Simple Functions Spreadsheet tool presentation

Mireia Grivé, Cristina Domènech, Vanessa Montoya,
David Garcia, Lara Duro
Amphos 21

September 2010

SKB

Simple Functions Spreadsheet tool presentation

Mireia Grivé, Cristina Domènech, Vanessa Montoya,
David Garcia, Lara Duro

Amphos 21

September 2010

Abstract

This document is a guide for users of the Simple Functions Spreadsheet tool.

The Simple Functions Spreadsheet tool has been developed by Amphos 21 to determine the solubility limits of some radionuclides and it has been especially designed for Performance Assessment exercises.

The development of this tool has been promoted by the necessity expressed by SKB of having a confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner. Its development started in 2005 and since then, it has been improved until the current version.

This document describes the accurate and preliminary study following expert criteria that has been used to select the simplified aqueous speciation and solid phase system included in the tool.

This report also gives the basic instructions to use this tool and to interpret its results. Finally, this document also reports the different validation tests and sensitivity analyses that have been done during the verification process.

Sammanfattning

Det här dokumentet är en guide till användare av verktyget Simple Functions.

Verktyget Simple Fuctions har utvecklats av Amphos 21 för att bestämma löslighetsgränser för några radionuklider och det har blivit specifikt utformat för att tillämpning i arbete med säkerhetsanalyser.

Utvecklingen av detta verktyg har drivits av SKB:s behov av en säker och lätthanterlig metod för att snabbt och smidigt beräkna löslighetsgränser. Utformningen av verktyget påbörjades år 2005 och sedan dess har det kontinuerligt utvecklats och förbättrats, vilket har resulterat i den version som presenteras i denna rapport.

Det här dokumentet beskriver hur kriterier, fastställda av experter, har väglett valet av radionuklid-speciering i de kemiska system som har inkluderats i verktyget.

Denna rapport ger också grundläggande instruktioner för hur verktyget ska användas och hur resultaten kan tolkas. Slutligen beskrivs även de metoder för validering och känslighetsanalys vilka har använts under den kontroll- och utvecklingsprocess som har ingått i utvecklingen av verktyget.

Contents

1   Introduction

The Simple Functions Spreadsheet is a tool to determine the solubility limits of radionuclides especially designed for Performance Assessment exercises. This tool has been developed in an Excel© spreadsheet, and as such, it belongs to category 4b according to the definition in the Model summary report /SKB 2010/.

The development of this tool was promoted by the necessity of having a confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner.

The tool was originally built up in the frame of the SR-Can project as a request by SKB. Amphos 21 developed the tool to determine the solubility limits and the solid phases likely to exert the solubility control of some radionuclides under specific conditions. This first version was able to reproduce the determination and assessment of the concentration limits obtained in the SR-Can project by using more complex geochemical tools /Duro et al. 2006/.

Later, and due to the need of assessing uncertainties associated to the calculated solubilities, a new version of the tool, including uncertainty calculation was developed.

The two versions presented here are updates of the version used in SR-Can. Both versions incorporate the thermodynamic data changes reported in /Grivé et al. 2010/, but they differ in the conditions under which the solubility assessment is done:

- VERSION A is designed to calculate radionuclide solubility limits in representative groundwater compositions supplied by the user.
- VERSION B is designed to calculate radionuclide solubility limits in a groundwater that has interacted with Fe-corrosion products.

In this document we describe the basis and criteria used to build this tool in its two versions and how it must be used. We also present different validation and sensitivity exercises to test the capabilities of the tool.

Appendix A lists the new set of representative groundwater compositions of interest for SKB and Appendix B, the results of the solubility assessment of some radionuclides in these groundwaters.

2 Suitability of the tool

This tool is an Excel© spreadsheet that contains the simple algorithms needed to determine the solid phase that may exert the solubility control under the conditions of interest for a given radionuclide and its solubility.

The methodology used for its development and the way it is conceptualized and implemented in Excel© are presented below.

1st step: Selection of the speciation scheme

One of the aims of the Simple Functions Spreadsheet is to facilitate the calculation of the solubility limits. Currently, there are plenty of geochemical codes able to calculate the speciation of many different elements in solution. These codes have an associated thermodynamic database containing the stoichiometry and stability of every aqueous and solid species.

Most thermodynamic databases are exhaustive, in an attempt to cover a wide range of water compositions. They contain information on aqueous species that only appear under very specific water compositions which may or not be of interest for the current solubility assessment for SKB.
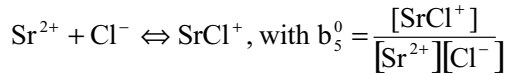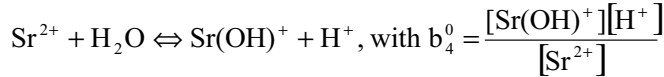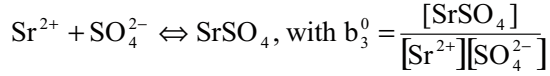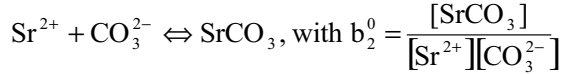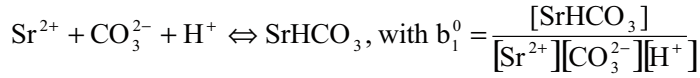
Although a generic code must contain all these data because it is intended for speciation calculations under all possible geochemical conditions, the Simple Functions Spreadsheet is tailored for the conditions of interest for SKB, and contains only those species accounting for at least 10% of the total element in solution under the following range of conditions:

- $T = 25°C$
- $I \leq 0.2$ m (ionic strength (I) in molality units (m))
- $6 < pH < 11$
- $-8 < pe < 14$
- $5 \cdot 10^{-5}$ m $< [SO_4] < 5 \cdot 10^{-2}$ m (range of interest for SKB)
- 10^{-4} m $< [CO_3] < 5 \cdot 10^{-3}$ m (range of interest for SKB)
- In VERSION A, $[Fe]_{aq}$ range given by the user; in VERSION B $[Fe]_{aq}$ is given by the equilibrium magnetite/goethite at the pH of interest.

The result of considering only those species that are relevant (that is, those representing more than 10% of the total aqueous concentration of the element in solution) is a much simpler calculation that can be easily implemented in an Excel spreadsheet. Besides, this provides the modeller with a much more hand able list of aqueous species, from where conclusions on the relative relevance of a change in a given parameter of the groundwater composition can be easily drawn.

Once the aqueous species have been selected, the steps described below have been followed to implement the speciation calculations in the Excel© spreadsheet:

1. Creation of a thermodynamic database including the stability constants for the selected aqueous species. For instance, in the case of strontium, the thermodynamic database includes the stability constants at $I = 0$ m (b_1^0 to b_5^0) of the selected aqueous species, being [ ] the activities of the aqueous species.

$$Sr^{2+} + CO_3^{2-} + H^+ \Leftrightarrow SrHCO_3, \text{ with } b_1^0 = \frac{[SrHCO_3]}{[Sr^{2+}][CO_3^{2-}][H^+]}$$

$$Sr^{2+} + CO_3^{2-} \Leftrightarrow SrCO_3, \text{ with } b_2^0 = \frac{[SrCO_3]}{[Sr^{2+}][CO_3^{2-}]}$$

$$Sr^{2+} + SO_4^{2-} \Leftrightarrow SrSO_4, \text{ with } b_3^0 = \frac{[SrSO_4]}{[Sr^{2+}][SO_4^{2-}]}$$

$$Sr^{2+} + H_2O \Leftrightarrow Sr(OH)^+ + H^+, \text{ with } b_4^0 = \frac{[Sr(OH)^+][H^+]}{[Sr^{2+}]}$$

$$Sr^{2+} + Cl^- \Leftrightarrow SrCl^+, \text{ with } b_5^0 = \frac{[SrCl^+]}{[Sr^{2+}][Cl^-]}$$

2. Introduction of the ionic strength correction equation proposed by Oelkers and Helgeson /Oelkers and Helgeson 1990/. This equation is used to calculate the value of the stability constants at ionic strengths other than 0. Following the example of Sr, the stability constant b_1 at I≠0 will be calculated according to Equation 1, where γ_i are the activity coefficients of the aqueous species i (Equation 2), z_i the ion charge and I, the ionic strength in molality units.

$$\log b_1 = \log b_1^0 - \log\gamma_{SrHCO_3} + \log\gamma_{Sr^{2+}} + \log\gamma_{CO_3^{2-}} + \log\gamma_{H^+} \qquad \text{Equation 1}$$

$$\log\gamma_i = -z_i^2 \times (0.5091 \times \sqrt{I}/(1+1.5 \times \sqrt{I})) - \log(1+0.0180153 \times I) + 0.064 \times I \qquad \text{Equation 2}$$

3. Introduction of the stoichiometric mass balance equations which allow the calculation of free concentrations of the species involved in the multiple equilibria. Because most equations are interconnected, this calculation is solved iteratively. Equation 3 shows the mass balance equation used to calculate the total aqueous concentration of Sr.

$$[Sr]_{TOT} = [Sr^{2+}] \begin{pmatrix} 1 + b_1[CO_3^{2-}][H^+] + b_2[CO_3^{2-}] \\ + b_3[SO_4^{2-}] + \dfrac{b_4}{[H^+]} + b_5[Cl^-] \end{pmatrix} \qquad \text{Equation 3}$$

The implementation of the mass balance equations in the PHREEQC code leads to the definition of a non-linear set of equations that the PHREEQC code solves by using a slightly modified Newton-Raphson method.

The effect of calculating solubility limits in solutions with higher ionic strengths than 0.2 m and/or at temperatures different from 25°C, have been properly evaluated by different sensitivity analyses reported in section 4 of this report. Likewise, the effect of calculating solubility limits in solutions with pH > 11 has been tested with the composition of the cement water (see Appendix B).

2nd step: Selection of the solubility limiting solid phase(s)

Depending on the studied conditions, there are different solids of a given element that may potentially form under specific conditions. It is not always the most stable solid phase which is more likely to precipitate, either due to kinetic constraints or other reasons. This is one of the issues extensively discussed in the solubility assessment document /Duro et al. 2006/. The selection of the most likely precipitating solid phases is, then, not only based on pure thermodynamic calculations but on an expert judgment.

In case that two or more of the selected solid phases can precipitate, the Simple Functions Spreadsheet selects the most stable under the conditions of interest. In case that no solid phase can be formed, the Simple Functions Spreadsheet renders a "Not solubility controlled" flag under the element of interest.

Different assumptions have been done concerning different parameters affecting solubility calculations:

Temperature: The Simple Functions Spreadsheet is engineered for calculations at room temperature (T = 25°C). A sensitivity study has been done to evaluate the influence of temperature within the range 0°C to 100°C on the final solubility value provided by Simple Functions Spreadsheet.

Ionic strength: The Simple Functions Spreadsheet is implemented for ionic strengths below 0.2 m. In order to simplify the calculations, we have introduced the ionic strength correction proposed in /Oelkers and Helgeson 1990/, which adopts Equation 2 for the calculation of activity coefficients (I is expressed in molality).

For I ≤ 0.2 m, the results of the application of Equation 2 are very similar to the ones obtained by the application of the Specific Interaction Theory (SIT), which is the one recommended by the NEA guidelines. The reason not to implement the SIT Theory is two-fold: i) the lack of interaction coefficients for some of the species and ii) the complexity that this implementation would add to the simplicity oriented character of the Simple Functions Spreadsheet.

To evaluate the influence that the activity correction approach can have on the final solubility calculation provided by the Simple Functions Spreadsheet, a sensitivity study has been done regarding ionic strength corrections (see section 4).

Specific constraints: There are some specific constraints in the Simple Functions Spreadsheet, mainly referring to redox equilibria. They are:

- The redox equilibrium CO_3^{2-}/CH_4 is decoupled. Carbonate is not allowed to reduce to methane, even for redox potentials lower enough as for the process to be thermodynamically favoured. The reason behind this decoupling is presented in /Duro et al. 2006/ and it is mainly based on the fact that reduction of carbonate is microbially mediated and microbes are not considered to have any relevance in the system of interest.

- Decoupling of the $SO_4^{2-}/S_2O_3^{2-}/HS^-$ redox systems. The same reasoning applies to this decoupling.

- No equilibrium with calcite is forced. In case the groundwater composition entered by the user results in an oversaturation with regards to calcite, the following warning flag will appear:
  WARNING!!! Calcite is oversaturated, check whether you allow a SI (calcite) = XXX
  where instead of XXX, the saturation index of calcite in the groundwater will appear.

3rd step: Calculation of uncertainties

We have used a derivative approach to calculate through error propagation algorithms the uncertainties associated with the calculated solubility limits. Derivative methods are fast and convenient for equilibrium reactions, although they have several limitations: variables are assumed to have a Gaussian uncertainty distribution, and they are also assumed to be independent (no covariance terms are included in the algorithm). More sophisticated methods are available (probabilistic approach with Monte Carlo simulations, as described for example in /Cabaniss 1999/, and even tailor-made software packages have been developed for assessing uncertainties in solubility calculations (e.g. /Ekberg and Ödegaard-Jensen 2004/ and references therein). However, these methods are considered to be out of the scope of the present work as it is focused on developing a simplified tool for assessing solubility uncertainties to be implemented in an Excel spreadsheet.

An element specific solubility model, that is, an analytical relationship between the maximum concentration of the element and all the variables and thermodynamic stability constants, can be generically described as in Equation 4, where S is the total solubility of the element of interest, that is, the sum of all the aqueous species of the element present in the solution, and Z_i are the different variables or input parameters needed to calculate the solubility.

$$S = f(pH, T, [ligands], K's, …) = f(Z_1, Z_2, …, Z_n) \qquad \text{Equation 4}$$

Using error propagation theory, the uncertainty of S and ΔS can be derived from uncertainties in input parameters (Equation 5).
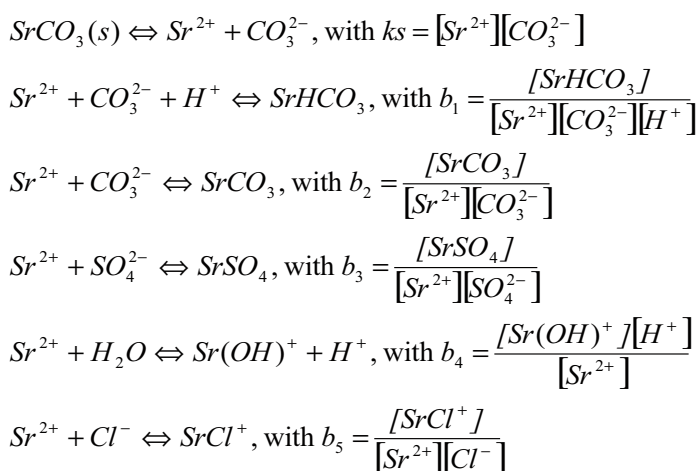
$$\Delta S = \sqrt{\left(\frac{\partial S}{\partial Z_1}\right)^2 \Delta Z_1{}^2 + \left(\frac{\partial S}{\partial Z_2}\right)^2 \Delta Z_2{}^2 + ... + \left(\frac{\partial S}{\partial Z_n}\right)^2 \Delta Z_n{}^2} \qquad \text{Equation 5}$$

As previously pointed out, the variables Z_i must be independent in order for this approximation to be valid. This is obviously not the case, as the concentrations of the free ligands depend on a range of equilibrium constants and, more importantly, they are mutually interdependent (this is why the spreadsheet uses an iterative method in the calculation). To overcome this problem we have followed the chain rule for the calculations of the derivatives (Equation 6) where Y_j represents variables in the solubility function that implicitly depend on the variable Z_i.

$$\frac{\partial S}{\partial Z_i} = \frac{\partial f}{\partial Z_i} + \sum_j \frac{\partial f}{\partial Y_j}\frac{\partial Y_j}{\partial Z_i} \qquad \text{Equation 6}$$

A review of published uncertainties in the equilibrium constants have been carried out in order to assign values to ΔZ_i (Equation 5). Where possible, the experimental error of the reported equilibrium constants in the related bibliography has been taken. If no error was reported in the original source, half of the range of variation between different bibliographic sources was taken as the uncertainty. Finally, if there was only one reference without an associated error, a default value of ± 0.3 log units has been taken as the uncertainty in $logK_i$.

An example will illustrate the procedure. Let's consider the solubility function of strontianite ($SrCO_3(s)$), which is given by Equation 7, where ks is the solubility product of strontianite and b_1-b_5 are the equilibrium constants of the reactions involved in the solubility calculation, as shown below:

$$SrCO_3(s) \Leftrightarrow Sr^{2+} + CO_3^{2-} \text{, with } ks = [Sr^{2+}][CO_3^{2-}]$$

$$Sr^{2+} + CO_3^{2-} + H^+ \Leftrightarrow SrHCO_3 \text{, with } b_1 = \frac{[SrHCO_3]}{[Sr^{2+}][CO_3^{2-}][H^+]}$$

$$Sr^{2+} + CO_3^{2-} \Leftrightarrow SrCO_3 \text{, with } b_2 = \frac{[SrCO_3]}{[Sr^{2+}][CO_3^{2-}]}$$

$$Sr^{2+} + SO_4^{2-} \Leftrightarrow SrSO_4 \text{, with } b_3 = \frac{[SrSO_4]}{[Sr^{2+}][SO_4^{2-}]}$$

$$Sr^{2+} + H_2O \Leftrightarrow Sr(OH)^+ + H^+ \text{, with } b_4 = \frac{[Sr(OH)^+][H^+]}{[Sr^{2+}]}$$

$$Sr^{2+} + Cl^- \Leftrightarrow SrCl^+ \text{, with } b_5 = \frac{[SrCl^+]}{[Sr^{2+}][Cl^-]}$$

$$S = \frac{ks}{[CO_3^{2-}]}\left(\begin{array}{c} 1 + b_1[CO_3^{2-}][H^+] + b_2[CO_3^{2-}] \\ + b_3[SO_4^{2-}] + \frac{b_4}{[H^+]} + b_5[Cl^-] \end{array}\right) \qquad \text{Equation 7}$$

The partial derivatives of S with respect the thermodynamic constants ks and b_1-b_5 are readily calculated. On the other hand, the concentration of carbonate is not an independent variable, as it depends on the concentration of bicarbonate (which is a fixed input), the pH (also a fixed input) and the equilibrium constant of the carbonate-bicarbonate reaction, namely K_c. Therefore, the source of uncertainty is this constant, and S must be derived with respect to this constant as shown in Equation 8.

$$\frac{\partial S}{\partial K_c} = \frac{\partial S}{\partial [CO_3^{2-}]}\frac{\partial [CO_3^{2-}]}{\partial K_c} \qquad \text{Equation 8}$$

Both derivatives in the previous equations can be easily calculated. The case of the sulphate ligand is more complicated, as its concentration derives from the total content of sulphate and a range of equilibria involving other free ligands concentrations such as $[Ca^{2+}]$, $[Na^+]$ and $[Fe^{2+}]$, as expressed in Equation 9.

$$[SO_4^{2-}] = \frac{[SO_4^{2-}]_{tot}}{\begin{pmatrix} 1 + K^{s,h}[H^+] + K^{s,ca}[Ca^{2+}] + K^{s,na}[Na^+] + K^{s,fe}[Fe^{2+}] \\ + K^{s,fe,h}[Fe^{2+}][H^+] \end{pmatrix}} \qquad \text{Equation 9}$$

In the above equation, $K_i^{s,ligand}$ are the equilibrium constants for all the reactions where sulphate is involved, and therefore the uncertainty in these constants have been dealt with in Equation 10, where we have taken into account that other ligands can be dependent on the equilibrium constants included in Equation 9.

$$\frac{\partial S}{\partial K^{s,ligand}} = \frac{\partial S}{\partial [SO_4^{2-}]} \frac{\partial [SO_4^{2-}]}{\partial K^{s,ligand}} + \frac{\partial S}{\partial [ligand]} \frac{\partial [ligand]}{\partial K^{s,ligand}} \qquad \text{Equation 10}$$

For example, the concentration of $[Na^+]$ can be expressed as in Equation 11, and therefore Equation 10 can be expressed as Equation 12 (noting that $K^{s,na} = K^{na,s}$).

$$[Na^+] = \frac{[Na^+]_{tot}}{(1 + K^{na,c}[CO_3^{2-}] + K^{na,c,h}[CO_3^{2-}][H^+] + K^{na,s}[SO_4^{2-}])} \qquad \text{Equation 11}$$

$$\frac{\partial S}{\partial K^{s,na}} = \frac{\partial S}{\partial [SO_4^{2-}]} \frac{\partial [SO_4^{2-}]}{\partial K^{s,na}} + \frac{\partial S}{\partial [Na^+]} \frac{\partial [Na^+]}{\partial K^{s,na}} \qquad \text{Equation 12}$$

Again, the derivatives in the previous equation are readily calculated from Equation 7, Equation 9 and Equation 11.

Following the same procedure equivalent expressions have been derived for all elements included in the analysis and derivatives calculated analytically. All the formulae obtained have been introduced in the Simple Functions Spreadsheet.

One useful output of the calculations has been the ranking of parameters according to the effect of their uncertainty on the overall solubility uncertainty. This can be done assuming that each term $\left(\frac{\partial S}{\partial Z_n}\right)^2 \Delta Z_n^2$ in Equation 5, which is the variance of Z_n, represents the degree of uncertainty that the variable Z_n gives to the overall uncertainty. This degree of uncertainty can be defined as a percentage, f_{Zi}, with the expression of Equation 13.

$$f_{Z_i}(\%) = \frac{\left(\frac{\partial S}{\partial Z_i}\right)^2 \Delta Z_i^2}{\Delta S^2} \cdot 100 \qquad \text{Equation 13}$$

Thus, the use of the formula above will give a ranking of parameters as a function of their impact on the overall uncertainty.

3 Usage of the tool

Before using the Simple Functions Spreadsheet tool it is important that the user activates the option **iteration** in the menu TOOLS/OPTIONS/CALCULATE (Figure 3-1) in Excel© Office 2003 program or in the menu OFFICE BUTTON/EXCEL OPTIONS/FORMULAS in Excel© Office 2007 program (Figure 3-2). With this selected item, the user allows Excel© to use the iterative method in the calculations.
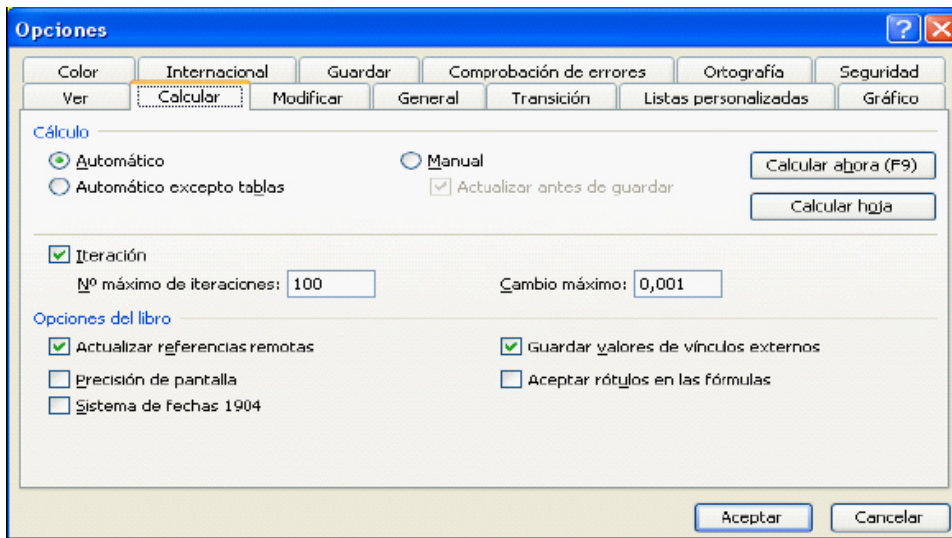

Figure 3-1. *Window showing the item that must be selected before using the Simple Functions Spreadsheet tool in the Excel program Office 2003.*
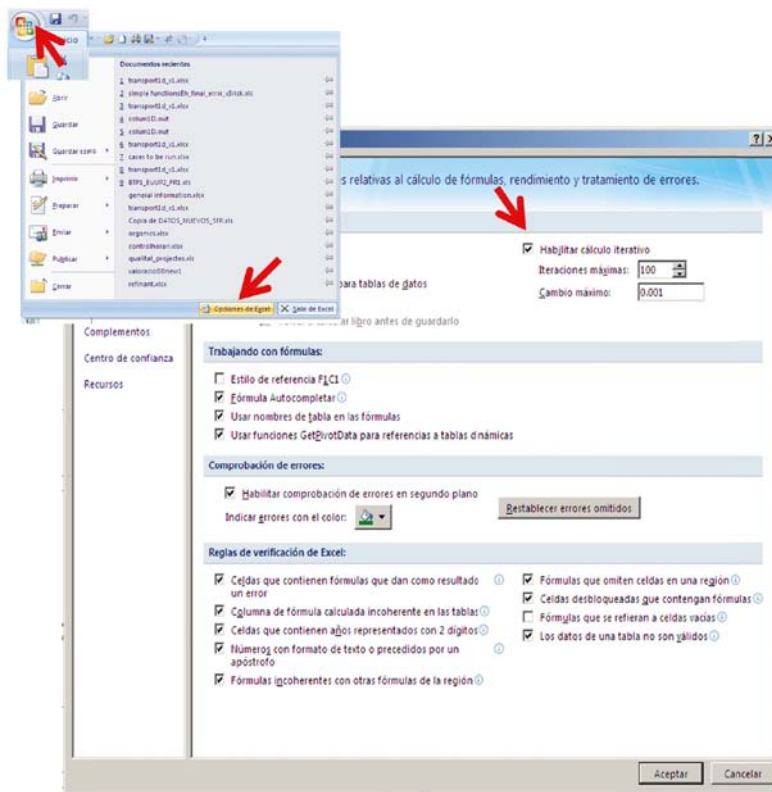

Figure 3-2. *Window showing the item that must be selected before using the Simple Functions Spreadsheet tool in the Excel program Office 2007.*

3.1 Description of VERSION A of the Simple Functions Spreadsheet

The Simple Functions Spreadsheet contains two general worksheets, "**INPUT DATA**" and "**DON'T TOUCH**", besides one worksheet per element of interest.

The user can only modify the worksheet named "**INPUT DATA**". The remaining worksheets are protected by a password in order to avoid unintentional modifications that may give rise to erroneous calculations.

The "**INPUT DATA**" worksheet contains the information shown in Figure 3-3.

The user can enter the composition of the groundwater of interest (**concentrations in m**) in the blue cells. All the numbers refer to total element content, except that for hydrogenocarbonate, where the **free HCO₃⁻** concentration is required. It is very important to enter this parameter in the sheet correctly.

All the concentrations must contain a value in the blue cells, otherwise, the spreadsheet does not calculate. This means that if, Si is missing in the composition of groundwater the user must fill in the concentration cell corresponding to Si with a very small concentration (not influencing the aqueous speciation) instead of zero (10^{-20} m, for example).

The total ionic strength (I) should be lower than 0.2 m to ensure that calculations are right. In case that the number introduced by the user in the blue cell besides I (mol/kg) is higher than 0.2 m, the following warning flag appears:

WARNING!!! Ionic Strength is over 0.2 m, your calculations will not be completely correct

In this case, the user may decide whether he/she wants to continue with calculations, considering the influence that a I higher than 0.2 m has on the final results (see section 4.2).

As explained above, another warning flag will appear in case that the groundwater composition results in an oversaturation of the system with respect to calcite:

WARNING!!! Calcite is oversaturated, check whether you allow a SI (calcite) = XXX

FILL THE BLUE CELLS, GW COMPOSITION

INPUT DATA	
pH	6
Eh (mV)	-143
I (mol/kg)	0.19
[HCO3-] (m)*	1.77E-03
[SO4-2]tot (m)**	6.80E-03
[Cl]tot (m)	1.53E-01
[Ca]tot (m)	2.33E-02
[Na]tot (m)	8.88E-02
[Fe]tot (m)	3.31E-05
[Si]tot (m)	1.85E-04

* free hydrogenocarbonate concentration, no calcite equilibrium, no reduction to methane
** sulphate concentration, no reduction to sulphide

CONSTRAINTS	
T = 25ºC	
I ≤ 0.2m	

Figure 3-3. View of the "INPUT DATA" worksheet.

Solubility calculations may be affected by the precipitation of calcite, and again, the user has the responsibility to decide whether he/she wants to go on with the calculation, bearing in mind that the results will not be completely correct.

The worksheet named "**DON'T TOUCH**" must not be modified by the user. This worksheet contains the thermodynamic database for the major components of the groundwater. It takes data introduced directly in the "**INPUT DATA**" worksheet and calculates:

- The stability constants and the given ionic strength by using the Oelkers and Helgeson equation for activity coefficients (Equation 2).

- The free concentration of the major elements in solution, by means of an iterative calculation
  $[HCO_3^{2-}]$
  $[SO_4^{2-}]$
  $[Cl^-]$
  $[Ca^{2+}]$
  $[Na^+]$
  $[Fe^{2+}]$

- The $pO_2(g)$

- The saturation index of calcite.

- Intermediate calculations related to the derivatives involving free ligands and their respective thermodynamic constants, together with their associated uncertainties.

The numbers calculated in the "**DON'T TOUCH**" worksheet are those that will be used by the spreadsheet to calculate the speciation and the solubility of the radionuclides in the other worksheets.

The **individual element worksheets** use the information generated in the "**DON'T TOUCH**" worksheet to:

- Calculate the aqueous speciation.

- Calculate the solubility of one or more solid phases selected as possible to control the concentration of a given element under the conditions of interest.

- Calculate the derivatives and the uncertainties for the thermodynamic constants affecting the solubility of each element.

- Select the solid phase resulting in lower solubility from the ones possibly forming as the solubility limiting solid phase.

- Render the value of the solubility limit under the conditions of interest.

- Render the value of the uncertainty of the solubility value both in linear and log units, and the contribution in percentage, f_{Zi}, that the uncertainty of each thermodynamic constant represents to the overall uncertainty in the solubility as defined in the previous section. This is useful as it gives an idea of the main equilibria that most affect the solubility, providing guidance on which constants should be the subject of the most comprehensive review in their uncertainty.

- In case that the solubility of the possible solid phases is over 0.01 m, the element is considered as non solubility limited and the following flag appears: "**No Solubility Limited**".

3.1.1   Example of application

For illustrative purposes, we have applied the methodology using the water composition given in Table 3-1. The results of the uncertainty analysis with these input data are summarised in Table 3-2.

Generally speaking, the most sensitive parameters are the solubility product of the solid phase and the formation constant of the main aqueous species.

Table 3-1. Input data for calculating solubilities and uncertainties.

INPUT DATA	
pH	6
Eh (mV)	-143
I (mol/kg)	0.19
$[HCO_3^-]$ (m)	1.77E-03
$[SO_4^{2-}]_{tot}$ (m)	6.80E-03
$[Cl]_{tot}$ (m)	1.53E-01
$[Ca]_{tot}$ (m)	2.33E-02
$[Na]_{tot}$ (m)	8.88E-02
$[Fe]_{tot}$ (m)	3.31E-05
$[Si]_{tot}$ (m)	1.85E-04

Table 3-2. Main results of the solubility uncertainty calculation. Log S stands for the log of the solubility of the solid phase, Δ Log S is the uncertainty in LogS, f_Z (%) stands for the contribution in percentage of the uncertainty of each thermodynamic constant to the overall uncertainty in the solubility.

Element	Solid phase	Solubility limit		Ranking of parameters most contributing to uncertainty	
		Log S	Δ Log S	Parameter	f_Z (%)
Sr	Celestite (SrSO$_4$)	−3.16	0.13	$K_{sp}(SrSO_4)$	94.64
				$K^0(CaSO_4(aq))$	4.34
Ra	RaSO$_4$ (s)	−6.76	0.05	$K_{sp}(RaSO_4)$	66.64
				$K^0(CaSO_4(aq))$	26.41
Ni	n.s.l				
Sn	SnO$_2$ (s)	−7.28	0.43	$K_{sp}(SnO_2)$	55.18
				$K^0(Sn(OH)_4(aq))$	44.12
Se	FeSe$_2$ (s)	−9.48	0.64	$K_{sp}(FeSe_2)$	91.06
				$K^0(HSe^-)$	8.92
Ag	AgCl (cr)	−5.08	0.16	$K^0(AgCl_4^{3-})$	58.33
				$K^0(AgCl_2^-)$	36.70
				$K^0(AgCl_3^{2-})$	3.78
U	UO$_2$·2H$_2$O(am)	−8.13	0.54	$K_{sp}(UO_2 \cdot 2H_2O(am))$	77.35
				$K^0(U(OH)_4(aq))$	22.20
Zr	Zr(OH)$_4$ (s)	−7.75	0.74	$K^0(Zr(OH)_4(aq))$	98.63
Nb	Nb$_2$O$_5$ (s)	−4.78	0.02	$K_{sp}(Nb_2O_5)$	100.00
Pa	Pa$_2$O$_5$ (s)	−6.47	0.44	$K_{sp}(Pa_2O_5)$	96.37
				$K^0(PaO_2(OH)(aq))$	3.63
Np	NpO$_2$·2H$_2$O (am)	−8.86	0.41	$K^0(Np(OH)_4)$	65.90
				$K_{sp}(NpO_2 \cdot 2H_2O(am))$	27.82
				$K^0(Np(OH)_3^+)$	5.45
Pu	Pu(OH)$_4$ (s)	−3.54	0.65	$K_{sp}(Pu(OH)_4(s))$	96.32
				$K^0(PuSO_4^+)$	3.03
Am	Am$_2$(CO$_3$)$_3$ (s)	−4.51	0.48	$K_{sp}(Am_2(CO_3)_3(s))$	98.62
				$K^0(Am(CO_3)^+)$	1.16
Cm	Cm$_2$(CO$_3$)$_3$ (s)	−4.51	0.48	$K_{sp}(Cm_2(CO_3)_3 (s))$	98.22
				$K^0(Cm(CO_3)^+)$	1.15
Tc	TcO$_2$:1.63H$_2$O	−8.13	0.23	$K_{sp}(TcO_2:1.63H_2O)$	92.44
				$K^0(TcCO_3(OH)_2)$	7.53
Pd	Pd(OH)$_2$(s)	−5.00	0.57	$K_{sp}(Pd(OH)_2(s))$	98.89
Sm	Sm(CO$_3$)(OH) (s)	−5.15	0.14	$K_{sp}(Sm(CO_3)(OH) (s))$	85.67
				$K^0(Sm(CO_3)^+)$	12.47
Ho	Ho$_2$(CO$_3$)$_3$(s)	−4.76	0.23	$K^0(Ho_2(CO_3)_3 (s))$	92.50
				$K^0(Ho(CO_3)^+)$	6.56
Th	ThO$_2$·2H$_2$O (am)	−8.04	0.43	$K_{sp}(ThO_2 \cdot 2H_2O(am))$	81.88
				$K^0(Th(CO_3)(OH)_3^-)$	15.30
Pb	Cerussite (PbCO$_3$)	−5.16	0.31	$K_{sp}(PbCO_3)$	95.16
				$K^0(PbCl^+)$	4.26

## 3.2 Description of VERSION B of the Simple Functions Spreadsheet

VERSION B is designed for solubility assessments in a groundwater that has interacted with Fe-corrosion products.

Fe corrosion processes are complex and kinetically controlled and therefore, the equilibration of a given groundwater with iron corrosion products is not simple. Because the objective of Simple Functions Spreadsheet tool is, within others, to provide a simple confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner, it is not possible to calculate with Simple Functions Spreadsheet tool the resulting groundwater composition after equilibrating it with the corrosion products. The user is thus, advised to use specialised geochemical codes if a true chemical equilibrium is desired to be calculated.

Experience gained when using specialised geochemical codes for this kind of calculations has shown that the parameters of the groundwater most affected by the interaction with Fe-corrosion products are pH, Eh and total iron aqueous concentration.

The conceptual model included in this tool does not aim at obtaining the composition of one of the reference groundwater in equilibrium with Fe corrosion products, but to calculate which would be the Eh and $[Fe]_{aq}$ that guarantee that the new chemical conditions are the most similar to the equilibrium with these Fe corrosion products. With this aim, the following assumptions have been considered:

- Groundwater equilibrates with the boundary magnetite/goethite, which are the Fe-bearing minerals assumed as corrosion products of the canister. This assumption allows the calculation of the Eh for the pH of interest, equal to the one of the initial groundwater entering the system (Figure 3-4).

- Fe^{2+} concentration is calculated from the equilibrium boundary magnetite-goethite at the pH and Eh of interest.
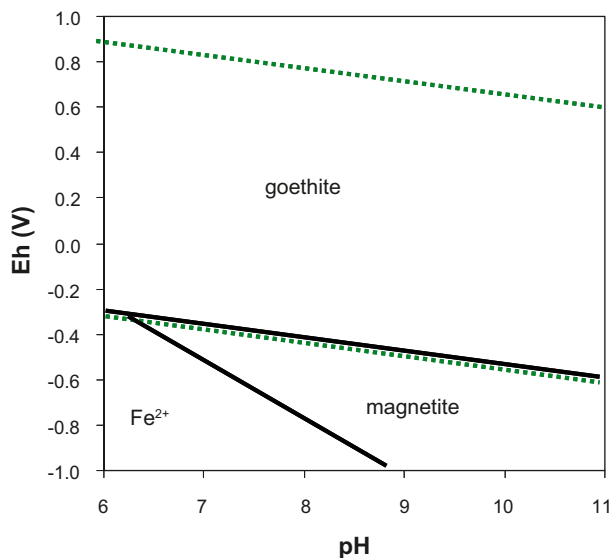
Figure 3-4. Predominance diagram Eh vs pH showing the stability fields of goethite and magnetite, and their theoretical equilibrium, by assuming an excess of both minerals. Dashed green lines correspond to the stability of water.

The calculations of Eh and of $[Fe]_{aq}$ have been implemented in the "**DON'T TOUCH**" worksheet. In this worksheet, the Eh(mV) and $pO_2(g)$ corresponding to the equilibrium magnetite-goethite (reaction 1) are calculated with Equation 14 to Equation 16, where logK46 and logK47 are respectively the equilibrium constants of reactions 2 and 3 at the ionic strength of interest.

$$Fe_3O_4 + 1.5H_2O + 0.25O_2(g) = 3FeOOH \qquad\qquad \text{reaction 1}$$

$$Eh\ (mV) = 59.16/4*(logpO_2+83.1–4pH) \qquad\qquad \text{Equation 14}$$

$$log(pO_2) = –4(logK46–3logK47) \qquad\qquad \text{Equation 15}$$

$$Eh\ (mV) = 59.16/4*[(–4(–logK46–3(–logK47)))+83.1–4pH] \qquad\qquad \text{Equation 16}$$

$$3Fe^{2+} + 3H_2O + 0.5O_2(g) = Fe_3O_4 + 6H^+ \qquad\qquad \text{reaction 2}$$

$$Fe^{2+} + 1.5H_2O + 0.25O_2(g) = FeOOH + 2H^+ \qquad\qquad \text{reaction 3}$$

$[Fe^{2+}]$ (in m) is then calculated with Equation 17, derived from reaction 3, and at the pH and $pO_2(g)$ previously obtained.

$$log[Fe^{2+}]= –logK47–2pH–0.25logpO_2 \qquad\qquad \text{Equation 17}$$

The only difference with respect VERSION A, is that the user is not able to give a value in the Eh(mV) cell neither in the [Fe]tot (m) cell of the "**INPUT DATA**" worksheet but they are internally calculated by assuming the equilibrium magnetite-goethite.

3.2.1 Validation of the VERSION B

Figure 3-5 and Figure 3-6 compare the values of $log[Fe^{2+}]$ and Eh(mV) calculated using the geochemical code PHREEQC and the approach implemented in the alternative version of the Simple Functions Spreadsheet. Results show the validity of the assumptions performed.
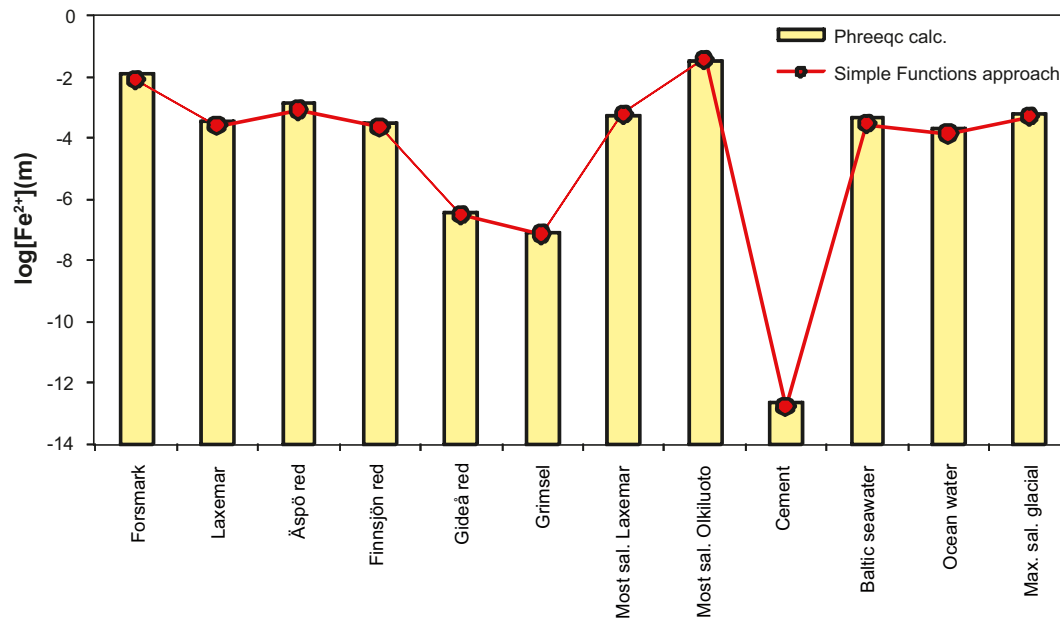
Figure 3-5. *Comparison of the $log[Fe^{2+}]$ calculated in equilibrium with goethite and magnetite at the pH and ionic strength of the different groundwater compositions (Table A-1) using the geochemical code PHREEQC and VERSION B of the Simple Functions Spreadsheet. The word "red" in the groundwater name accounts for reducing conditions (in terms of Eh) (see Table A-1).*
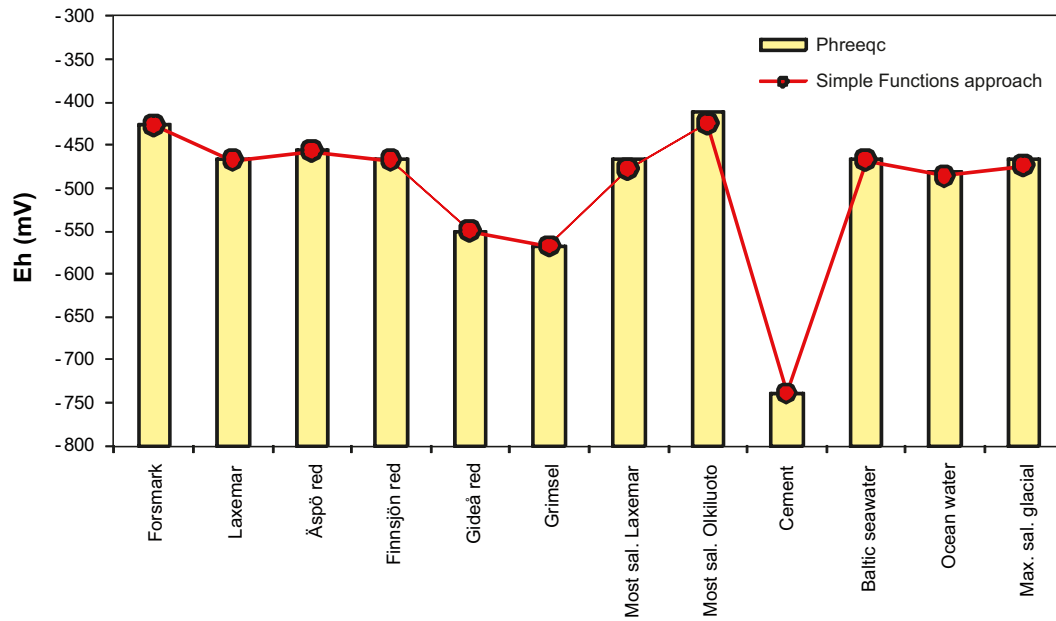
Figure 3-6. *Comparison of the Eh(mV) calculated in equilibrium with goethite and magnetite at the pH and ionic strength of the different groundwater compositions (Table A-1) using the geochemical code PHREEQC and using VERSION B of the Simple Functions Spreadsheet. The word "red" in the ground-water name accounts for reducing conditions (in terms of Eh) (see Table A-1).*

4 Development process and verification

4.1 Validation of solubility calculations

The Simple Functions Spreadsheet has been developed as an easy-handling tool to calculate ranges and distributions of solubility limits to be used in the radionuclide transport calculations. Because of its simplicity, calculations are less complete than those used in other geochemical codes. But it is the main aim of this tool to obtain results still valid under all the conditions of interest for Performance Assessments.

In this section we present the results of a benchmarking exercise in which the solubilities calculated with the VERSION A of the Simple Functions Spreadsheet for each radionuclide and for each groundwater composition of interest (see Appendix A) have been compared with the solubilities calculated with the code PHREEQC /Parkhurst and Appelo 2001/ and in some cases calculated with the code HYDRA-MEDUSA /Puigdomènech 2002/.

Calculations with PHREEQC and HYDRA-MEDUSA have been done assuming in agreement with the Simple Functions Spreadsheet that neither CO_3^{2-} nor SO_4^{2-} can be reduced to CH_4 nor to HS^- respectively; that is, assuming that the CO_3^{2-}/CH_4 and the $SO_4^{2-}/S_2O_3^{2-}/HS^-$ redox systems are decoupled. Given that the Simple Functions Spreadsheet does not take into account the precipitation of calcite in case it is oversaturated, benchmarking calculations with PHREEQC or with HYDRA-MEDUSA have neither considered the precipitation of calcite.

The calculated solubilities for the different groundwater compositions (12 in total, listed in Table A-1, Appendix A) are shown in Figure 4-1 to Figure 4-3 and listed in Tables B-1 to B-6 of Appendix B). As can be seen in Figure 4-1 to Figure 4-3 the benchmarking exercise shows that the Simple Functions Spreadsheet is able to properly identify the limiting solubility phase of each radionuclide in the groundwater of interest. We must always recall that the solubility limiting solid phases included in Simple Functions have been selected from a prior expert judgement. Therefore, formally speaking it is not the excel spreadsheet the one selecting the solid phase likely to limit the solubility, but selecting the less soluble phase from the limited set of solid phases allowed to form in the Simple Functions Spreadsheet.

This exercise has also shown that radionuclide concentrations calculated using the Simple Functions Spreadsheet agree, within the uncertainties ranges, with the concentrations calculated with PHREEQC and HYDRA-MEDUSA codes.

As expected, the main differences are observed in saline groundwaters (Laxemar and Olkiluoto). The reason is strongly related to the high ionic strength of these groundwaters, which significantly differs from the maximum ionic strength for which the Simple Functions Spreadsheet was designed.
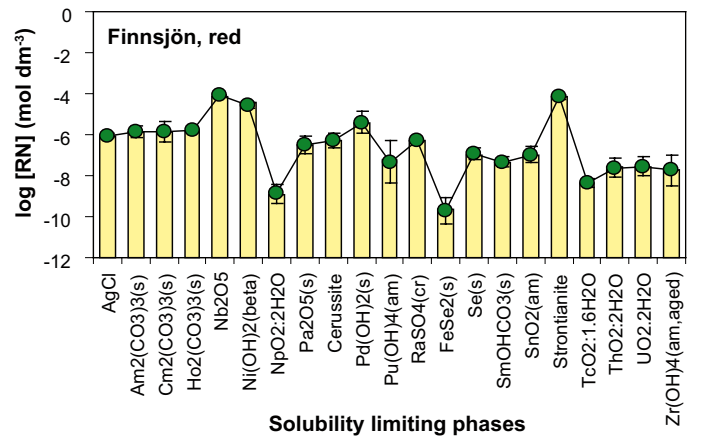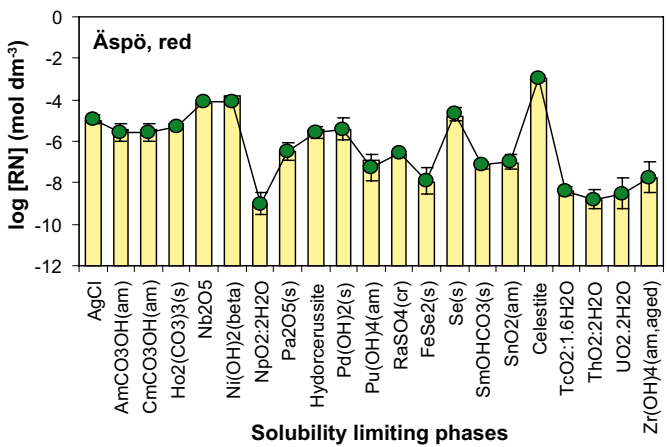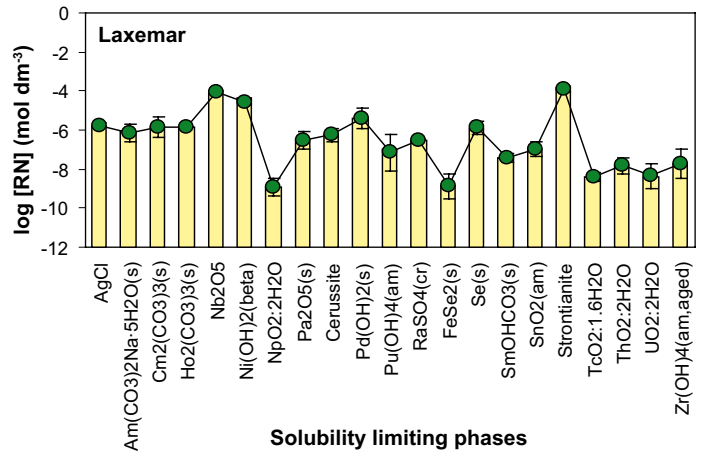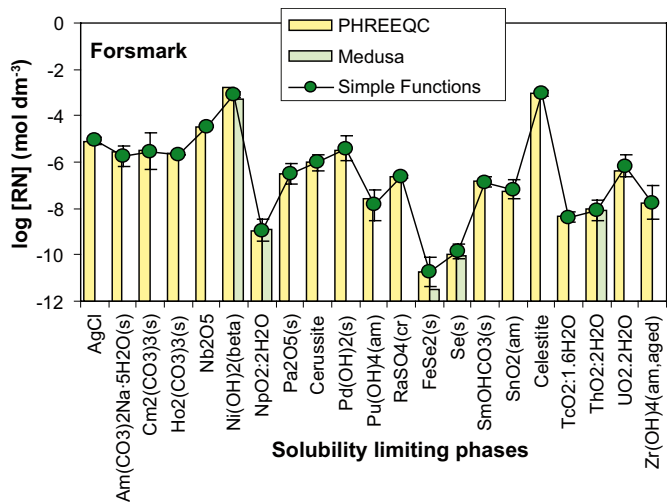
Figure 4-1. *Solubility limiting phases and radionuclide concentrations calculated with the VERSION A of Simple Functions Spreadsheet (symbols), PHREEQC code (yellow bars) and HYDRA-MEDUSA code (green bars) for Forsmark, Laxemar, Äspö (most reducing Eh of Table A-1) and Finnsjön (most reducing Eh of Table A-1) groundwater compositions.*
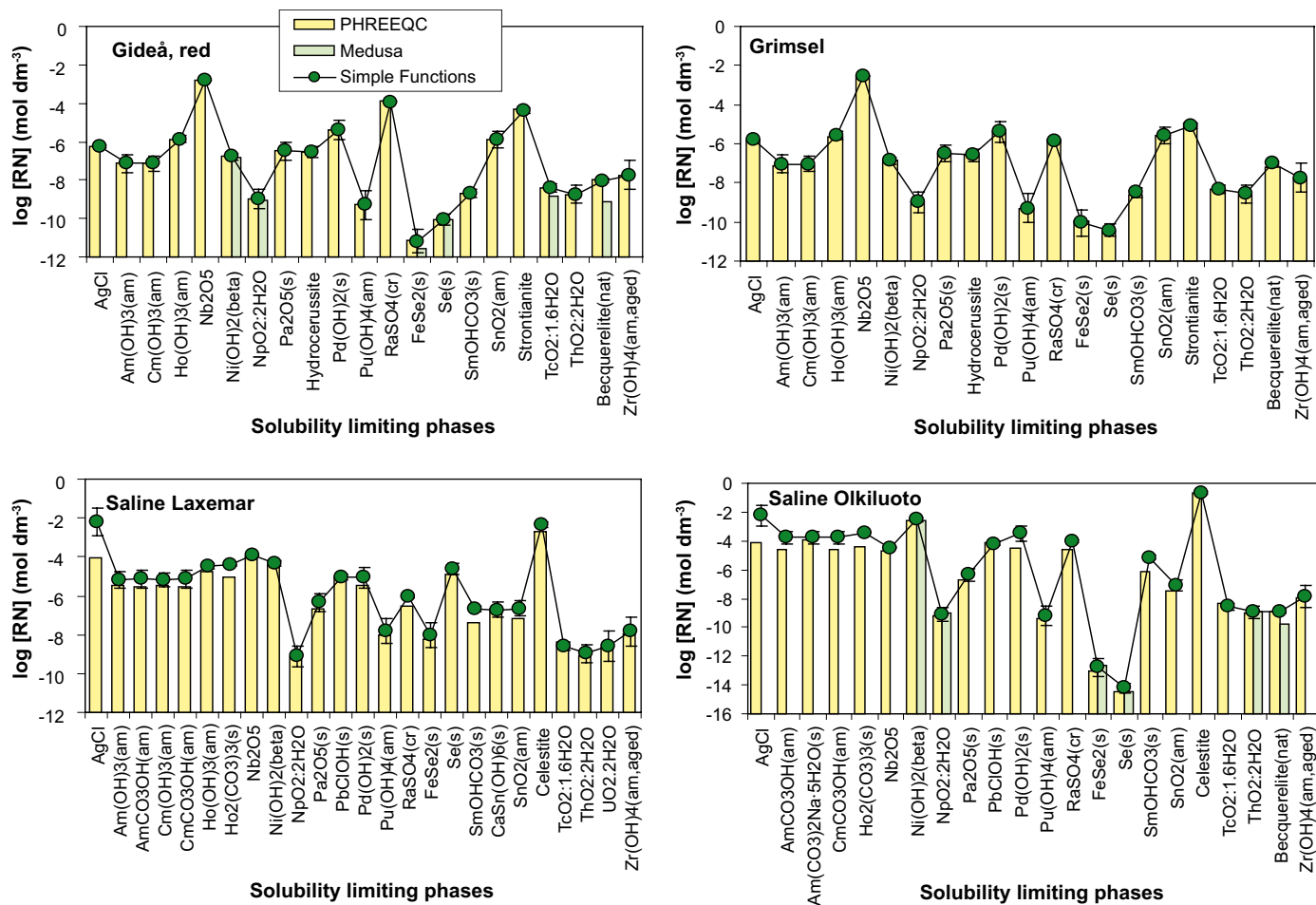
Figure 4-2. *Solubility limiting phases and radionuclide concentrations calculated with the VERSION A of Simple Functions Spreadsheet (dots), PHREEQC code (yellow bars) and HYDRA-MEDUSA code (green bars) for Gideå (most reducing Eh of Table A-1), Grimsel, Saline Laxemar and Saline Olkiluoto groundwater compositions.*
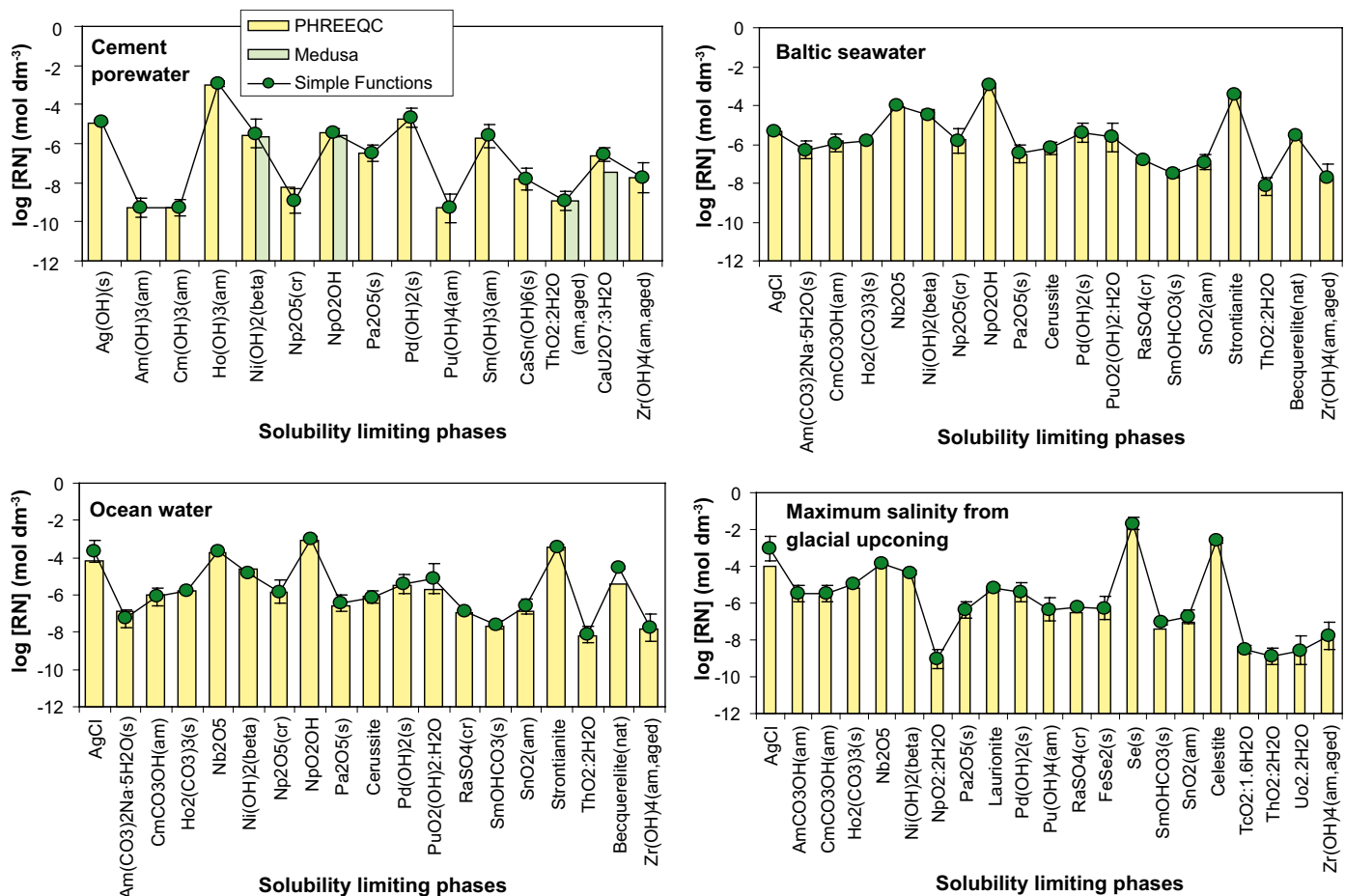
Figure 4-3. *Solubility limiting phases and radionuclide concentrations calculated with the VERSION A of Simple Functions Spreadsheet (symbols), PHREEQC code (yellow bars) and HYDRA-MEDUSA code (green bars) for cement porewater, Baltic seawater, Ocean water and maximum salinity from glacial upconing groundwater compositions.*

4.2   Sensitivity study concerning activity corrections

The Simple Functions Spreadsheet was initially designed to calculate radionuclide concentrations in groundwaters at 25°C in solutions with a maximum ionic strength of 0.2 m. In some cases, though, the groundwater of interest might have a higher salinity (see Table A-1 in Appendix A).

In this chapter we test the validity of the activity correction approach used in the Simple Functions Spreadsheet to calculate solubility values at higher ionic strengths.

The methodology used to perform this sensitivity analyses has consisted on:

1. Calculating the radionuclide concentration in equilibrium with the corresponding solubility limiting solid phase with the VERSION A Simple Functions Spreadsheet, where the activity correction approach used is Oelkers and Helgeson /Oelkers and Helgeson 1990/, see section 2.

2. Calculating the radionuclide concentration in equilibrium with the corresponding solubility limiting solid phase with the HYDRA-MEDUSA code, but using the SIT approach for ionic strength corrections.

3. Calculating the radionuclide concentration in equilibrium with the corresponding solubility limiting solid phase with the PHREEQC code that by default uses the Davies equation.

4. Comparing the calculated concentrations.

The comparison has only been done for some of the groundwaters and for some of the radionuclides of interest, covering the ionic strength range 6·10⁻³ to 1.89 m. Selected groundwater compositions are:

- Gideå (red) (as an example of very diluted groundwater).

- Forsmark groundwater (representative of the final selected site and very similar to Laxemar, Finnsjön and Äspö groundwater).

- Cement porewater (representative of cementitious conditions).

- Saline Olkiluoto (the most saline groundwater).

Radionuclide selection has been done considering the availability of reliable thermodynamic data (SIT interaction coefficients and enthalpy data). The final selected radionuclides are U, Th, Se, Np and Ni.

Figure 4-4 shows the concentrations calculated with the VERSION A of the Simple Functions Spreadsheet compared to those obtained with the HYDRA-MEDUSA code (SIT approach) and the PHREEQC code (Davies approach). As can be seen, no significant deviations are identified for any of the studied radionuclides in the different groundwater compositions.

We can conclude that despite the theoretical limit of validity of the activity correction approach used in the Simple Functions Spreadsheet, there are no significant differences in the calculated solubilities in the range 6·10⁻³ < I < 1.89 m.
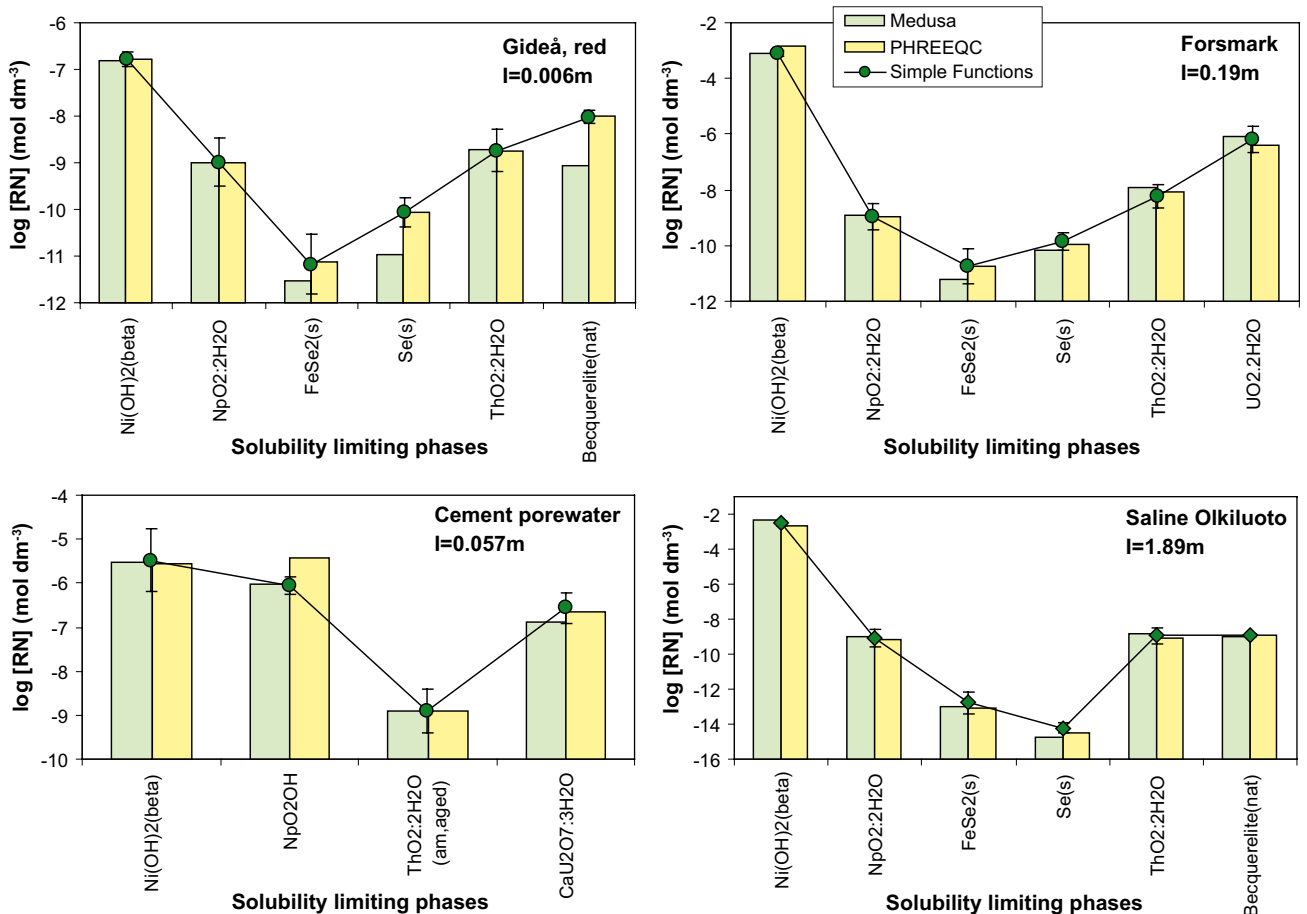
Figure 4-4. Solubility limiting phases and radionuclide concentrations calculated with the VERSION A of Simple Functions Spreadsheet (Oelkers and Helgeson activity correction), PHREEQC code (Davies activity correction) and HYDRA-MEDUSA code (SIT activity correction) for Gideå groundwater (most reducing Eh of Table A-1), Forsmark groundwater, Cement porewater and Saline Olkiluoto groundwater compositions.

4.3 Sensitivity study concerning the temperature effect in the range 0–100°C

The Simple Functions Spreadsheet is designed to calculate radionuclide concentrations at 25°C. In this chapter we test the uncertainty associated with the Simple Functions Spreadsheet calculations in the case of groundwater temperatures in the range 0 to 100°C.

The methodology used to perform these sensitivity analyses has consisted on:

1. Calculating the radionuclide concentration in equilibrium with the corresponding solubility limiting solid phase with the VERSION A of the Simple Functions Spreadsheet at 25°C.

2. Calculating the radionuclide concentration in equilibrium with the corresponding solubility limiting solid phase with the HYDRA-MEDUSA code, but using the van't Hoff equation to correct the log K (T = 25°C) to the temperature of interest.

3. Comparing the results of both calculated concentrations.

The groundwater compositions and radionuclides considered in this sensitivity analyses are the same as those in the activity correction sensitivity analyses: Gideå (red), Forsmark, Cement porewater and Saline Olkiluoto groundwaters and U, Th, Se, Np and Ni.

HYDRA-MEDUSA calculations have been done at the following temperatures: 0, 10, 25, 40, 70 and 100°C.

Figure 4-5 plots the radionuclide concentrations calculated with the VERSION A of Simple Functions Spreadsheet at 25°C compared to those obtained with the HYDRA-MEDUSA code at 0, 10, 25, 40, 70 and 100°C.

As can be seen, there is a dependence of the solubility on the temperature, which differs from one radionuclide to another and from one groundwater composition to another, as it is a complex function of the enthalpy values of the solid phases and also of the different aqueous species.

After this sensitivity study, one can conclude that calculations done with the Simple Functions Spreadsheet for temperatures different from 25°C might differ up to 2 log units from the expected solubilities, especially at 0 and 100°C.

There are, though some exceptions that deserve additional explanations. In the case of Selenium, the reader can see that the solubility of $FeSe_2$ and $Se(cr)$ solid phases significantly increases from $T > 70$°C. The reason for this increase bears on the increase of the stability range of selenite species as temperature increases. In the case of Ni, the increase of Ni solubility as $T \rightarrow 0$°C is due to the exothermic character of the main reaction taken place ($Ni(OH)_2 + 2H^+ = Ni^{2+} + 2H_2O$), but also to the fact that in the calculations presented in this report, the pH of groundwater is maintained constant. If the pH was allowed to change, Ni aqueous concentration in equilibrium with $Ni(OH)_2(s)$ would not change so dramatically with a temperature decrease.

In other cases, the enthalpy gaps for some aqueous species and solid phases can lead to apparently confusing results. In the case of Thorium, there is a lack of enthalpy data for $Th(OH)_4(aq)$, aqueous Th carbonates, or $ThO_2:2H_2O$ (am,aged). Calculations shown in Figure 4-5 are done assuming these limitations. In this case, given that $Th(OH)_4(aq)$ is the predominant aqueous species under the studied conditions, only small variations are observed in the calculated solubility of $ThO_2:2H_2O$ (am,aged) at different temperatures. If the enthalpy gaps were filled, one could expect a variation with the temperature.

It is then important to bear in mind that the confidence degree of solubility changes with temperature is subjected to the availability of enthalpy data. In a further step, it would be recommendable to make estimations of those enthalpy gaps when possible together with an uncertainty analysis assessing if the fact to estimate enthalpy data decreases or not the uncertainty with respect to calculations with data gaps.

Therefore, the influence of temperature appears to be more important than that of the ionic strength, but in view of the results of this sensitivity case, the Simple Functions Spreadsheet can be considered a good tool for an easy and fast calculation of the solubility of radionuclides under the different groundwater compositions and temperatures of interest for Performance Assessment, always used with caution and keeping in mind its limitations.
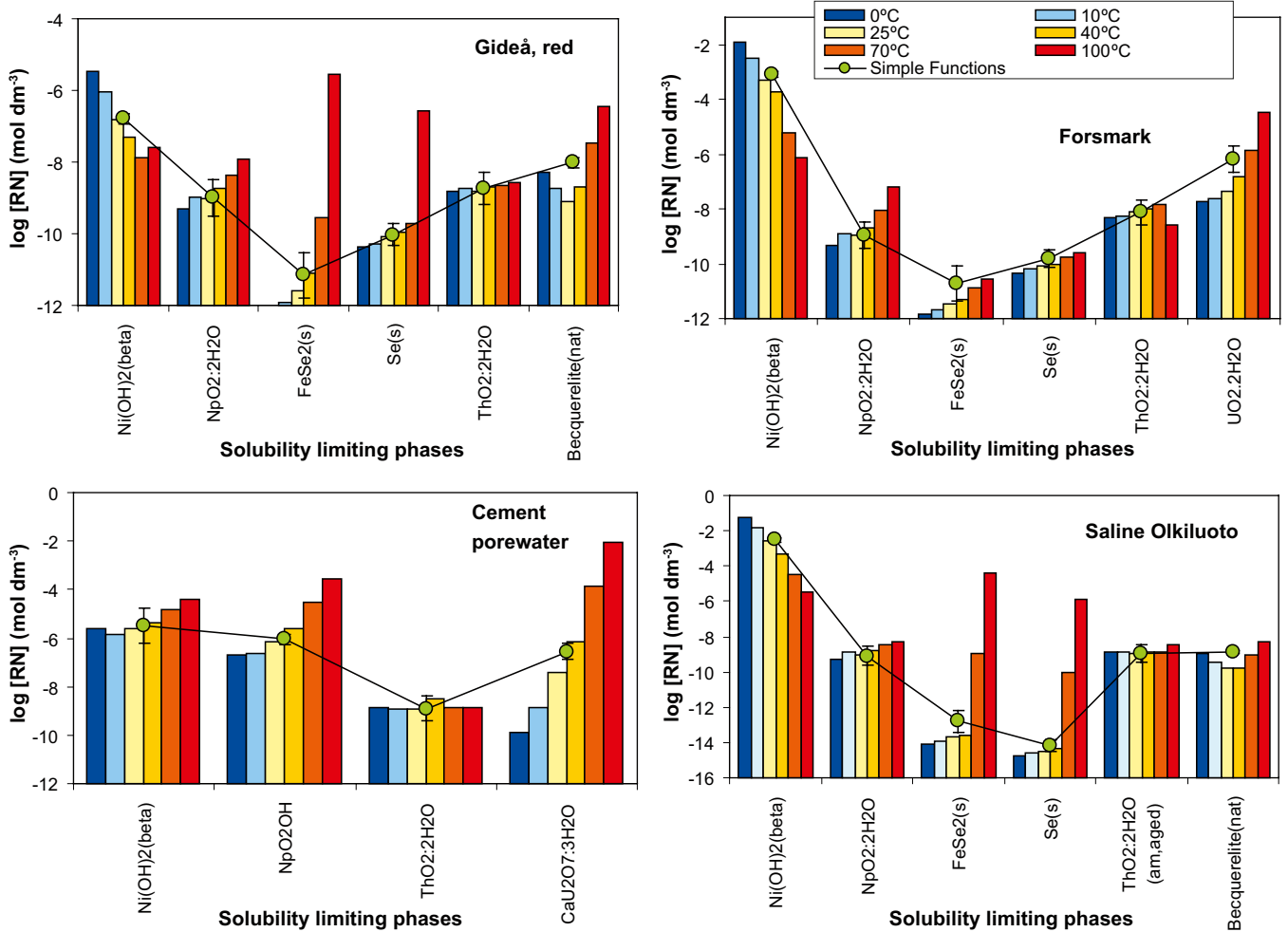
Figure 4-5. *Solubility limiting phases and radionuclide concentrations calculated with the VERSION A of the Simple Functions Spreadsheet (25°C), and HYDRA-MEDUSA code (0, 10, 25, 40, 70 and 100°C) for Gideå groundwater (most reducing Eh of Table A-1), Forsmark groundwater, Cement porewater and Saline Olkiluoto groundwater compositions.*

5   Transferring data between codes

This tool is an easy tool that needs the input of a groundwater composition and provides the concentration of radionuclides in equilibrium with their respective solubility limiting phases under the conditions of the groundwater composition. Therefore, any groundwater composition (calculated or measured) can be introduced in the tool.

Calculated radionuclide concentrations can be directly used in other codes.

6 Rationales for using the tool in the assessment

The SR-Site team has selected the Simple Functions Spreadsheet for the SR-Site safety assessment since it is a tailor-made tool for the production of probabilistic distributions of radioelement solubilities. The results produced by the tool are in good agreement with those from conventional geochemical codes (e.g. PHREEQC).

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

Bruno J, Cera E, de Pablo J, Duro L, Jordana S, Savage D, 1997. Determination of radio-nuclide solubility limits to be used in SR 97. Uncertainties associated to calculated solubilities. SKB TR-97-33, Svensk Kärnbränslehantering AB.

Cabaniss S E, 1999. Uncertainty propagation in geochemical calculations: non-linearity in solubility equilibria. Applied Geochemistry, 14, pp 255–262.

Duro L, Grivé M, Cera E, Gaona X, Domènech C, Bruno J, 2006. Determination and assessment of the concentration limits to be used in SR-Can. SKB TR-06-32, Svensk Kärnbränslehantering AB.

Ekberg C, Ödegaard-Jensen A, 2004. Computer programs for uncertainty analysis of solubility calculations: Windows version and other updates of the SENVAR and UNCCON. Program description and handling instructions. SKI Report 2004:20, Statens kärnkraftinspektion (Swedish Nuclear Power Inspectorate).

Grivé M, Domènech C, Montoya V, Garcia D, Duro L, 2010. Determination and assessment of the concentration limits to be used in SR-Can. Supplement to TR-06-32. SKB R-10-50, Svensk Kärnbränslehantering AB.

Oelkers E H, Helgeson H C, 1990. Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions. Geochimica et Cosmochimica Acta, 54, pp 727–738.

Parkhurst D L, Appelo C A J, 2001. User's guide to PHREEQC (Version 2.4.6). A computer program for speciation, batch reaction, one dimensional transport and inverse geochemical calculations. Denver, Co: U.S. Geological Survey.

Pitkänen P, Lukkonen A, Ruotsalainen P, Leino-Forsman H, Vuorinen U, 1999. Geochemical modelling of groundwater evolution and residence time at the Olkiluoto site. Posiva 98-10, Posiva Oy, Finland.

Puigdomènech I, 2002. MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) Windows interface to the MS-DOS versions of INPUT, SED and PREDOM (FORTRAN programs drawing chemical equilibrium diagrams) Vers. 31 July 2002. Royal Institute of Technology, Stockholm, Sweden.

SKB, 2005. Hydrogeochemical evaluation. Preliminary site description Forsmark area – version 1.2. SKB R-05-17, Svensk Kärnbränslehantering AB.

SKB, 2006a. Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. SKB TR-06-09, Svensk Kärnbränslehantering AB.

SKB, 2006b. Hydrogeochemical evaluation. Preliminary site description Laxemar subarea – version 1.2. SKB R-06-12, Svensk Kärnbränslehantering AB.

SKB, 2010. Model summary report for the safety assessment SR-Site. SKB TR-10-51, Svensk Kärnbränslehantering AB.

Groundwater compositions

The groundwater compositions considered are those reported in Table A-1, extracted from /SKB 2006a/.

We have completed some of these groundwater compositions by adding information on redox potentials taken from the original sources.

Table A-1. Groundwater compositions used in the calculations (from /SKB 2006a/). Shadowed cells: redox data for groundwater compositions used in this work (original data in bold). Concentrations in kmol/m³.

	Forsmark	Laxemar	Äspö	Finnsjön	Gideå	Grimsel: interacted glacial meltwater	"Most Saline" groundwater at Laxemar	"Most Saline" groundwater at Olkiluoto	Cement pore water	Baltic seawater	Ocean water	Maximun salinity from glacial upconing
pH	7.2	7.9	7.7	7.9	9.3	9.6	7.9	7	12.5	7.9	8.15	7.9
Na	0.089	0.034	0.091	0.012	0.0046	0.00069	0.349	0.415	0.002	0.089	0.469	0.25
Ca	0.023	0.0058	0.047	0.0035	0.00052	0.00014	0.464	0.449	0.018	0.0024	0.0103	0.27
Mg	0.0093	0.00044	0.0017	0.0007	0.000045	6×10^{-7}	0.0001	0.0053	≤ 0.0001	0.010	0.053	0.0001
K	0.0009	0.00014	0.0002	0.00005	0.00005	0.000005	0.0007	0.0007	0.0057	0.002	0.01	0.0005
Fe	33×10^{-6}	8×10^{-6}	4×10^{-6}	32×10^{-6}	9×10^{-7}	3×10^{-9}	8×10^{-6}	6×10^{-5}	$\leq 10\times10^{-6}$	3×10^{-7}	4×10^{-8}	2×10^{-6}
HCO_3^-	0.0022	0.0031	0.00016	0.0046	0.00023	0.00045	0.00010	0.00014	≈ 0	0.0016	0.0021	0.00015
Cl^-	0.153	0.039	0.181	0.0157	0.0050	0.00016	1.283	1.275	≈ 0	0.106	0.546	0.82
SO_4^{2-}	0.0052	0.0013	0.0058	0.00051	0.000001	0.00006	0.009	0.00009	≈ 0	0.0051	0.0282	0.01
HS^-	≈ 0	3×10^{-7}	5×10^{-6}	–	$\leq 3\times10^{-7}$	–	$\leq 3\times10^{-7}$	$\leq 1.6\times10^{-7}$	≈ 0	–	–	$\leq 3\times10^{-7}$
Ionic Strength (kmol/m³)	0.19	0.053	0.24	0.025	0.006	0.0013	1.75	1.76	0.057	0.13	0.65	1.09
Eh (mV)	**−140**	**−280**	*−307/−73*	*−250/−68*	*−201/−60*	**−200**	**−314**	**−3**				**−400**
pe	*−2.37*	*−4.75*	**−5.21/−1.24**	**−4.23/−1.16**	**−3.41/−1.01**	*−3.39*	*−5.32*	*−0.05*				*−6.78*
Ref.Eh/pe	*1*	*2*	*3*	*3*	*3*	*4*	*4*	*5*				*2*

1) /SKB 2005/. 2) /SKB 2006b/. 3) /Bruno et al. 1997/ 4). /Duro et al. 2006/ 5). /Pitkänen et al. 1999/

Radionuclide solubilities

Tables B-1 to B-6 show the solid phases identified as the most likely to exert a solubility control for every single groundwater composition listed in Table A-1, as well as the corresponding radionuclide concentration in equilibrium with them. The calculated concentrations with the VERSION A of the Simple Functions Spreadsheet and with the PHREEQC code are listed for comparison. When indicated, values calculated with the HYDRA-MEDUSA code are also shown.

Table B-1. Solubility limiting phases and log radionuclide concentrations (in m) calculated for Forsmark and Laxemar groundwater compositions. * Values calculated with HDYRA-MEDUSA code.

	Solubility limiting phase	Forsmark PHREEQC/Medusa*	Simple Functions	Laxemar PHREEQC	Simple Functions
Ag	AgCl	–5.11	–5.08±0.16	–5.77	–5.76±0.12
Am	$Am(CO_3)_2Na \cdot 5H_2O(s)$	–5.57	–5.76±0.26	–6.05	–6.13±0.26
Cm	$Cm_2(CO_3)_3(s)$	–5.46	–5.53±0.76	–5.85	–5.86±0.50
Ho	$Ho_2(CO_3)_3(s)$	–5.64	–5.69±0.26	–5.84	–5.83±0.28
Nb	Nb_2O_5	–4.51	–4.46±0.02	–4.09	–4.03±0.02
Ni	$Ni(OH)_2(beta)$	–2.81/–3.26*	–3.09±0.12	–4.36	–4.55±0.12
Np	$NpO_2:2H_2O$	–8.96/–8.93*	–8.96±0.48	–8.93	–8.93±0.46
Pa	$Pa_2O_5(s)$	–6.52	–6.48±0.44	–6.51	–6.50±0.44
Pb	Cerussite	–5.97	–6.03±0.32	–6.25	–6.26±0.36
Pd	$Pd(OH)_2(s)$	–5.46	–5.41±0.52	–5.41	–5.40±0.52
Pu	$Pu(OH)_4(am)$	–7.57	–7.86±0.68	–6.99	–7.15±0.94
Ra	$RaSO_4(cr)$	–6.62	–6.63±0.05	–6.51	–6.51±0.04
Se	$FeSe_2(s)$	–10.74/–10.45*	–10.73±0.64	–8.82	–8.8±0.64
	$Se(s)$	–9.95/–10.04*	–9.83±0.31	–5.93	–5.88±0.31
Sm	$SmOHCO_3(s)$	–6.84	–6.86±0.21	–7.44	–7.40±0.21
Sn	$SnO_2(am)$	–7.23	–7.18±0.39	–6.99	–6.96±0.38
Sr	Celestite	–3.01	–3.01±0.14		
	Strontianite			–3.82	–3.91±0.13
Tc	$TcO_2:1.6H_2O$	–8.37	–8.39±0.22	–8.38	–8.39±0.22
Th	$ThO_2:2H_2O$ (am,aged)	–8.05/–8.10*	–8.06±0.43	–7.82	–7.83±0.43
U	$UO_2.2H_2O$	–6.38	–6.17±0.47	–8.37	–8.34±0.63
Zr	$Zr(OH)_4(am,aged)$	–7.76	–7.75±0.74	–7.75	–7.74±0.74

Table B-2. Solubility limiting phases and log radionuclide concentrations (in m) calculated for Äspö and Finnsjön groundwater compositions (the Eh used in the calculations is the most reducing of Table B-1). * Values calculated with HDYRA-MEDUSA code.

	Solubility limiting phase	Äspö (red) PHREEQC	Simple Functions	Finnsjön (red) PHREEQC	Simple Functions
Ag	AgCl	–5.01	–4.94±0.20	–6.06	–6.06±0.10
Am	$Am_2(CO_3)_3(s)$			–5.88	–5.88±050
	$AmCO_3OH(am)$	–5.43	–5.58±0.44		
Cm	$Cm_2(CO_3)_3(s)$			–5.88	–5.88±0.50
	$CmCO_3OH(am)$	–5.43	–5.58±0.44		
Ho	$Ho_2(CO_3)_3(s)$	–5.17	–5.26±0.24	–5.83	–5.82±0.30
Nb	Nb_2O_5	–4.20	–4.11±0.02	–4.11	–4.06±0.02
Ni	$Ni(OH)_2(beta)$	–3.79	–4.07±0.12	–4.44	–4.57±0.12
Np	$NpO_2:2H_2O$	–9.02	–9.01±0.52	–8.89	–8.89±0.44
Pa	$Pa_2O_5(s)$	–6.52	–6.48±0.44	–6.50	–6.50±0.44
Pb	Cerussite	–5.42	–5.50±0.31	–6.05	–6.05±0.33
	Hydrocerussite	–5.45	–5.59±0.29		
Pd	$Pd(OH)_2(s)$	–5.42	–5.41±0.52	–5.40	–5.40±0.52
Pu	$Pu(OH)_4(am)$	–6.92	–7.26±0.65	–7.24	–7.33±1.04
Ra	$RaSO_4(cr)$	–6.60	–6.58±0.06	–6.31	–6.31±0.05
Se	$FeSe_2(s)$	–7.94	–7.94±0.64	–9.65	–9.71±0.64
	Se(s)	–4.77	–4.67±0.31	–6.99	–6.94±0.31
Sm	$SmOHCO_3(s)$	–7.11	–7.15±0.17	–7.36	–7.32±0.22
Sn	$SnO_2(am)$	–7.08	–6.99±0.38	–7.00	–6.98±0.38
Sr	Celestite	–2.98	–2.96±0.14		
	Strontianite			–4.11	–4.18±0.13
Tc	$TcO_2:1.6H_2O$	–8.40	–8.42±0.22	–8.37	–8.38±0.22
Th	$ThO_2:2H_2O$ (am,aged)	–8.80	–8.80±0.46	–7.61	–7.61±0.43
U	$UO_2.2H_2O$	–8.52	–8.51±0.77	–7.60	–7.55±0.48
Zr	$Zr(OH)_4(am,aged)$	–7.76	–7.75±0.74	–7.74	–7.74±0.74

Table B-3. Solubility limiting phases and log radionuclide concentrations (in m) calculated for Gideå (the Eh used in the calculations is the most reducing of Table B-1) and Grimsel groundwater compositions. * Values calculated with HDYRA-MEDUSA code.

	Solubility limiting phase	Gideå (red) PHREEQC/ Medusa*	Simple Functions	Grimsel PHREEQC	Simple Functions
Ag	AgCl	–6.27	–6.27±0.07	–5.79	–5.81±0.02
Am	Am(OH)$_3$(s)	–7.11	–7.15±0.38	–7.16	–7.03±0.40
Cm	Cm(OH)$_3$(s)	–7.11	–7.15±0.38	–7.16	–7.03±0.40
Ho	Ho(OH)$_3$(am)	–5.86	–5.86±0.16	–5.66	–5.57±0.19
Nb	Nb$_2$O$_5$	–2.83	–2.80±0.02	–2.54	–2.53±0.02
Ni	Ni(OH)$_2$(beta)	–6.77/–6.81*	–6.79±0.15	–6.87	–6.87±0.16
Np	NpO$_2$:2H$_2$O	–9.00/–9.04*	–8.99±0.52	–8.99	–8.99±0.51
Pa	Pa$_2$O$_5$(s)	–6.50	–6.50±0.44	–6.50	–6.50±0.44
Pb	Hydrocerussite	–6.52	–6.53±0.31	–6.55	–6.58±0.32
Pd	Pd(OH)$_2$(s)	–5.40	–5.40±0.52	–5.40	–5.40±0.52
Pu	Pu(OH)$_4$(am)	–9.30	–9.30±0.73	–9.30	–9.30±0.73
Ra	RaSO$_4$(cr)	–3.91	–3.94±0.04	–5.82	–5.87±0.04
Se	FeSe$_2$(s)	–11.12/–11.58*	–11.18±0.64	–9.99	–10.04±0.65
	Se(s)	–10.06/–10.04*	–10.05±0.31	–10.42	–10.42±0.31
Sm	SmOHCO$_3$(s)	–8.70	–8.68±0.21	–8.59	–8.50±0.26
Sn	SnO$_2$(am)	–5.87	–5.87±0.42	–5.57	–5.58±0.42
Sr	Strontianite	–4.32	–4.38±0.13	–4.95	–5.10±0.13
Tc	TcO$_2$:1.6H$_2$O	–8.39/–8.82*	–8.39±0.22	–8.35	–8.34±0.23
Th	ThO$_2$:2H$_2$O (am,aged)	–8.73	–8.73±0.45	–8.62	–8.57±0.44
U	Becquerelite	–8.00/–9.12*	–8.01±0.14	–7.22	–7.01±0.08
Zr	Zr(OH)$_4$(am,aged)	–7.74	–7.74±0.74	–7.74	–7.74±0.74

Table B-4. Solubility limiting phases and log radionuclide concentrations (in m) calculated for Saline Laxemar and Saline Olkiluoto groundwater compositions. *Values calculated with HDYRA-MEDUSA code.

	Solubility limiting phase	Saline Laxemar		Saline Olkiluoto	
		PHREEQC	Simple Functions	PHREEQC/Medusa*	Simple Functions
Ag	AgCl	−4.08	−2.21±0.71	−4.10	−2.22±0.71
Am	Am(OH)$_3$(s)	−5.44	−5.20±0.35		
	AmCO$_3$OH(am)	−5.53	−5.14±0.44	−4.60	−3.75±0.43
	Am(CO$_3$)$_2$Na·5H$_2$O(s)				−3.76±0.43
Cm	Cm(OH)$_3$(s)	−5.44	−5.20±0.35		
	CmCO$_3$OH(am)	−5.53	−5.14±0.44	−4.60	−3.75±0.43
Ho	Ho(OH)$_3$(am)	−4.74	−4.46±0.13		
	Ho$_2$(CO$_3$)$_3$(s)	−5.07	−4.43±0.22	−4.38	−3.43±0.22
Nb	Nb$_2$O$_5$	−3.95	−3.89±0.02	−4.66	−4.46±0.02
Ni	Ni(OH)$_2$(beta)	−4.41	−4.32±0.13	−2.63/−2.58*	−2.52±0.13
Np	NpO$_2$:2H$_2$O	−9.18	−9.10±0.52	−9.16/−8.97*	−9.09±0.51
Pa	Pa$_2$O$_5$(s)	−6.70	−6.34±0.44	−6.70	−6.34±0.44
Pb	PbClOH(s)	−5.03	−5.05±0.15	−4.15	−4.17±0.15
Pd	Pd(OH)$_2$(s)	−5.44	−5.07±0.51	−4.51	−3.48±0.50
Pu	Pu(OH)$_4$(am)	−8.04	−7.83±0.64	−9.36	−9.22±0.68
Ra	RaSO$_4$(cr)	−6.54	−6.05±0.09	−4.56	−4.06±0.09
Se	FeSe$_2$(s)	−8.23	−8.01±0.64	−13.05/−12.67*	−12.79±0.64
	Se(s)	−4.87	−4.61±0.31	−14.51/−14.54*	−14.22±0.31
Sm	SmOHCO$_3$(s)	−7.41	−6.69±0.13	−6.16	−5.14±0.13
Sn	CaSn(OH)$_6$(s)	−6.68	−6.72±0.40		
	SnO$_2$(am)	−7.16	−6.67±0.39	−7.46	−7.08±0.40
Sr	Celestite	−2.73	−2.34±0.15	n.s.l.	n.s.l.
Tc	TcO$_2$:1.6H$_2$O	−8.39	−8.57±0.22	−8.38	−8.54±0.22
Th	ThO$_2$:2H$_2$O (am,aged)	−9.06	−8.97±0.48	−9.04/−8.88*	−8.96±0.48
U	UO$_2$.2H$_2$O	−8.69	−8.60±0.77	−8.94/−9.82*	−8.91±0.08
Zr	Zr(OH)$_4$(am,aged)	−7.93	−7.85±0.74	−7.93	−7.85±0.74

Table B-5. Solubility limiting phases and log radionuclide concentrations (in m) calculated for Cement porewater and Baltic seawater compositions. * Values calculated with HDYRA-MEDUSA code.

	Solubility limiting phase	Cement porewater PHREEQC/Medusa*	Simple Functions	Baltic seawater PHREEQC	Simple Functions
Ag	Ag(OH)$_3$	–4.98	–4.92±0.05		
	AgCl			–5.33	–5.31±0.13
Am	Am(OH)$_3$(s)	–9.28	–9.29±0.41		
	Am(CO$_3$)$_2$Na·5H$_2$O(s)			–6.07	–6.31±0.26
Cm	Cm(OH)$_3$(s)	–9.28	–9.29±0.41		
	CmCO$_3$OH(am)			–5.84	–5.93±0.46
Ho	Ho(OH)$_3$(am)	–3.01	–2.92±0.16		
	Ho$_2$(CO$_3$)$_3$(s)			–5.82	–5.83±0.27
Nb	Nb$_2$O$_5$	n.s.l.	n.s.l.	–4.06	–3.98±0.02
Ni	Ni(OH)$_2$(beta)	–5.57/–5.64*	–5.48±0.72	–4.24	–4.50±0.12
Np	Np$_2$O$_5$	–8.27	–8.91±0.63		
	NpO$_2$OH (aged)	–5.41/–5.59*	–5.46±0.20	–2.93	–2.98±0.11
Pa	Pa$_2$O$_5$(s)	–6.51	–6.50±0.44	–6.51	–6.49±0.44
Pb	Cerussite	n.s.l.	n.s.l.	–6.19	–6.21±0.35
Pd	Pd(OH)$_2$(s)	–4.76	–4.67±0.51	–5.41	–5.41±0.52
Pu	Pu(OH)$_4$(am)	–9.31	–9.30±0.73		
	PuO$_2$(OH)$_2$:H$_2$O			–5.65	–5.64±0.76
Ra	RaSO$_4$(cr)	n.s.l.	n.s.l.	–6.77	–6.78±0.05
Se		n.s.l.	n.s.l.	n.s.l	n.s.l.
Sm	Sm(OH)$_3$(am)	–5.70	–5.62±0.61		
	SmOHCO$_3$(s)			–7.52	–7.50±0.21
Sn	CaSn(OH)$_6$(s)	–7.85	–7.81±0.54		
Sn	SnO$_2$(am)			–6.98	–6.91±0.39
Sr	Strontianite	n.s.l.	n.s.l.	–3.36	–3.46±0.13
Tc	TcO$_2$:1.6H$_2$O	n.s.l.	n.s.l.	n.s.l.	n.s.l.
Th	ThO$_2$:2H$_2$O (am,aged)	–8.91/–8.91	–8.90±0.49	–8.15	–8.16±0.44
U	CaU$_2$O$_7$:3H$_2$O	–6.66/–7.44	–6.56±0.34		
	Becquerelite			–5.55	–5.55±0.08
Zr	Zr(OH)$_4$(am,aged)	–7.73	–7.74±0.74	–7.76	–7.75±0.74

Table B-6. Solubility limiting phases and log radionuclide concentrations (in m) calculated for the Ocean water and the maximum salinity from glacial upcoming groundwater compositions.

	Solubility limiting phase	Ocean water PHREEQC	Simple Functions	Maximum salinity from glacial upcoming PHREEQC	Simple Functions
Ag	AgCl	–4.18	–3.68±0.57	–4.04	–3.02±0.66
Am	AmCO$_3$OH(am)			–5.63	–5.49±0.44
	Am(CO$_3$)$_2$Na·5H$_2$O(s)	–6.90	–7.27±0.26		
Cm	CmCO$_3$OH(am)	–6.01	–6.10±0.46	–5.63	–5.49±0.44
Ho	Ho$_2$(CO$_3$)$_3$(s)	–5.81	–5.77±0.28	–5.19	–4.94±0.22
Nb	Nb$_2$O$_5$	–3.76	–3.67±0.02	–3.97	–3.88±0.02
Ni	Ni(OH)$_2$(beta)	–4.61	–4.86±0.13	–4.25	–4.34±0.13
Np	Np$_2$O$_5$	–5.89	–5.84±0.61		
	NpO$_2$OH (aged)	–3.07	–3.00±0.12		
	NpO$_2$:2H$_2$O			–9.11	–9.06±0.52
Pa	Pa$_2$O$_5$(s)	–6.57	–6.45±0.44	–6.62	–6.41±0.44
Pb	Cerussite	–6.09	–6.11±0.33		
	PbClOH(s)			–5.13	–5.22±0.15
Pd	Pd(OH)$_2$(s)	–5.46	–5.43±0.52	–5.46	–5.38±0.52
Pu	Pu(OH)$_4$(am)			–6.24	–6.35±0.64
	PuO$_2$(OH)$_2$:H$_2$O	–5.67	–5.13±0.80		
Ra	RaSO$_4$(cr)	–6.98	–6.89±0.05	–6.53	–6.26±0.08
Se	FeSe$_2$(s)	n.s.l.	n.s.l.	–6.39	–6.27±0.64
	Se(s)			–1.87	–1.68±0.31
Sm	SmOHCO$_3$(s)	–7.68	–7.62±0.21	–7.37	–7.05±0.14
Sn	SnO$_2$(am)	–6.86	–6.62±0.40	–7.07	–6.75±0.39
Sr	Celestite			–2.82	–2.57±0.15
	Strontianite	–3.42	–3.43±0.13		
Tc	TcO$_2$:1.6H$_2$O	n.s.l.	n.s.l.	–8.39	–8.50±0.22
Th	ThO$_2$:2H$_2$O (am,aged)	–8.18	–8.13±0.43	–8.94	–8.89±0.47
U	UO$_2$.2H$_2$O			–8.61	–8.56±0.77
	Becquerelite	–5.38	–4.56±0.08		
Zr	Zr(OH)$_4$(am,aged)	–7.81	–7.78±0.74	–7.85	–7.80±0.74