	27.5	1070	216	5330	511	93	1.4
KFM03A/642	8273	Chem	639-646.12	2004-02-23	4.35	7.38	0.12	7.48	0.32	7.55	7.55	13.05	<0.01	-196	12			-235	1660	14.3	1440	53	5430	197	22	-2.8
KFM03A/943	8281	Chem	939.5-946.6	2004-03-29	8.80	7.32	0.15	7.53	0.12	7.78				-245	12				1890	10.4	3100	18	8560	74	9	-0.8
KFM03A/990	8152	Chem	980-1001.19	2003-12-08	3.05	(8)				8.26	8.26	10.00	<0.01	(-130)		77	-250	-300	1980	6.9	3550	8	9690	47	6	-1.0
KFM04A/234-incline	8267	Chem	230.5-237.64	2004-02-10	7.45			7.36	0.09	7.16	7.16					172		-221	1820	25.6	1340	224	5580	514	110	-1.3
KFM04A/357-inclin	8287	Chem	354-361.13	2004-05-10	6.50			7.33	0.12	7.27	7.27	5.57	<0.01	(100)				-241	1980	13.8	1540	165	5780		78	3.8
KFM05A-inclined at	8601	Chem	712.6-722		2.10	(-7.5)		7.00					(<0.01)	(-274)	~100								(4500)			
KFM06A/357-incline	8838	Chem	353.5-360.6		7.10	6.91	1.53	7.33	0.63	7.41			<0.01	-155	7				1470	13.4	1280	74	4850	157	48	-2.3
KFM06A/771-inclin	8785	Chem	768.0-775.1		1.60	8.31	0.32	8.22	0.17	8.26			<0.01	(-200)	51				1690	6.8	2500	4	7080	36	6	-0.3
KFM07A/925-incline	8879	Chem	848-1001.6		0.35	8.04	0.30	8.05	0.15	8.00			<0.01	9	7				2050	13.7	5040	20	14000	99	6	-0.1
LAXEMAR																										
KLX01/274	1537	Chem	272-277	1988-12-08	4.60	8.50				8.10	8.10								1040	6.20	243	20.0	2050	40	83	-0.2
KLX01/458	1528	Chem	456-461	1988-11-23	13.70			8.70		8.20	8.20								860	6.10	223	18.0	1700	106	78	-1.2
KLX01/691	1516	Chem	680-702.11	1988-11-03	2.60					8.10	8.10								1680	7.10	1400	23.0	4870	351	24	0.1
KLX01/691	1633		680-702.11	1989-11-01	1.99	7.90				7.60	7.60								1610	7.30	1330	24.0	4680	390	24	-0.6
KLX01/835	1761	Chem	830-841	1990-10-09	0.14					8.10	8.10								2750	7.60	3000	15.4	9180	670	6	-0.3
KLX01/915	1773	Chem	910-921	1990-10-30	0.85					8.40	8.40								3100	7.00	3800	9.6	11200	770	6	-0.9
KLX01/915	1774	Chem	910-921	1990-10-31	0.87					8.40	8.40								3100		3700	9.7				
KLX01/1038	1785		999-1077.99	1990-11-19	1.83					8.20	8.20								3350	9.90	4500	6.9	12600	695	12	0.3
KLX02/318	2738	Chem	315-321.5	1994-02-10	0.22					7.80	7.80			(-100)		(-339 in TR-95-05)			111	3.10	24	4.6	73	43	223	-0.9
KLX02/337	2705	Chem	335-340.8	1993-11-08	0.24					8.20	8.20			(-40)		(-200)(-307 in TR-95-05)			206	3.10	36	5.9	235	84	201	-1.5
KLX02/800	2712	Chem	798-803.8	1993-11-23	0.18					7.60	7.60			(-120)		(-317 in TR-95-05)			288	4.50	123	10.6	548	105	111	0.6
KLX02/800	3719	Chem	798-802	2002-03-14						7.90	7.90	19.8		(-125)									73.2		217	
KLX02/1093	2722	Chem	1090-1096.2	1993-12-16						8.50	8.50			(-170)		(-207 in TR-95-05)			3800	10.40	5620	2.1	15800	1010	8	-2.1
KLX02/1160	2934		1155-1165	1999-09-15						7.60	7.60								3730	10.50	5250	5.0	15130	860	12	-2.2
KLX02/1350	2931		1345-1355	1999-08-10						7.90	7.90								8210	17.90	11200	2.7	31230	1024	9	-4.1
KLX02/1389	3030		1385-1392	1999-12-06																						
KLX02/1560	2723	Chem	1420-1700.5			(8)				6.40		18		(-400)												
KLX02/1560	2731	Chem	1420-1700.5	1994-01-17	0.14					7.90	7.90			(-300)		(-334 in TR-95-05)			8030	29.00	18600	2.7	45500	832	9	-0.7
KLX03/35	7340	PTest	11.95-60	2004-05-04						8.50	8.50												33	13	341	
KLX03/56	7341	PTest	11.95-100.3	2004-05-04						8.46	8.46												21	10	352	
KLX03/180	7441	Wirelin	103-218.02	2004-06-04	1.02					8.18	8.18								330	3.3	47	7	507	30	271	-5.4
KLX03/412		Chem	408-415.3			7.9								-275												
KLX03/548	7669	Wirelin	497.02-599.8	2004-08-14	5.15					8.27	8.27								288	3.5	43	6	381	43	300	-4.1
KLX03/647	7673	Wirelin	600-695.24	2004-08-17	102.00																					
KLX03/726	7675	Wirelin	692.86-761.1	2004-08-23	30.30					6.09	6.09								1260	8.1	924	12	3550	392	41	-3.1

* Sample type codes: PB = percussion borehole, PVB = pressurised sampler in downhole PVP sampling unit in Chemmac string, LTMS = Long-term monitoring system, Tube = Tubing sampler, PSS = Pipe string double packer system,
SWIW = single well injection-withdrawal test, Ptest = Pumping test, Calc = calculated by correcting for flushing water content, Chem = Full chemical characterisation Class 5, Return = drilling water return,
Wireline = wireline sampler, MP1 = pumped with MP1 pump, HTHB = hydraulic test in percussion holes

Sample	SKB No	Type*	Depth range	Date	Drill water	pH Chem mac	+/-	pH surf Chem	+/-	pH lab	pH for model	Temp Chem-mac	Diss O$_2$	Eh Chem mac	+/-	Eh Fe^{3+}/Fe^{2+}	Eh SO$_4^{2-}$/S^{2-}	Eh Fe(OH)$_3$/Fe^{2+}	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	Charge bal
			m bgl		%							°C	mg/L	mV								mg/L				%
KLX04/107	7856	PSS	104-109	2004-09-30	0.09					7.73									95	2.7	27	6	24	16	324	-2.3
KLX04/158	7253	Wirelin	103-213.14	2004-03-25	7.76					8.12	8.12								118	2.4	17	4	29	17	318	0.1
KLX04/269	7300	Wirelin	210-329.14	2004-04-18	40.70					8.63	8.63												42	27	277	
KLX04/366	7347	Wirelin	329-403.82	2004-05-07	66.70																					
KLX04/458	7386	Wirelin	401-515.1	2004-05-24	96.60																					
KLX04/513	7776	PSS	510.6-516.6	2004-09-29	4.41					7.83									691	3.2	234	7	1480	104	51	-2.6
KLX04/657	7490	Wirelin	614-701.16	2004-06-11	97.60																					
KLX04/774	7505	Wirelin	690.2-850.4	2004-06-20	91.10																					
KLX04/921	7563	Wirelin	849-993.49	2004-06-29	105.00																					
KLX04/974	7752	PSS	971.2-976.2	2004-09-16	3.98					7.61									2010	7.7	710	5	7910	845	8	-32.2
KLX06/153	7722	Wirelin	103-202		17.40																		25			
KLX06/255	7760	Wirelin	200-310		47.50																					
KLX06264	7759	Wirelin	260-268		4.30																		16			
KLX06/361	7798	Wirelin	307-415		66.50																					
KLX06/347	7775	Wirelin	331-364		35.60																		73			
KLX06/564	7859	Wirelin	514-613		74.70																					
SIMPEVARP																										
KSH01A/161	5263	Chem	156.5-167		2.39			8.17	0.16	7.36	8.1	6.3		-257	20	50			2200	14.7	960	71	5590	32	25	-1.7
KSH01A/253	5260	Chem	245-261.5		0.02			8.00	0.17	7.34	8.05			-160	36	63			2430	13.2	1180	65	6298	51	17	-2.4
KSH01A/556	5280-3	Calc	548-565							7.97	7.97	3		(-230 est)					3699	13.0	2530	51	10113	243	10	0.3
KSH01A/556	5280-5	Calc	548-565							7.97	7.97	3		(-230 est)					3674	13.6	2521	50	10049	249	10	0.3
KSH01A/556	5288	Chem	548-565		10.74			8.15	0.16	7.63	8.2	3		-173	20	77			3500	77.0	1900	47	8876	230	11	-0.4
KSH01A/556	5288-3	Calc	548-565							8.019	8.019	3		(-230 est)					3901	85.8	2126	52	9933	248	10	-0.5
KSH01A/556	5288-5	Calc	548-565							8.019	8.019	3		(-230 est)					3882	85.6	2120	51	9884	252	10	-0.5
KSH02/116	5653	Tube	91-141		2.35					7.94	7.94								463	3.4	309	4	1114	122	219	-2.1
KSH02/216	5655	Tube	191-241		5.88					7.47	7.47								1020	6.6	798	6	2960	165	148	-2.5
KSH02/421	5810	PSS	419-424	2003-09-05	1.48					6.83	6.83								3100	9.8	1710	11	7803	227	5	-0.7
KSH02/423			422.3-423.3																							
KSH02/577	5056	PSS	575-580	2003-09-15	0.13					8.13	8.13								3310	10.2	1790	7	8262	303	6	-1.0
KSH03A/50	5001	PSS	0-100.6							7.72	7.72								292	6.9	94	23	510	64	240	-0.5
ASPO																										
KAS02/208	1548		202-214.5					7.5		7.4	7.4			-257					1300	6.6	990	65	3820	106	71	0.3
KAS02/532	1433		530-535					7.73		8	8	15.3		-308					2200		1890		6330	550	10	0.1
KAS02/892	1560		860-924.04					8.5		8.3	8.3			-150					3000	10.9	3830	31	11100	519	11	0.2
KAS03/131	1569		129-134					8		8	8	10.2		-275					613	2.4	162	21	1220	31	61	0.7
KAS03/931	1582		860-1002.06					8		8.1	8.1	20.5		-275					3020	7.3	4380	50	12300	709	11	-1.0
KAS04/338	1603		334-343							8	8	12.15		-275					1180	6.1	740	30	3030	220	69	-0.1
KAS04/460	1588		440-480.98					8.1		8.1	8.1			-280					1890	7.8	1660	61	5840	407	21	-0.9
AVRO																										
KAV01/560	1374		550-563					7.2			7.2	15		-225					1500	6.0	1100	60	4300	220	42	-0.4
KAV01/609	1354		635-743.6									16.8		-120					3200		2800		9700	390	10	-0.4

* Sample type codes: PB = percussion borehole, PVB = pressurised sampler in downhole PVP sampling unit in Chemmac string, LTMS = Long-term monitoring system, Tube = Tubing sampler, PSS = Pipe string double packer system,
SWIW = single well injection-withdrawal test, Ptest = Pumping test, Calc = calculated by correcting for flushing water content, Chem = Full chemical characterisation Class 5, Return = drilling water return,
Wireline = wireline sampler, MP1 = pumped with MP1 pump, HTHB = hydraulic test in percussion holes

Sample	SKB No	Type*	Depth range	SI calcite	$\log P_{CO_2}$ calc	Model $\log P_{CO_2}$ at SI=0	Model pH at SI=0	Fe ICP	Fe(tot)	Fe^{2+}	Fe^{3+} calc	Mn	S^{2-}	DOC/ TOC	NH_4	CH_4 (diss)		H_2 (diss)		O_2 (diss)	U (ICP)	Refs
			m bgl									mg/L				mL/L	mmol/L	µL/L	µmol/L		µg/L	
FORSMARK																						
KFM01A/115	4530	Chem	110.1-120.77	0.05	-2.92	-2.06	7.41	0.79	1.00	0.95	0.04	0.69	-0.03	1.5	1.07		0		0.00		1.5	P-03-94
KFM01A/180	4724	Chem	176.8-183.9	0.39	-2.85	-2.46	7.21	0.52	0.54	0.48	0.06	1.02	-0.03	2.3	1.01		0		0.00		14.9	P-03-94
KFM02A/59	4398	HTHB	18-100.4	0.36	-2.52	-2.14	7.61				0.00						0		0.00			P-03-48
KFM02A/116	8100	PTest	106.5-126.5	0.37	-2.11	-1.74	7.16	1.37	1.35		1.35	0.25	0.01	11.0	0.51		0		0.00		5.4	P-04-70
KFM02A/423	8272	PTest	413.5-433.5	0.25	-2.64	-2.39	7.12	0.74	0.75	0.73	0.02	1.81		-1.0	1.88		0		0.00		13.9	P-04-70
KFM02A/512	8016	Chem	509-516.08	0.13	-2.31	-2.19	7.06	1.70	1.85	1.84	0.01	2.16	0.01	2.1	2.30	0.04	0.0018	199.0	8.88	0.12	88.6	P-04-70
KFM03A/388	8012	PTest	386-391	0.13	-2.53	-2.39	7.17	0.74	0.79		0.79	1.13		1.3	2.33		0		0.00		3.5	P-04-108
KFM03A/450	8017	PTest	440-453	0.31	-2.76	-2.46	7.19	0.91	0.92	0.92	0.00	1.17	-0.03	1.2	2.33		0		0.00		2.2	P-04-108
KFM03A/452	8284	Chem	448.5-456.6						1.10	1.11	-0.01	1.25	0.05									P-04-108
KFM03A/642	8273	Chem	639-646.12	-0.04	-3.44			0.24	0.23	0.23	0.00	0.32		1.6	0.16		0		0.00		46.1	P-04-108
KFM03A/943	8281	Chem	939.5-946.6						0.22	0.21	0.01	0.11	0.06									P-04-108
KFM03A/990	8152	Chem	980-1001.19	0.31	-4.00	-4.41	7.07	0.03	0.03	0.03	0.01	0.01	0.03	1.4		0.05	0.0022	-3.0	-0.17	0.04	0.4	P-04-108
KFM04A/234-incline	8267	Chem	230.5-237.64	0.17	-2.36	-2.20	7.00	2.01	2.13	2.12	0.01	2.81	0.00	1.5	1.59		0		0.00		62.0	P-04-109
KFM04A/357-incline	8287	Chem	354-361.13	0.13	-2.64	-2.51	7.14	2.13	2.10	2.16	-0.06	1.31					0		0.00			P-04-109
KFM05A-inclined at	8601	Chem	712.6-722																			P-05-79
KFM06A/357-incline	8838	Chem	353.5-360.6																			P-05-178
KFM06A/771-incline	8785	Chem	768.0-775.1										0.02									P-05-178
KFM07A/925-incline	8879	Chem	848-1001.6																			P-05-170
LAXEMAR																						
KLX01/274	1537	Chem	272-277						0.13	0.13	0.00	0.20	0.53	1.5	0.08		0		0.00			TR-98-03
KLX01/458	1528	Chem	456-461						0.04	0.04	0.00	0.16	0.46	1.4	0.06		0		0.00			TR-02-19 (p 246), TR-98-03
KLX01/691	1516	Chem	680-702.11						0.03	0.03	0.00	0.20	2.50	1.2	0.00		0		0.00			R-06-10 (p 376), TR-98-03
KLX01/691	1633		680-702.11						0.14	0.14	0.00	0.21	0.65	3.3	0.04		0		0.00			TR-98-03
KLX01/835	1761	Chem	830-841						0.22	0.21	0.01	0.11	0.07		0.01		0		0.00			
KLX01/915	1773	Chem	910-921						0.05	0.05	0.00	0.09	0.29		0.01		0		0.00			
KLX01/915	1774	Chem	910-921						0.05	0.05	0.00	0.09	0.34				0		0.00			
KLX01/1038	1785		999-1077.99						0.36	0.36	0.01	0.05	0.10		0.01		0		0.00			
KLX02/318	2738	Chem	315-321.5					1.06	1.05	1.04	0.01	0.15	0.04	5.5	0.10		0		0.00		1.090	TR-95-05, Table 3-4; R-04-74 spreadsheet
KLX02/337	2705	Chem	335-340.8					0.47	0.46	0.46	0.00	0.14	-0.01				0		0.00		0.470	TR-95-05, Table 3-4, TR-02-19 (p 246), R-04-74 spreadsheet
KLX02/800	2712	Chem	798-803.0					1.03	1.73	1.71	0.02	0.39	-0.01	5.0	0.07		0		0.00		0.760	TR-95-05, Table 3-4
KLX02/800	3719	Chem	798-802								0.00						0		0.00			R-06-10 (p 376), R-04-74 spreadsheet
KLX02/1093	2722	Chem	1090-1096.2					-0.01			0.00	0.01	-0.01	1.1	-0.01		0		0.00			TR-95-05, Table 3-4
KLX02/1160	2934		1155-1165					1.06	1.04	1.03	0.01	0.25	-0.01	10.0	0.03		0		0.00			
KLX02/1350	2931		1345-1355					0.20	0.23	0.20	0.03	0.00	-0.01	90.0	0.00		0		0.00			
KLX02/1389	3038		1385-1392																			
KLX02/1560	2723	Chem	1420-1700.5																			R-04-74 spreadsheet
KLX02/1560	2731	Chem	1420-1700.5					0.41	0.43	0.43	0.00	0.14	-0.01	0.9	-0.01		0		0.00		0.020	TR-95-05, Table 3-4
KLX03/35	7340	PTest	11.95-60								0.00						0		0.00			P-05-167
KLX03/56	7341	PTest	11.95-100.3								0.00						0		0.00			P-05-167
KLX03/160	7441	Wirelin	103-218.02					0.25			0.00	0.08					0		0.00			P-05-167
KLX03/412		Chem	400-415.3											2.2								R-06-110
KLX03/548	7669	Wirelin	497.02-599.89					4.83			0.00	0.23					0		0.00			P-05-167
KLX03/647	7673	Wirelin	600-695.24								0.00						0		0.00			P-05-167
KLX03/726	7675	Wirelin	692.86-761.11					11.00			0.00	0.50					0		0.00			P-05-167

Sample	SKB No	Type*	Depth range	SI calcite	$\log P_{CO_2}$ calc	Model $\log P_{CO_2}$ at SI=0	Model pH at SI=0	Fe ICP	Fe(tot)	Fe^{2+}	Fe^{3+} calc	Mn	S^{2-}	DOC/TOC	NH_4	CH_4 (diss)		H_2 (diss)		O_2 (diss)	U (ICP)	Refs
			m bgl									mg/L				mL/L	mmol/L	µL/L	µmol/L		µg/L	
KLX04/107	7856	PSS	104-109					0.16	0.16	0.14		0.16	0.01	9.9	0.12							P-05-271
KLX04/158	7253	Wirelin	103-213.14					3.79			0.00	0.12					0		0.00			P-05-111
KLX04/269	7300	Wirelin	210-329.14								0.00						0		0.00			P-05-111
KLX04/366	7347	Wirelin	329-403.82								0.00						0		0.00			P-05-111
KLX04/450	7306	Wirelin	401-515.1								0.00						0		0.00			P-05-111
KLX04/513	7776	PSS	510.6-516.6					0.09	0.10	0.08		0.11	0.01	2.2	0.032						0.3	P-05-271 & R-06-110
KLX04/657	7490	Wirelin	614-701.16								0.00						0		0.00			P-05-111
KLX04/774	7505	Wirelin	698.2-850.4								0.00						0		0.00			P-05-111
KLX04/921	7563	Wirelin	849-993.49								0.00						0		0.00			P-05-111
KLX04/974	7752	PSS	971.2-976.2					0.16	0.17	0.15		0.07	0.02	<1	0.006						0.3	P-05-271
KLX06/153	7722	Wirelin	103-202																			P-05-234
KLX06/255	7760	Wirelin	200-310																			P-05-234
KLX06264	7750	Wirelin	260-288																			P-05-234
KLX06/361	7798	Wirelin	307-415																			P-05-234
KLX06/347	7775	Wirelin	331-384																			P-05-234
KLX06/564	7859	Wirelin	514-613																			P-05-234
SIMPEVARP																						
KSH01A/161	5263	Chem	156.5-167	0.3	-4.0	-3.84	7.79		1.413	1.397	0.02	0.54	0	0.9	0.095	0.060	0.0027	-3.400	-0.15	0.900	0.1	P-04-12
KSH01A/253	5260	Chem	245-261.5	0.2	-4.1	-3.90	7.05		1.310	1.296	0.02	0.66	0	-1.0	0.079		0		0.00		0.2	P-04-12
KSH01A/556	5288-3	Calc	548-565								0.00	0.53					0		0.00			P-04-12
KSH01A/556	5288-5	Calc	548-565								0.00	0.51					0		0.00			P-04-12
KSH01A/556	5288	Chem	548-565	0.2	-4.5	-4.25	8.00		0.523	0.511	0.01	0.4		-1.0	0.048	0.040	0.0018	81.000	3.62	0.170	0.1	P-04-12
KSH01A/556	5288-3	Calc	548-565								0.00	0.44					0		0.00			P-04-12
KSH01A/556	5288-5	Calc	548-565								0.00	0.43					0		0.00			P-04-12
KSH02/116	5653	Tube	91-141								0.00	0.15					0		0.00			P-03-88
KSH02/216	5655	Tube	191-241								0.00	0.31					0		0.00			P-03-88
KSH02/421	5810	PSS	419-424						0.08	0.016	0.06	0.13		-1.0	0.015		0		0.00		0.8	P-04-281
KSH02/423			422.3-423.3																			
KSH02/577	5856	PSS	575-580						0.04	0.002	0.04	0.14		-1.0	0.005		0		0.00		0.1	P-04-281
KSH03A/50	5801	PSS	0-100.6								0.00	2.08					0		0.00			P-04-233
ÄSPÖ																						
KAS02/208	1548		202-214.5	0.3	-2.9	-2.57	7.20		0.502	0.483	0.02	0.91	0.5	6	0.4		0		0.00		0.246	TR-92-31; TR-98-03
KAS02/532	1433		530-535	0.1	-4.3	-4.16	7.00		0.244	0.24	0.00		0.10		0.03		0		0.00		0.23	TR-92-31; TR-98-03
KAS02/892	1560		860-924.04	0.6	-5.0	-4.11	7.77		0.051	0.049	0.00	0.23	0.72	-0.5	0.01		0		0.00			TR-92-31; TR-98-03
KAS03/131	1569		129-134	0.1	-3.4	-3.26	7.00		0.125	0.123	0.00	0.1	0.71	2	0.04		0		0.00			TR-92-31; TR-98-03
KAS03/931	1582		860-1002.06	0.3	-4.4	-3.96	7.60		0.078	0.077	0.00	0.2	1.28		0.005		0		0.00			TR-92-31; TR-98-03
KAS04/330	1603		334-343	0.6	-3.3	-2.63	7.30		0.327	0.324	0.00	0.31	0.41	5.3	0.09		0		0.00		0.404	TR-92-31; TR-98-03
KAS04/460	1588		440-480.98	0.4	-4.1	-3.58	7.64		0.259	0.256	0.00	0.44	0.6	1.3	0.05		0		0.00			TR-92-31; TR-98-03
ÄVRÖ																						
KAV01/560	1374		558-563	-0.2	-2.8				1.02	1.02	0.00	1.7	0.81		0.08		0		0.00			R-04-74
KAV01/689	1354		635-743.6	-0.7	-3.3						0.00						0		0.00			R-04-74

Appendix 4: Comparison of log K values

Comparison of log K values for selected complexes and solid phases as extracted and calculated from different thermodynamic databases used in PHREEQCI. Corresponding values from the PSI/NAGRA and HYDRA databases have been introduced for comparison.

Reaction / Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\lvert Maxdiff_{Hydra} \rvert$/ Comments
1 Fe^{3+} $Fe^{3+}+e^-=Fe^{2+}$	--	13.032(0.012)/ 13.032(0.012)	13.02(0)	13.02(0)	13.02(0)	13.02	0.012(1.0x)/ Mv4/OK
2 $Fe(OH)_2{}^+$ $Fe^{3+}+2H_2O= Fe(OH)_2{}^++2H^+$	-5.67(0)	-5.67(0)/ -4.594(1.076)	-5.67(0)	-5.67(0)	-5.67(0)	-5.67	1.08(12.0x)/ Mv4/OK
3 $Fe(OH)^+$ $Fe^{2+}+H_2O^-= Fe(OH)^++H^+$	--	--/ -9.379(0.821)	-9.5(0.7)	--	-9.5(0.7)	-10.2	0.82(6.6x)/ Mv4/OK
4 $Fe(OH)_3{}^-$ $Fe^{2+}+3H_2O=$ $Fe(OH)_3{}^-$ $+3H^+$	-31(1.40)	-31(1.40)/ -28.991(4.409)	-31.0(1.40)	--	--	-33.40	4.409(25645x)/ Mv4/NOT OK
5 $Fe(OH)_4{}^-$ $Fe^{3+}+4H_2O=$ $Fe(OH)_4{}^-+4H^+$	--	--/--	--	--	-21.6	--	--
6 $Fe(OH)_2$ $Fe^{2+}+2H_2O=$ $Fe(OH)_2+2H^+$	-20.6 (0.2)	-20.57(0.23)/ -20.494(0.306)	-20.57(0.23)	--	--	-20.8	0.306(2.0x)/ Mv4/OK
7 $Fe(OH)_2$ (c) $Fe^{2+}+2OH^-=Fe(OH)_2$	--	--/--	--	--	--	-12.996	--
8 $Fe(OH)_3$ $Fe^{3+}+3H_2O=$ $Fe(OH)_3+3H^+$	--	--/--	--	--	-12.56	--	--
9 $Fe(OH)_3$ (mic) $Fe^{3+}+3H_2O=$ $Fe(OH)_3$(mic)$+3H^+$	--	--/--	--	--	-3	--	--
10 $Fe(OH)_3$ (am) $Fe^{3+}+3H_2O=$ $Fe(OH)_3$(am)$+3H^+$	--	--/--	-4.891	-4.891	-5	--	--
11 Goethite $FeOOH+3H^+=$ $Fe^{3+}+2H_2O$	0.5345 (0.0345)	0.5(0)/ 0.491(0.009)	-1.0(1.5)	-1.000(1.5)	-1(1.5)	0.5	1.5(32x)/ Ph/OK
12 Hematite $Fe_2O_3+6H^+=$ $2Fe^{3+}+3H_2O$	0.1086 (0.2994)	-4.008(4.416)/ -1.418(1.826)	-4.008 (4.416)	-4.008 (4.416)	1.12$^{*)}$(0.712)	0.408	4.42(26303x)/ M/NOT OK

Reaction / Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\lvert Maxdiff_{Hydra}\rvert$/ Comments
13 Magnetite Fe_3O_4+$8H^+$= $2Fe^{3+}$+Fe^{2+}+$4H_2O$	10.4724 (0.5776)	3.737(7.323)/ 3.4028(7.6472)	3.737 (7.323)	--	10.02(1.03)	11.05	7.65/ Mv4/NOT OK
14 $FeCO_3$ HCO_3^-+Fe^{2+}= $FeCO_3$+H^+	-5.5988 (0.3502)	--/--	-5.949(0)	-5.949(0)	-5.949(0)	-5.949	0.35(2.2x)/ llnl/OK
15 $FeCO_3$ Fe^{2+}+CO_3^{2-}=$FeCO_3$	4.73 (0.35)	--/--	4.38(0)	4.38(0)	--	4.38	0.35(2.2x)/ llnl/OK
16 Siderite $FeCO_3$=Fe^{2+}+CO_3^{2-}	-10.5208	-10.55/-10.24	-10.89	-10.890	--	--	0.65(4.5x)/ OK
17 $FeCl^+$ Fe^{2+}+Cl^-=$FeCl^+$	-0.1605 (0.3005)	--/--	0.14(0)	0.14(0)	0.14(0)	0.14	0.30(2.0x)/ llnl/OK
18 $FeCl^{2+}$ Fe^{3+}+Cl^-=$FeCl^{2+}$	-0.8108 (2.29)	1.48(0)/1.48(0)	1.48(0)	1.48(0)	1.48(0)	1.48	2.29(195x)/ llnl/OK
19 $FeCl_2$ $2Cl^-$+Fe^{2+}=$FeCl_2$	-2.4541	--/--	--	--	--	--	??
20 $FeCl_3$ $3Cl^-$+Fe^{3+}=$FeCl_3$	--	--/--	--	--	1.13	--	--
21 $FeCl_2^+$ $2Cl^-$+Fe^{3+}=$FeCl_2^+$	2.1300 (0)	2.13(0)/2.13(0)	2.13(0)	2.13(0)	2.13(0)	2.13	0.00(1x)/OK
22 $FeCl_4^-$ $4Cl^-$+Fe^{3+}=$FeCl_4^-$	-0.79 (0.13)	--/--	--	--	--	-0.92	0.13(1.3x)/ llnl/OK
23 $FeCl_4^{2-}$ $4Cl^-$+Fe^{2+}=$FeCl_4^{2-}$	-1.9	--/--	--	--	--	--	??
24 Pyrite FeS_2+H_2O= $0.25H^+$+$0.25SO_4^{2-}$ +Fe^{2+}+$1.75HS^-$	-24.6534 (2.2486)	--/--	--	--	--	-26.902	2.2486(177x)/ llnl/ DOUBTFUL
25 Pyrite FeS_2+$2H^+$+$2e^-$= Fe^{2+}+$2HS^-$	--	-18.479(0)/ -18.5082 (0.0292)	-18.479 (0)	-18.479(0)	-18.5(0.021)	-18.479	0.0292(1.1x)/ Mv4/OK

Reaction / Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\vert\text{Maxdiff}_{\text{Hydra}}\vert$/ Comments
26 FeS (ppt) $FeS+H^+=Fe^{2+}+HS^-$	-3.8184 (0.0966)	-3.915(0)/ -2.95(0.965)	-3.915(0)	-3.915(0)	-5.31(1.395)	-3.915	1.395(25x)/ PSI/OK?, Troilite
27 Na_2CO_3 $Na_2CO_3+H^+= HCO_3^-+2Na^+$	11.1822 (0.7282)	9.02(1.434)/ 9.018(1.436)	--	--	--	10.454	1.436(27.3x)/ Mv4/OK
28 $NaHCO_3$ $HCO_3^-+Na^+=NaHCO_3$	--	--/--	--	--	-0.25	--	--
29 $CaCO_3$ $HCO_3^-+Ca^{2+}= CaCO_3+H^+$	-7.0017 (0.1033)	-7.179(0.074)/ -7.1(0.005)	-7.105 (0)	-7.105(0)	--	-7.105	0.1033(1.3x)/ llnl/OK
30 Calcite $CaCO_3+H^+= Ca^{2+}+HCO_3^-$	1.8487 (0.0013)	1.854(0.004)/ 1.85(0)	--	1.849 (0.001)	--	1.85	0.0013(1.0x)/ llnl/OK
31 $CaCO_3$ $CaCO_3=Ca^{2+}+CO_3^{2-}$	--	--/--	-8.48	--	--	--	--
32 Dolomite (ord) $CaMg(CO_3)_2+2H^+= Ca^{2+}+Mg^{2+}+2HCO_3^-$	2.5135 (1.0565)	3.7(0.13)/ 3.57(0)	3.57(0)	3.568 (0.002)	3.568 (0.002)	3.57	1.06(11.5x)/ llnl/OK
33 Dolomite (ord) $CaMg(CO_3)_2= Ca^{2+}+Mg^{2+}+2CO_3^{2-}$	--	--/--	-16.54	--	--	--	--
34 $CO_2(g)$ $CO_2+H_2O=H^++HCO_3^-$	-7.8136 (0.0124)	-7.83(0.004)/ -7.83(0.004)	--	-7.790 (0.036)	--	-7.826	0.036(1.1x)/ Ph/OK
35 $CO_2(g)$ $CO_2+H_2O=2H^++CO_3^{2-}$	-18.1424 (0.0126)	-18.16(0.005)/ -18.16(0.005)	--	-18.049 (0.106)	..	-18.155	0.106(1.3x)/ Ph/OK
36 CO_2 $HCO_3^-+H^+=CO_2+H_2O$	6.3447	--/--	--	6.322	--	--	0.027(1.1x)/ llnl/OK
37 CO_3^{2-} $HCO_3^-=CO_3^{2-}+H^+$	-10.3288 (0.0002)	-10.33(0.001)/ -10.329(0)	-10.329(0)	-10.329(0)	--	-10.329	0.0012(1.0x)/ M/OK
38 H_2CO_3 $CO_3^{2-}+2H^+=H_2CO_3$	--	16.681(0.002)/ 16.681(0.002)	16.681 (0.002)	16.681 (0.002)	--	16.683	0.002(1.0x)/ OK

Reaction / Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\lvert\text{Maxdiff}_{\text{Hydra}}\rvert$/ Comments
39 $CuCO_3$ $HCO_3^-+Cu^{2+}= CuCO_3+H^+$	-3.3735 (0.1865)	-0.70(2.86)/ 1.2(4.76)	-3.60(0.04)/ -0.70(2.86)	--	--	-3.56/0.82	4.76(57543x)/ Mv4/NOT OK
40 Azurite $Cu_3(CO_3)_2(OH)_2+4H^+=$ $2H_2O+2HCO_3^-+3Cu^{2+}$	9.1607 (4.4107)	3.74(1.01)/ 3.752(0.998)	3.750 (1.000)	--	--	4.750	4.4107 (25745x)/ llnl/ NOT OK
41 $CuCl^+$ $Cu^{2+}+Cl^-=CuCl^+$	0.4370 (0.203)	0.43(0.21)/ 0.2(0.44)	0.43(0.21)	--	--	0.64	0.44(2.8x)/ Mv4/OK
42 $CuCl_2$ $2Cl^-+Cu^{2+}=CuCl_2$	0.1585 (0.0415)	0.16(0.04)/ -0.26(0.46)	0.16(0.04)	--	--	0.2	0.87(7.4x)/ Mv4/OK
43 $CuCl_2^-$ $2Cl^-+Cu^+=CuCl_2^-$	4.8212 (0.8688)	5.5(0.19)/ 5.42(0.27)	--	--	--	5.690	0.27(1.9x)/ llnl/OK
44 $CuCl_4^{2-}$ $4Cl^-+Cu^{2+}=CuCl_4^{2-}$	-4.5681 (0.9681)	-4.59(0.99)/ -4.59(0.99)	-4.59(0.99)	--	--	-3.6	0.99(9.8x)/ Mv4mfl/OK
45 $CuCl_3^{2-}$ $3Cl^-+Cu^+=CuCl_3^{2-}$	5.6289 (0.6089)	5.7(0.68)/ 4.75(0.27)	--	--	--	5.020	0.68(4.8x)/ M/OK
46 Covellite $CuS+H^+=Cu^{2+}+HS^-$	-22.8310 (0.771)	-23.038 (0.978)/ -22.3(0.24)	-22.270 (0.21)	--	--	-22.06	0.978(9.51x)/ M/OK
47 Chalcocite $Cu_2S+H^+=HS^-+2Cu^+$	-34.7342 (0.7242)	-34.619 (0.609)/-34.92 (0.91)	-34.619 (0.609)	--	--	-34.01	0.91(8.1x)/ Mv4/OK
Reaction\ Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\lvert\text{Maxdiff}_{\text{Hydra}}\rvert$/ Comments
48 CrO_4^{2-} $CrO_4^{2-}+6H^++3e^-=$ $Cr(OH)_2^++2H_2O$	--	67.376(0.856)/ 67.376(0.856)	--	--	--	66.52	0.856(7.2x)/ M/OK

Reaction / Data base	llnl	Minteq/ minteqv4	wateq4f	phreeqc	PSI/Nagra (Comparison)	HYDRA (Comparison)	$\lvert Maxdiff_{Hydra} \rvert$/ Comments
49 MnO_4^- $Mn^{2+}+4H_2O=$ $MnO_4^-+8H^++5e^-$	--	-127.824(0)/--	-127.824(0)	--	--	-127.824	0,00(1x)/ OK
50 MnS(green) $MnS+H^+=Mn^{2+}+HS^-$	--	3.8(0)/3.8(0)	3.8(0)	--	--	3.8	0(1x)/ OK
51 O_2(g) $O_2+4H^++4e^-=2H_2O$	85.9951 (0.0061)	86.08(0.091)/ 85.9951 (0.0061)	86.08 (0.091)	86.08 (0.091)	--	85.989	0.091(1.2x)/ M/OK
52 SO_4^{2-} $SO_4^{2-}+H^+=HS^-+2O_2$	-138.16	--/--	--	--	--	--	--
53 SO_4^{2-} $SO_4^{2-}+10H^++e^-=H_2S+4H_2O$	--	--/--	40.644	--	--	--	--
Number of values	36//90	33//83/ 32//80	34//85	22//55	19//48	38//95	40/100%

*) In the PSI/NAGRA data base the complex ion $Fe(OH)_4^-$ is considered in this case which strongly influences the Log K value.

Some comments on the comparisons of thermodynamic databases

- Appendix 4 constitutes a selection of log K values that could be of importance for PHREEQCI calculations. Only log K data were evaluated.

- Some values are directly extracted and others are calculated from other values.

- Databases llnl, Minteq/Minteqv4, Wateq4f and phreeqc are available directly within the PHREEQCI package. Data from HYDRA [5] are inserted here for external comparison as is also the PSI/Nagra database [14].

- The values within parentheses are absolute differences to the HYDRA value, $|\mathrm{diff}_{\mathrm{hydra}}|$. Those are calculated in order to generate a basis for data comparison.

- The $|\mathrm{Maxdiff}_{\mathrm{hydra}}|$ values are the maximum calculated absolute differences between the actual tabulated data found in the indicated PHREEQCI database and the corresponding HYDRA value.

- Thus HYDRA is used as an external reference. HYDRA also is the ‘best equipped’ database containing the largest number of values.

- The llnl database has most values available within the PHREEQCI package.

- The phreeqc database has least values available within the PHREEQCI package.

- The Minteqv4 (Mv4) database has the largest deviation from HYDRA in 35% of the cases.

- The Minteq (M) database has the largest deviation from HYDRA in 15% of those cases when a difference to HYDRA has been calculated.

- The phreeqc (Ph) database has the largest deviation from HYDRA in 8% of those cases when a difference to HYDRA has been calculated.

- The llnl database has the largest deviation from HYDRA in 30% of those cases when a difference to HYDRA has been calculated.

- Comparisons could not be made in 12% of those cases when a difference to HYDRA has been calculated.

- Deviations were considered to be NOT OK or DOUBTFUL in a total of 15% of those cases when a difference to HYDRA has been calculated, distributed on ‘Mv’ 7.5%, ‘M’ 2.5 %, ‘Ph’ 0% and ‘llnl’ 5%.

- As the total number of observations is small the statistics should be viewed with caution.

Appendix 5: E_h-pH diagrams calculated for selected Forsmark samples

Parameters used for modelling each diagram with the MEDUSA program and HYDRA thermodynamic database. Note that a selection only of these model runs is illustrated in the following E_h-pH diagrams.

Sample/Depth(m)	pH/E_h (mV)	[Fe] mg/l;µM	[S] mg/l;mM	[Cl] mg/l;µM	Figure nr
KFM01A/115 Only Fe	7.47/ -175	1.00; 17.90	-	-	x1
KFM01A/115 Only S	7.47/ -175	-	316; 3.30	-	x2
KFM01A/115 Fe species shown	7.47/ -175	1.00; 17.90	316; 3.30	-	x3
KFM01A/115 S species shown	7.47/ -175	1.00; 17.90	316; 3.30	-	x4
KFM01A/115 Only dissolved Cl species shown	7.47/ -175	1.00; 17.90	316; 3.30	4563; 128.5	r1
KFM01A/115 Only dissolved Fe species shown	7.47/ -175	1.00; 17.90	316; 3.30	4563; 128.5	r2
KFM01A/115 Only dissolved S species shown	7.47/ -175	1.00; 17.90	316; 3.30	4563; 128.5	r3
KFM01A/180	7.60/ -170	0.54; 9.68	-	-	x5
KFM01A/180	7.60/ -170	-	547; 5.70	-	x6
KFM01A/180 S species shown	7.60/ -170	0.54; 9.68	547; 5.70	-	x7
KFM01A/180 Fe species shown	7.60/ -170	0.54; 9.68	547; 5.70	-	x8
KFM01A/180 Only dissolved Cl species shown	7.60/ -170	0.54; 9.68	547; 5.70	5330; 150.1	s1
KFM01A/180 Only dissolved Fe species hown	7.60/ -170	0.54; 9.68	547; 5.70	5330; 150.1	s2
KFM01A/180 Only dissolved S species shown	7.60/ -170	0.54; 9.68	547; 5.70	5330; 150.1	s3
KFM02A/116	7.52/ -225	1.35; 24.20	-	-	y1
KFM02A/116	7.52/ -225		90; 0.49	-	y2
KFM02A/116 S species shown	7.60/ -170	1.35; 24.20	90; 0.49	-	y3
KFM02A/116 Fe species shown	7.60/ -170	1.35; 24.20	90; 0.49	-	y4
KFM02A/116 Only dissolved Cl species shown	7.52/ -225	1.35; 24.20	90; 0.94	642; 18.08	t1

Sample/Depth(m)	pH/E_h (mV)	[Fe] mg/l;μM	[S] mg/l;mM	[Cl] mg/l;μM	Figure nr
KFM02A/116 Only dissolved Fe species shown	7.52/ -225	1.35; 24.20	90; 0.94	642; 18.08	t2
KFM02A/116 Only dissolved S species shown	7.52/ -225	1.35; 24.20	90; 0.94	642; 18.08	t3
KFM02A/512	7.18/ -140	1.85; 33.20	-	-	y5
KFM02A/512	7.18/ -140	-	498; 5.20	-	y6
KFM02A/512 S species shown	7.18/ -140	1.85; 33.20	498; 5.20	-	y7
KFM02A/512 Fe species shown	7.18/ -140	1.85; 33.20	498; 5.20	-	y8
KFM02A/512 Only dissolved Cl species shown	7.18/ -140	1.85; 33.2	498; 5.20	5410; 152.6	v1
KFM02A/512 Only dissolved Fe species shown	7.18/ -140	1.85; 33.2	498; 5.20	5410; 152.6	v2
KFM02A/512 Only dissolved S species shown	7.18/ -140	1.85; 33.2	498; 5.20	5410; 152.6	v3
KFM03A/450	7.49/ -250	0.92; 16.50	-	-	p1
KFM03A/450	7.49/ -250	-	472; 4.90	-	p2
KFM03A/450 S species shown	7.49/ -250	0.92; 16.50	472; 4.90	-	p3
KFM03A/450 Fe species shown	7.49/ -250	0.92; 16.50	472; 4.90	-	p4
KFM03A/450 Only dissolved Cl species shown	7.49/ -250	0.92; 16.50	472; 4.90	5430; 153.2	h1
KFM03A/450 Only dissolved Fe species shown	7.49/ -250	0.92; 16.50	472; 4.90	5430; 153.2	h2
KFM03A/450 Only dissolved S species shown	7.49/ -250	0.92; 16.50	472; 4.90	5430; 153.2	h3
KFM03A/642	7.55/ -200	0.23; 4.12	-	-	q1
KFM03A/642	7.55/ -200	-	197; 2.10	-	q2
KFM03A/642 S species shown	7.55/ -200	0.23; 4.12	197; 2.10	-	q3
KFM03A/642 Fe species shown	7.55/ -200	0.23; 4.12	197; 2.10	-	q4
KFM03A/642 Only dissolved Cl species shown	7.55/ -200	0.23; 4.12	197; 2.10	5430; 153.2	k1
KFM03A/642 Only dissolved Fe species shown	7.55/ -200	0.23; 4.12	197; 2.10	5430; 153.2	k2

Sample/Depth(m)	pH/E_h (mV)	[Fe] mg/l;μM	[S] mg/l;mM	[Cl] mg/l;μM	Figure nr
KFM03A/642 Only dissolved S species shown	7.55/ -200	0.23; 4.12	197; 2.10	5430; 153.2	k3
KFM03A/990	8.26/ -150	0.03; 0.53	-	-	z1
KFM03A/990	8.26/ -150	-	47; 0.49	-	z2
KFM03A/990 S species shown	8.26/ -150	0.03; 0.53	47; 0.49	-	z3
KFM03A/990 Fe species shown	8.26/ -150	0.03; 0.53	47; 0.49	-	z4
KFM03A/990 Only dissolved Cl species shown	8.26/ -150	0.03; 0.50	47; 0.49	9690; 273	u1
KFM03A/990 Only dissolved Fe species shown	8.26/ -150	0.03; 0.50	47; 0.49	9690; 273	u2
KFM03A/990 Only dissolved S species shown	8.26/ -150	0.03; 0.50	47; 0.49	9690; 273	u3

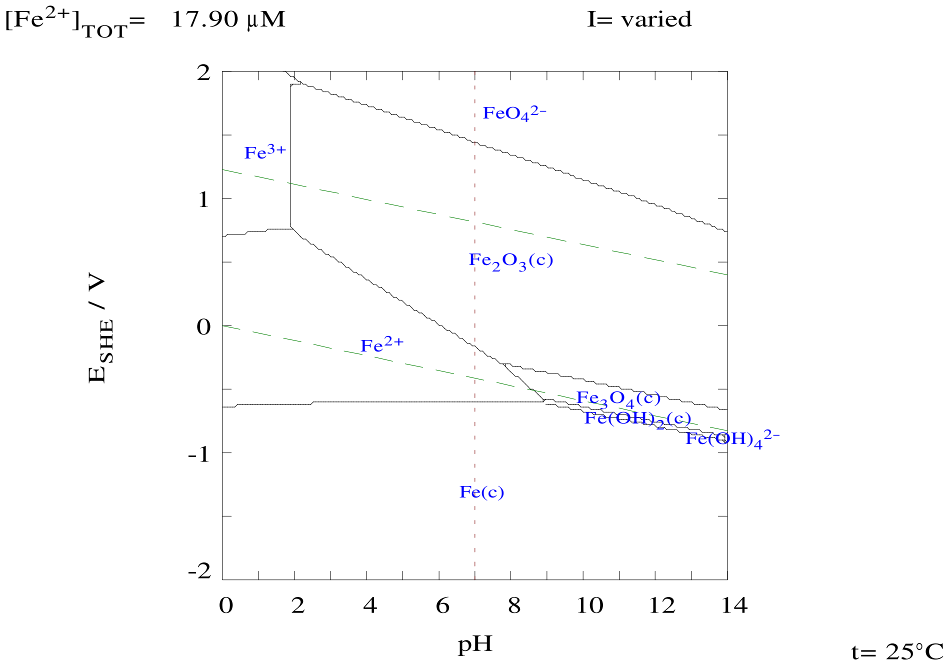

Figure x1 KFM01A/Depth = 115 m, pH = 7.47, E_h = -175 mV, Total conc. Fe = 1.00 mg/l (17.90 µM).

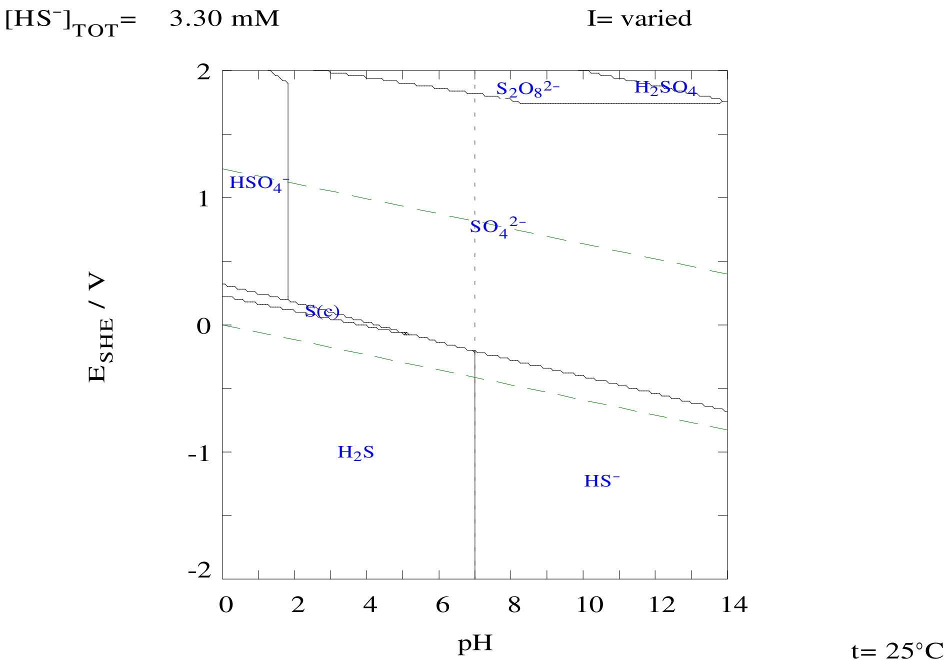

Figure x2 KFM01A/Depth = 115 m, pH = 7.47, E_h = -175 mV, Total conc. S = 316 mg/l (3.30 mM).

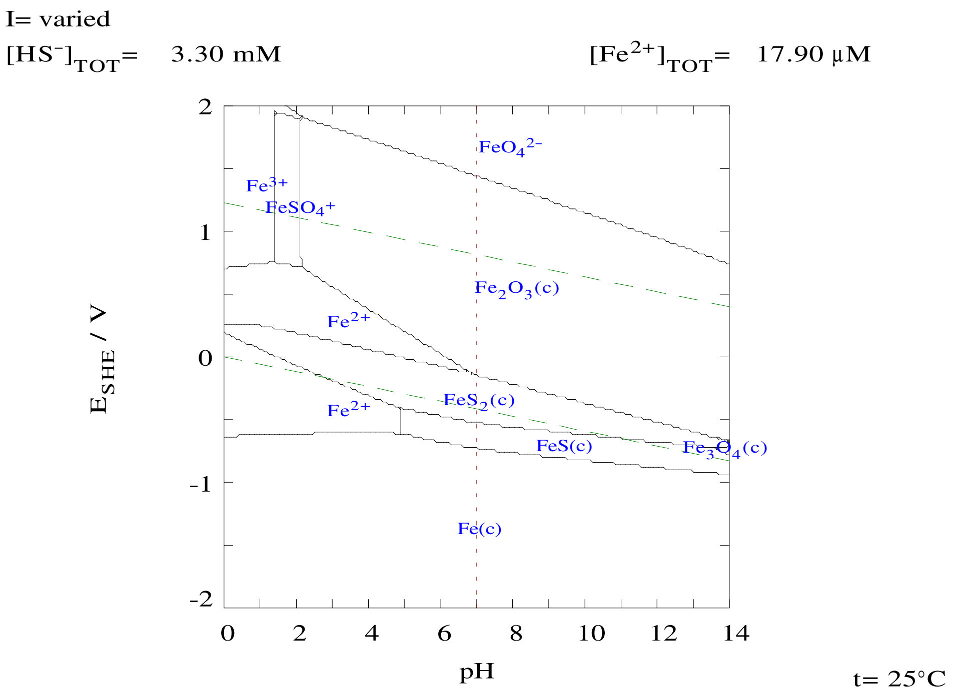

Figure x3 KFM01A/Depth = 115 m, pH = 7.47, E_h = -175 mV, Total conc. S = 316 mg/l (3.30 mM), Total conc. Fe = 1.00 mg/l (17.90 µM). Fe species shown.

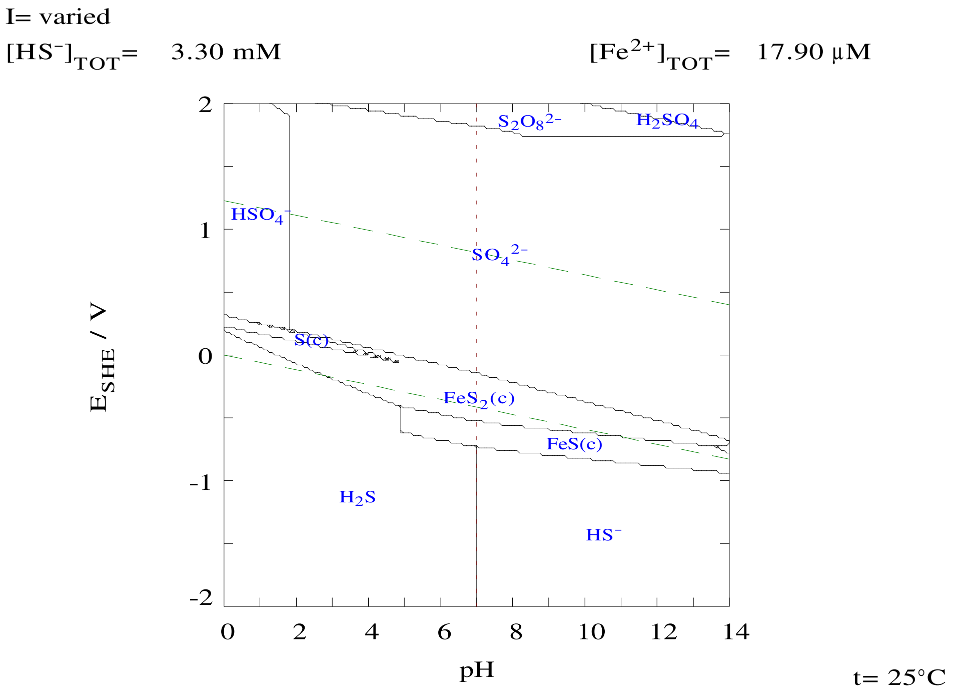

Figure x4 KFM01A/Depth = 115 m, pH = 7.47, E_h = -175 mV, Total conc. S = 316 mg/l (3.30 mM), Total conc. Fe = 1.00 mg/l (17.90 µM). S species shown.

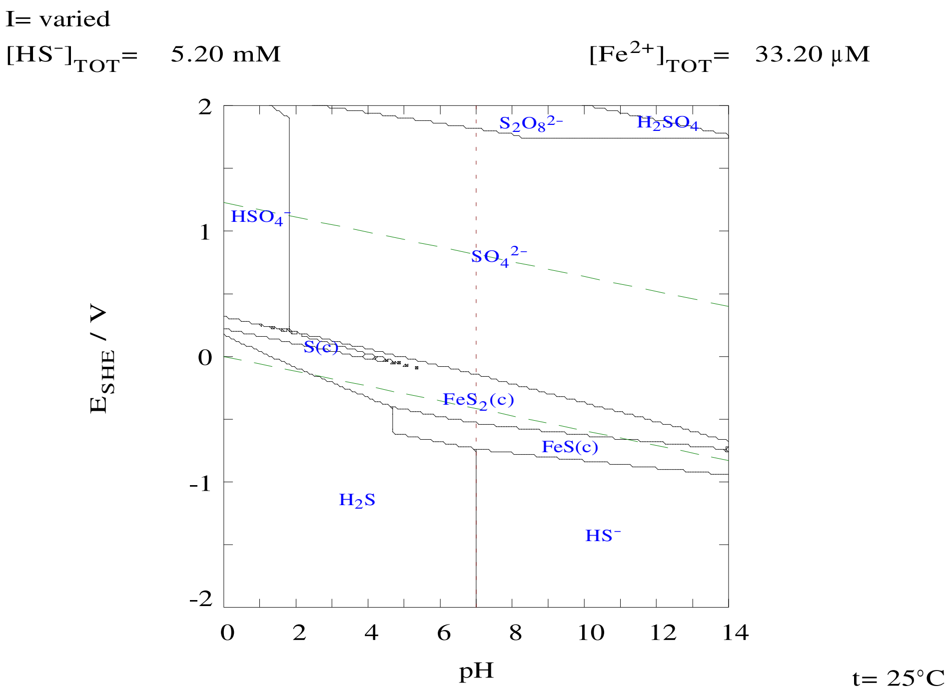

Figure y7 KFM02A/Depth = 512 m, pH = 7.18, E_h = -140 mV, Total conc. Fe = 1.85 mg/l (33.20 µM). Total conc. S = 498 mg/l (5.20 mM). S species shown.

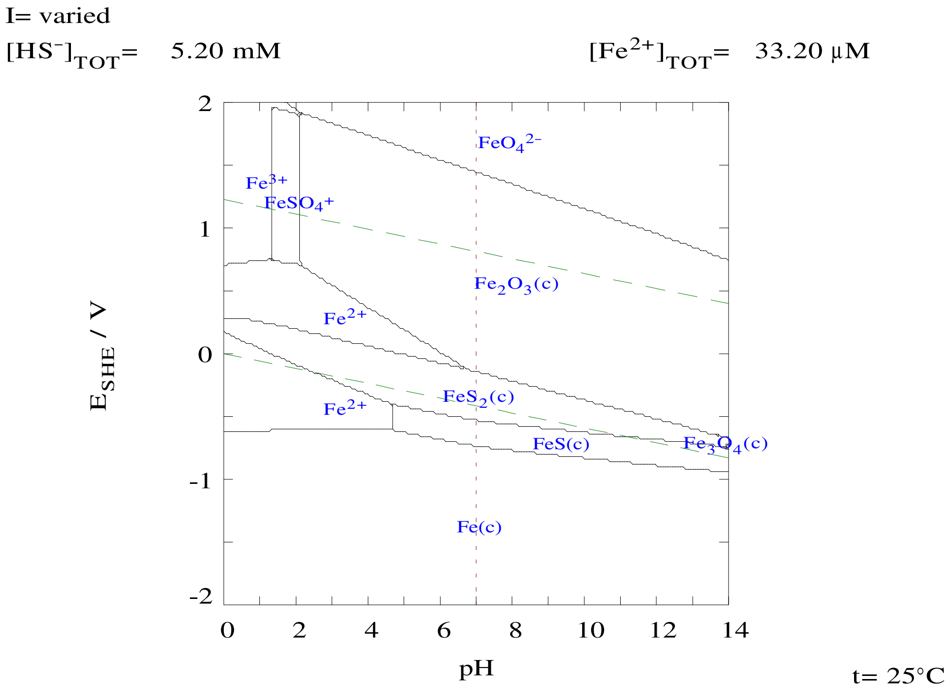

Figure y8 KFM02A/Depth = 512 m, pH = 7.18, E_h = -140 mV, Total conc. Fe = 1.85 mg/l (33.20 µM). Total conc. S = 498 mg/l (5.20 mM). Fe species shown.

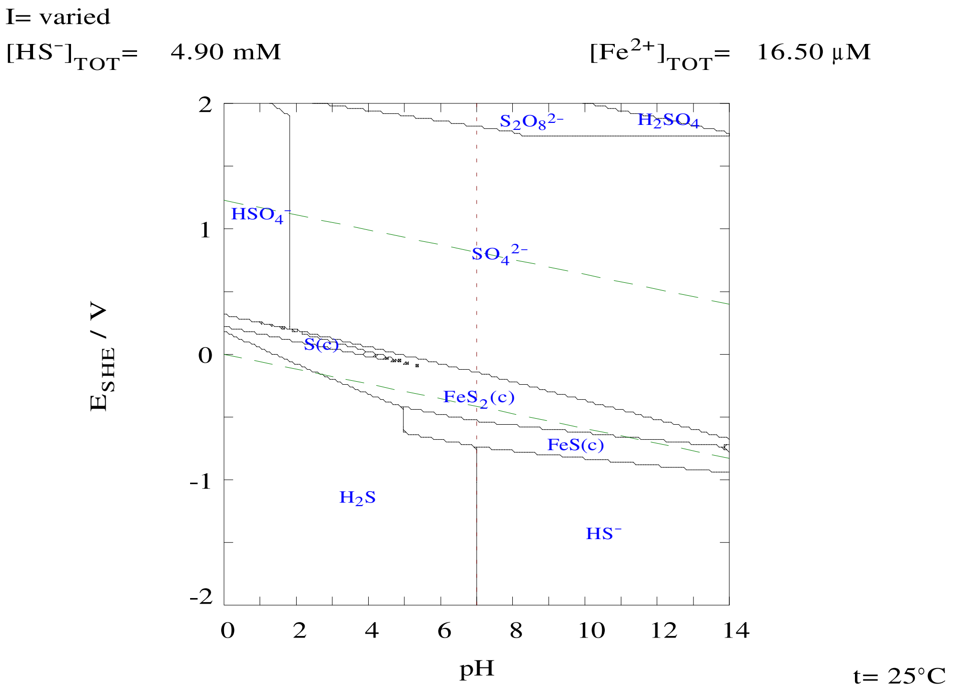

Figure p3 KFM03A/Depth = 450m, pH = 7.49, E_h = -250 mV, Total conc. Fe = 0.92 mg/l (16.50 µM). Total conc. S = 472 mg/l (4.90 mM). S species shown.

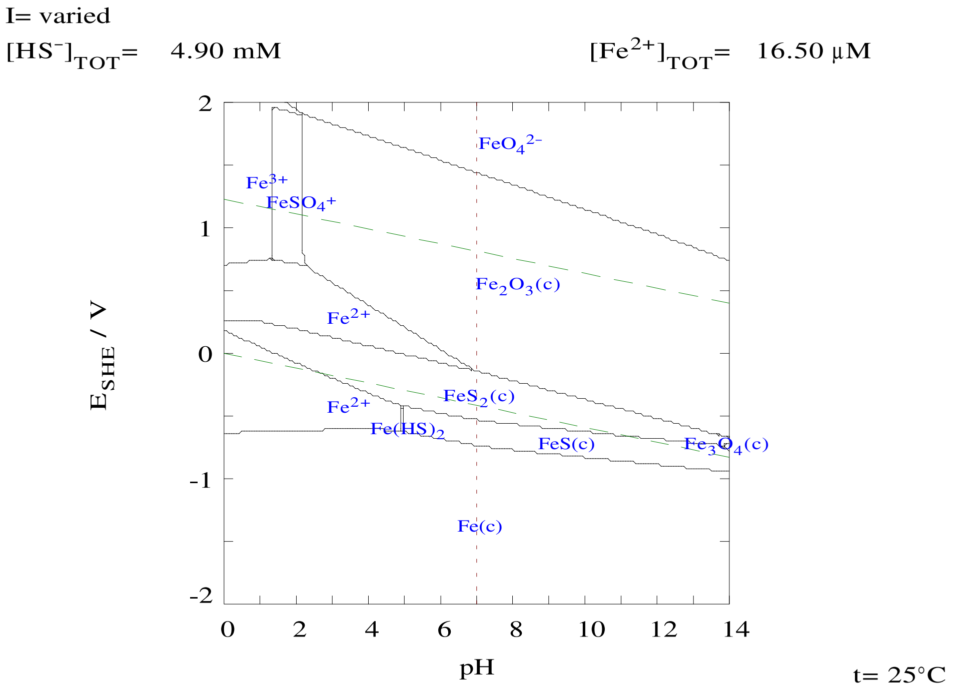

Figure p4 KFM03A/Depth = 450m, pH = 7.49, E_h = -250 mV, Total conc. Fe = 0.92 mg/l (16.50 µM). Total conc. S = 472 mg/l (4.90 mM). Fe species shown.

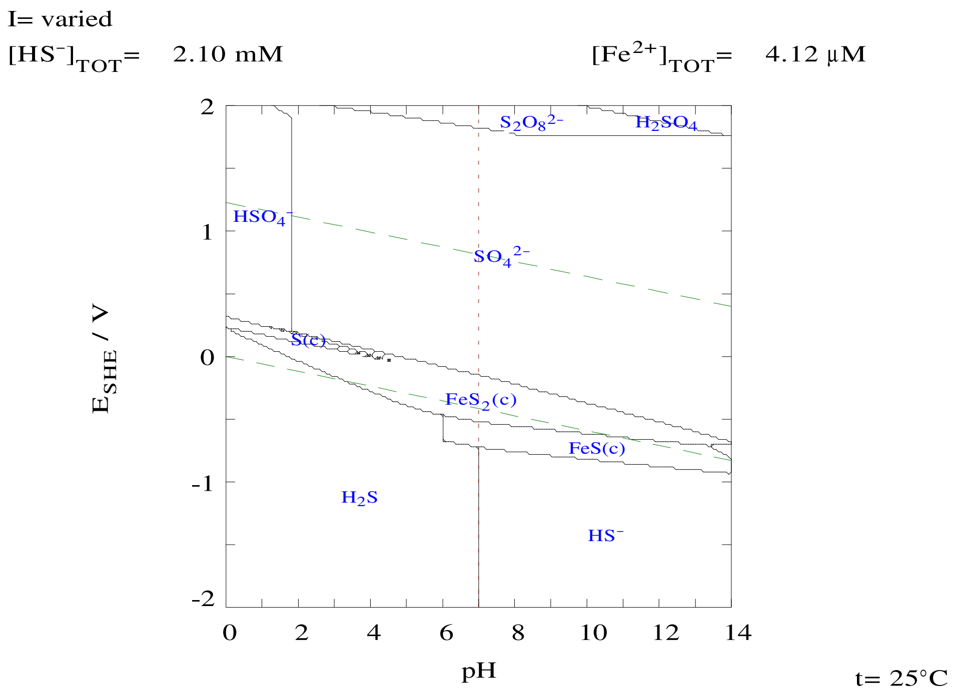

Figure q3 KFM03A/Depth = 642m, pH = 7.55, E_h = -200 mV, Total conc. Fe = 0.23 mg/l (4.12 µM). Total conc. S = 197 mg/l (2.10 mM). S species shown.

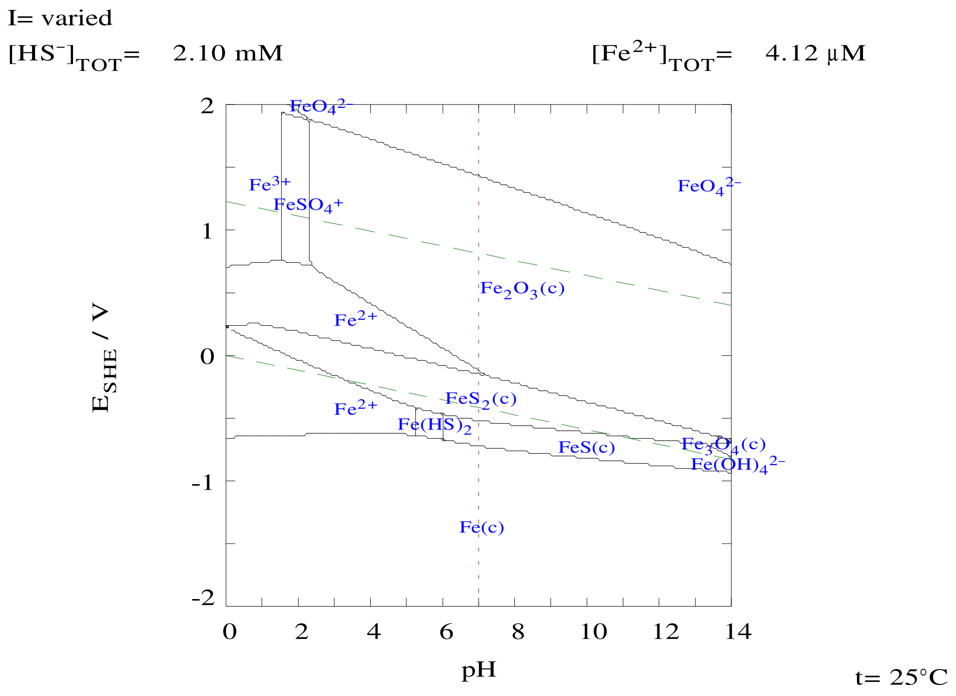

Figure q4 KFM03A/Depth = 642m, pH = 7.55, E_h = -200 mV, Total conc. Fe = 0.23 mg/l (4.12 µM). Total conc. S = 197 mg/l (2.10 mM). Fe species shown.

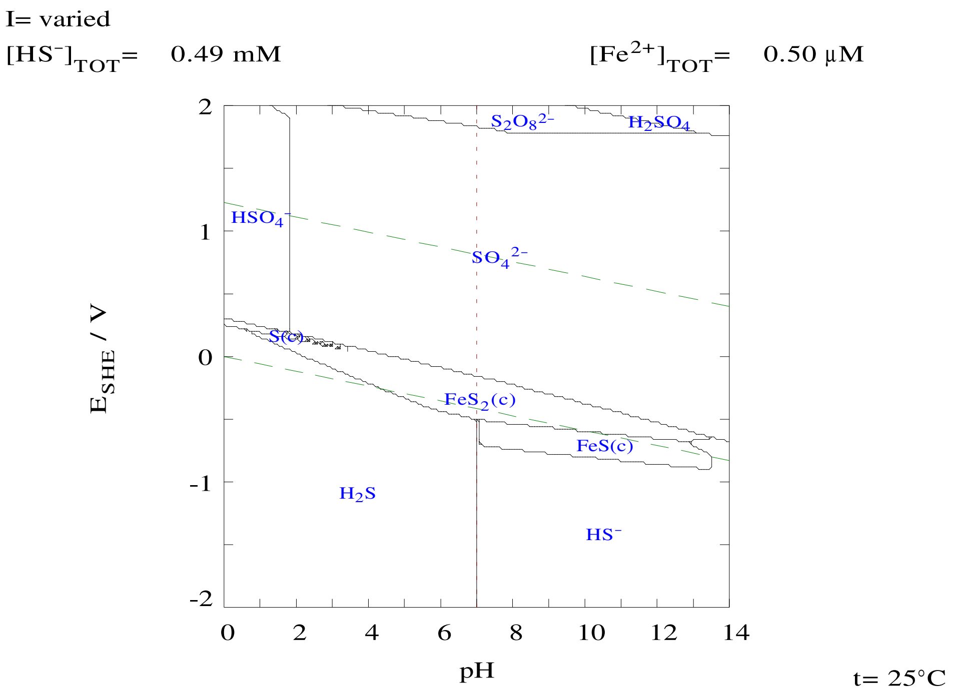

Figure z3 KFM03A/Depth = 990m, pH = 8.26, E_h = -150 mV, Total conc. Fe = 0.03 mg/l (0.53 µM). Total conc. S = 47 mg/l (0.49 µM). S species shown.

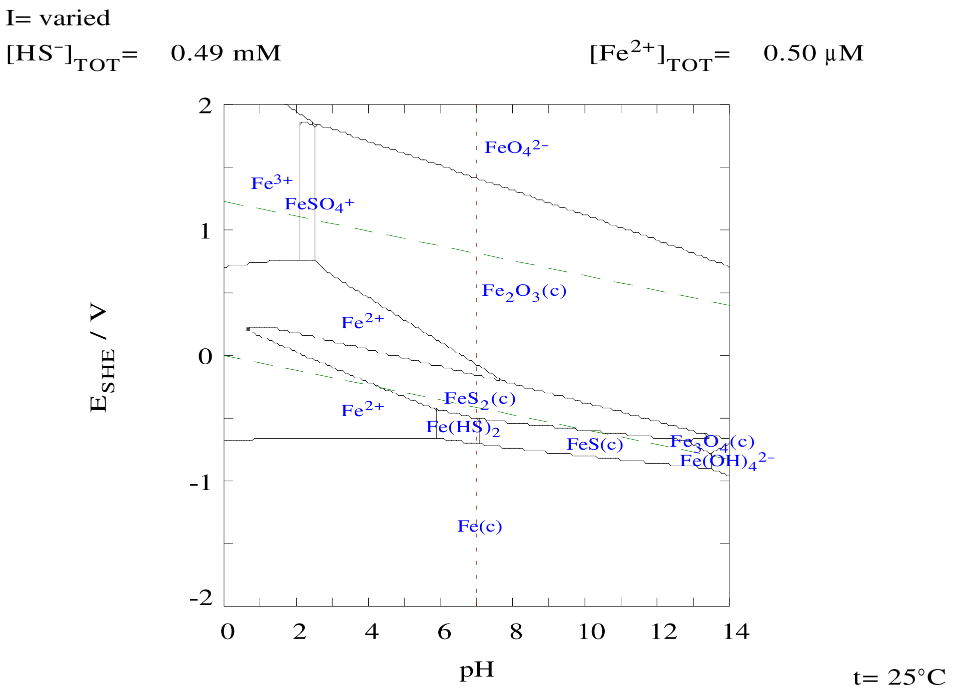

Figure z4 KFM03A/Depth = 990m, pH = 8.26, E_h = -150 mV, Total conc. Fe = 0.03 mg/l (0.53 µM). Total conc. S = 47 mg/l (0.49 µM). Fe species shown.

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