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Infiltration of dilute groundwaters and resulting groundwater compositions at repository depth

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SSM perspective

Background

The planned Swedish concept for final disposal of spent nuclear fuel includes copper canisters placed in deposition holes at about 500 m depth in granitic bedrock. The copper canisters will be surrounded by bentonite buffer with the objective of inhibiting groundwater flow adjacent to the canister. It has been discovered that dilute glacial melt-water may induce erosion of the buffer material. A very dilute groundwater chemical condition promotes colloidal stability, which may aggravate erosional processes. It is therefore of interest to analyze chemical and physical processes, which affect groundwater chemical composition from the infiltration at the surface to a level in the bedrock corresponding to the repository depth.

The infiltrating groundwater from a melting glacier may be affected by mixing with older more saline water and matrix water, as well as weathering reactions related to minerals in the bedrock. This report provides a preliminary assessment of two different modeling approaches to account for the reactions between dilute groundwater and primary silicates as well as secondary minerals in the bedrock. The first modeling approach focus on kinetic rate expression for main mineral components of the bedrock, and the other on local equilibrium conditions.

Objectives

The objective of this assignment was to evaluate geochemical processes that may affect groundwater conditions at repository depth for the case with infiltrating dilute glacial melt-water at the surface above the repository. This report focus on the chemical reactions that affect alkali and alkaline earth cation concentrations in groundwater, of which the latter have the most pronounced effect on colloidal stability.

Results

Most modeling runs suggest that concentration of Ca2+ increases relative to concentration of Na+ giving groundwater ionic strengths compatible with currently available criteria for colloidal stability (Σ [M2+]> 10-3 M). However, certain cases such as infiltration of very dilute Norwegian glacier water suggested that mineral reaction in the bedrock would be insufficient to prevent the dilute water conditions associated with buffer erosion. Some of the modeling runs were accompanied by pH increases that can be regarded as unrealistic. Modeled pH conditions can thus be used as one indicator of model performance.

Need for further research

Uncertainties related to the conceptual models for rock water interactions and their quantification in the context of a deep repository for nuclear wastes may at present be regarded as considerable. Further efforts are recommended to if possible better constrain the range of groundwater composition at repository depth directly following a glacial melt water intrusion event. Modeling results from this type of efforts also have to be integrated in an overall picture involving other aspects of groundwater evolution such as mixing with older groundwater and other events related to the progress of a glacial cycle. To what extent these objectives are critical for the safety evaluation depend on the status of buffer erosion research, results from groundwater flow simulation and other aspects of the safety case.

Project information

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Content

Executive Summary

The purpose of this study has been to simulate the hydrochemical evolution of dilute water, typical of melt-water in a glaciation scenario, infiltrating into bedrock. The focus is on the alkali and alkaline earth cation compositions because these might affect the performance of bentonite buffer.

A geochemical model of batch reactions between dilute water and rock minerals has been constructed. Two approaches to simulating these hydrogeochemical reactions have been implemented using the PHREEQC program. The first approach has simulated the dissolution reactions of various aluminosilicate minerals in terms of the rates of each reaction. The potential for continued dissolution is governed by the calculated state of thermodynamic equilibrium for each mineral phase, but the progress of dissolution is calculated using empirical kinetics expressions. The second approach has assumed that local equilibria are achieved rapidly between water and reactive minerals so that hydrochemical evolution is governed by equilibria with different assemblages of minerals. Sequential equilibria with various permutations of mineral assemblages have simulated how the resulting groundwater compositions, specifically the pH and the $[Ca^{2+}+Mg^{2+}]/[Na^{+}]$ ratio, depend on the selected mineral assemblages.

The equilibrating secondary minerals for both modelling approaches are calcite, chalcedony, kaolinite, illite and chlorite, plus montmorillonite in the local equilibrium model. The minerals selected for kinetic dissolution reactions are albite, anorthite, K-feldspar and biotite. The minerals selected for dissolution-only equilibration are laumontite, saponite, prehnite, albite, anorthite and K-feldspar. Model runs were constructed to represent various combinations of these minerals in three stages of local equilibrium.

The main conclusions to be drawn from this modelling study are: (i) The realistic and most likely scenarios for hydrogeochemical evolution would result in divalent cation concentrations and (Ca+Mg)/Na ratios that would not challenge the safety function indicator criterion, $\Sigma[M^{2+}]\geq 10^{-3}$ M; (ii) There are specific hydrogeochemical scenarios that in theory could result in groundwater compositions at repository depth that are depleted in Ca^{2+} and Mg^{2+} concentrations.

This modelling study provides some insights about the hydrogeochemical evolution of dilute water if it reaches repository depth without having mixed with pre-existing brackish or saline groundwaters. Such an influx of dilute water is perceived to be particularly possible due to melt water infiltration during a future glacial period. The issues, illustrated by this study, of reactions between minerals and dilute water should be further explored to better understand the hydrogeochemical aspects of the glacial meltwater intrusion scenario. The present study indicates potential issues but has not had the scope for a sensitivity analysis and an investigation of uncertainties.

1 Introduction

This first part of this work was commissioned in 6/2009 from Intellisci Ltd by SSM, Project nr. 1725, on contract SSM 2009/2261. A continuation was commissioned in 5/2010, SSM Project nr. 3037008-05, on contract SSM 2010/1807.

The possibility of dilute water at repository depth has a number of potential implications for long-term safety and for SSM's review of SR-Site:

- Very dilute waters could have cation (Ca^{2+}, Mg^{2+}) concentrations lower than the threshold values required by the safety function for bentonite buffer stability and performance, potentially resulting in dispersion of bentonite.

- Dilute waters may have a different pH range in comparison with the measured existing conditions in repository depth range, also the buffering of pH by dissolved constituents, primarily the carbonate system, will be different in a dilute water.

- Dilute waters may have different redox characteristics from the observed present redox conditions in existing groundwaters at repository depth, because the concentrations of redox-active species (Fe, S, DOC) will be different and also the populations and activities of microorganism populations may be different, also the buffering of redox by water-rock reactions may be different.

- Fast infiltration and downflow of dilute waters could be associated with influx of dissolved oxygen that has resisted consumption by reaction with reducing solutes and minerals (attenuation of dissolved oxygen has already been considered in previous reports by Glynn & Voss [1] and Bath & Hermansson [2] for SKI/SSM).

- Dilute water could introduce or stimulate different populations of microorganisms which in turn would change the prevailing balance in redox equilibria (this topic has been considered in a previous report for SSM by Bath & Hermansson).

- Dilute water would change the chemical conditions for wasteform dissolution and radionuclide speciation in the EBS, and could also change the speciation and mobility/retention of radionuclides in the near-field geosphere.

Aims:

- To assess the potential hydrochemical impacts of drawdown of dilute waters to repository depth during the operational period of the repository and of recovery after closure.

- To estimate the evolution of water compositions at repository depth over the initial few thousands of years after closure when surficial changes such as land rise and shoreline regression and the associated hydrogeological changes of enhanced fresh water infiltration and migrating flow paths would cause groundwaters at repository depth and along discharge paths to be more dilute.

- To model the potential range of chemical compositions for waters at repository depth resulting from the infiltration of dilute melt waters in the glaciation phase of the normal evolution scenario.

- To use the obtained ranges of dilute compositions for groundwaters at repository depth for preliminary review and assessment of SKB's treatment of these issues in SR-Site documentation, especially with regard to safety functions and other interpretations of potential impacts of dilute waters on performance of the Engineered Barriers of the KBS-3 repository.

Tasks:

i. Describe potential future hydrogeological and environmental conditions in which dilute water might flow to repository depth. The output will be scenarios and conceptual models for groundwater flow at repository depth. Descriptions will include recharge and discharge parts of scenarios for future flow systems.

ii. Estimate the potential ranges of fresh water compositions at the surface and in near-surface groundwaters, referring to literature and using expert judgement. This will be done for various infiltration conditions, e.g. temperate meteoric waters, sub-glacial melt water, future sea water.

iii. Develop conceptual models for the geochemical evolution of water under the various types of infiltration conditions mentioned above. The conceptual models will cover homogeneous and heterogeneous geochemical reactions, as described in 'background science' above, which will modify the composition of dilute infiltration as it flows from surface to repository depth.

iv. Carry out modelling of these hydrogeochemical reactions and of how they would control the composition and geochemical state of dilute groundwaters, i.e. with respect to pH, Na, K, Ca, Mg, SO_4, HCO_3, Cl at repository depth. The modelling will be carried out using the PHREEQC computer code with the phreeq.dat or llnl.dat thermodynamic databases. The outputs will be groundwater compositions that represent the potential variability of parameters that affect safety functions for EBS performance and radionuclide mobility.

2 Background

In the normal evolution scenario for the KBS-3 repository, the chemical composition of groundwater at repository depth will change due to hydrochemical changes in infiltration and shallow groundwater sources that flow towards the repository location. Source regions of downflowing groundwater flow paths and trajectories of discharging flow paths may also change as the hydrogeology of the system changes in response to land rise, shoreline recession and other environmental-climatic changes. There will also be shorter-term hydrogeological changes during the construction and operation stages when the repository will be dewatered.

In the longer-term, dilute water intrusion from melt waters during the glaciation stage of the normal evolution scenario will likely be the largest potential impact on groundwater compositions at repository depth. There is abundant evidence that such ‘cold-climate waters’ penetrated to repository depth during past ice ages. However there is significant uncertainty about the compositions of such waters and the potential ranges of compositions that occurred as a result of geochemical evolution between infiltration and repository depth, and likewise uncertainty about the potential ranges of water compositions during such hydrological events in the future.

The natural processes of geochemical evolution that would influence the final composition and chemical conditions at repository depth include:

- Assimilation of CO_2 and O_2 from the soil zone (if present) and subsequent reaction of CO_2 with minerals;

- Dissolution and equilibration with rapidly-reacting minerals in the soil and near-surface rocks, e.g. calcite, gypsum (if present), pyrite, other Fe^{2+} minerals;

- Ion exchange reactions with clay minerals in soils and as fracture fillings;

- Assimilation of dissolved organic carbon and microorganisms from the soil zone;

- Reaction of dissolved O_2 with dissolved and mineral sources of reduced species, e.g. sulphide, Fe^{2+}, DOC, producing oxidised solutes, e.g. SO_4, Fe^{3+}, HCO_3;

- Mixing with pre-existing older, less mobile and more mineralised groundwaters in fractures and in rock matrix pores;

- Alteration reactions with aluminosilicate minerals in rock matrix and in fractures, consuming H^+ and CO_2, releasing solutes, precipitating secondary minerals, exchanging ions.

There will be reactions with the components of the EBS, e.g. bentonite and cementitious engineering materials, that modify the composition of water further as it penetrates through backfill and buffer towards the canisters in a repository. However the geochemical modelling reported here is concerned only with the natural processes.

The present study is concerned with the evolution, by water-rock reaction, of the cation composition, alkalinity and pH of dilute infiltration flowing towards repository depth. Specifically, it focuses on the variability of the concentrations and relative proportions of the dominant divalent and monovalent cations, i.e. Ca^{2+} & Mg^{2+} and Na^{+} & K^{+} respectively, because this is one of the factors in near-field groundwater chemistry that would influence the development of material properties of the bentonite buffer. Other divalent cations, principally Sr^{2+} and Fe^{2+}, are not considered here because at their low natural abundances the potential effects on ion exchange in the EBS is minor relative to the major divalent cations though it is be noted that this may not be the case for Fe^{2+} derived from steel engineering materials, e.g. in the KBS-3H design. Evolution of groundwater mineralisation by mixing with pre-existing brackish/saline groundwaters is excluded in this modelling because the aim is to understand the range of possible outcomes for groundwater composition in the variant scenario where glacial melt water or other very dilute water enters the system with such flux that it displaces pre-existing groundwater and penetrates to repository depth without such mixing. Thus the modelling of the ‘unmixed’ scenario carried out here is studying an extreme case in a wide range of possibilities for future evolution of groundwater flows and compositions at repository depth.

The present modelling does not couple redox reactions into the water-rock reactions because their inclusion would introduce complications and potential into interpretation of the possible outcomes from reactions with carbonate and silicate minerals which are not redox-active. Evolution of redox has been discussed and modelled in a previous study for SSM [2].

Therefore the modelling done for this study concerns the first, second, third and seventh of the geochemical processes in the above bullet list, but does not take into account the fourth, fifth and sixth in the list.

3 Scenarios for Dilute Groundwaters

3.1 Fresh water inflow during temperate climate

As land uplift progresses, the hydraulic gradient between the inland water table and the Baltic Sea will increase. As a result the existing brackish groundwater that occupies most of the target volume will tend to be displaced by infiltrating fresh meteoric water. Shallow brackish water is, presumably, already being flushed and the depth of flushing will increase progressively as the density of the freshening groundwater column decreases and dilute groundwater penetrates deeper. How deep this process will penetrate in the long term will depend on a number of factors: e.g. how the hydraulic gradient develops as uplift slows down, the stability of underlying brackish-saline groundwaters due to density stratification, permeability of connection between Baltic seawater and groundwaters in the target volume, and permeability for lateral regional-scale flow of dilute groundwaters from further inland.

3.2 Melt water inflow during future glaciation

Much has already been written about the scenario whereby melt water under an ice sheet or on the fringe of a melting ice sheet might infiltrate into underlying rock [3, 4, 5, 6, 7]. Melt water at the base of a 'warm-based' ice sheet will have a pressure head between atmospheric pressure and the head of a water column through the thickness of the overlying ice sheet. In the latter case, the driving force of melt water infiltration will be substantially higher than under normal infiltration conditions and the inflow and penetration depth of melt water will be proportionately greater.

There is isotopic evidence, primarily low stable isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in water, which indicates that such palaeohydrogeological conditions existed during, or in their regression phases of, past glaciations. Most or all of the groundwater with this isotopic signature presumably originates from the last, end-Pleistocene, glaciation, though deeper groundwaters and pore waters in rock matrix may contain minor components of melt water from previous Pleistocene ice ages. Typically, the isotopic evidence at Forsmark indicates that glacial melt water penetrates to at least 500-600 m depth, and perhaps with only partial flushing to 1000 m or more. Thus it is probable that melt water from future ice sheets could also reach to repository depth.

As described above, melt water that would infiltrate under anomalously high hydraulic gradient and high flux would derive from the base of the ice sheet. Its chemical composition would therefore reflect the particular hydrochemical conditions in that environment.

3.3 Groundwater flow under permafrost

An uncertain hydrogeological scenario for deepening of dilute water flow would arise if permafrost were to divert fresh water circulation to greater depths. There is a large degree of uncertainty in this scenario [8, 9].

The possibility of it would depend, amongst other factors, on there being sufficient sustained lateral flow through the target volume despite downwards infiltration being inhibited by permafrost. It is likely that lateral regional flow will only persist below a permafrosted landscape if it is recharged in locations unaffected by permafrost, for example in talik areas (i.e. unfrozen gaps in permafrost, for example beneath river beds). It is conceivable, in that case, that downwards development of permafrost towards repository depth, e.g. to several hundred metres depth, could deflect the flow lines of dilute groundwater downwards, thus flushing pre-existing brackish groundwaters at repository depth. The composition of the dilute water in this case would reflect its remote source, possibly related to infiltration through talik features. In addition to water-rock reactions, the composition might also be affected by mixing with sub-permafrost water.

A hydrochemical process related to permafrost formation that has hydrodynamic implications is the generation of saline groundwaters due to salt rejection [10, 11, 12]. By this process, saline groundwater is expected to accumulate ahead of a deepening front of perennially frozen bedrock as salt is rejected from groundwater as it is frozen. Such a saline groundwater ‘lens’ would tend to flow downwards due to its relatively greater density, thus dissipating the salinity. SKB has carried out scoping calculations for salt rejection in this type of bedrock that indicate that permafrost penetrating to 300 m depth might result in salinity of about 12000 mg/L Cl^- if contained in a lens about 10 m-thick [13]. Considerable uncertainty remains in the actual occurrence, distribution and hydrogeochemical and hydrodynamic implications of this salinization process, especially in crystalline bedrock [14]. Its potential effects on deep groundwater compositions during glacial periods are not considered further in this report.

4 Chemical Compositions of Dilute Groundwaters

SKB's hydrochemical database for waters sampled from soil pipes (i.e. piezometers) at Forsmark shows that groundwaters at very shallow depths, <10 m, already have a substantial component from a brackish water source. The majority of water samples taken from percussion boreholes and cored boreholes at depths <100 m are brackish with >3000 mg/L Cl^- (see Figure 4-1 in [15]). Only a small number of water samples from 0 to 100 m depth are dilute, having <1000 mg/L Cl^-.

This brackish contribution is almost certainly due to Baltic/Littorina water. The trends of individual major ions versus the chloride concentrations for soil pipe water samples that have <50 mg/L Cl^- indicate the likely general ionic compositions in the dilute water component in these groundwaters:

- Ca^{2+} is at 90-200 mg/L (2-5 mM) in the dilute component;

- Na^+ is relatively low, <10 mg/L (0.5 mM) in the dilute component and increases in correlation with Cl^-;

- K^+ is low at 2-10 mg/L (0.05-0.2 mM) and remains at around 5 mg/L as Cl^- increases;

- Mg^{2+} similarly remains around 5-10 mg/L (0.2-0.4 mM), independent of Cl^- in this range;

- HCO_3^- is in the range 200-500 mg/L (3.5-8 mM) in the most dilute waters and remains between 300-400 mg/L within this range of Cl^- increase;

- SO_4^{2-} values are scattered especially in the most dilute waters, between 0 and 130 mg/L (0-1.5 mM).

These trends provide some background information about the hydrochemical effects of in-mixing of brackish water. It improves confidence about the hydrochemical changes in very dilute waters that occur due to water-rock reaction alone. These cause the dilute infiltration water, initially having rainfall/snowfall composition, to evolve towards $Ca\text{-}HCO_3$ with lesser proportions of Na, Mg, K and SO_4. Calculations with the PHREEQC geochemical model code [16] indicate that most of these shallow groundwaters are already saturated or oversaturated with respect to calcite and also with respect to silica. DOC (dissolved organic carbon) concentrations tend to be rather high, 15-30 mg/L. Concentrations of Fe^{2+} and, in some cases, HS^-, suggest that reducing conditions might already occur, albeit patchily, and probably being correlated with the amounts of DOC.

Stream waters, although they might have a component from effluent shallow groundwater, probably provide the best indication of the composition of infiltration water that has not undergone substantial reaction with soil and rock.

Na^+ concentrations are around 0.02 to 0.7 mM and Ca^{2+} is similar at 0.15 to 0.7 mM. These cation concentrations are balanced by HCO_3^- at 0.25 to 1.3 mM, Cl^- at 0.15 to 0.7 mM and also some minor SO_4^{2-}. Comparing these compositions with those of shallow groundwaters from soil pipes indicates that early hydrogeochemical evolution primarily involves increases of HCO_3^-, Ca^{2+} and SO_4^{2-}, small decrease of Na^+, and small increases of Mg^{2+} and K^+. Possible sources of SO_4^{2-} are discussed in R-07-55 where it is concluded that there are mixed sources: oxidation of pyrite in soils, atmospheric fallout and leached relict marine sulphate. Similarly, the same report concludes that Ca^{2+} increase is derived mainly from dissolution of calcite in Quaternary sediment deposits and soils and possible also from weathering reactions with Ca-aluminosilicates; ion exchange release of Ca^{2+} also probably has a role in the decrease of Na^+. However the Na^+ budget may also be more complex, including inputs from weathering of Na-aluminosilicates. HCO_3^- is thought to derive from calcite dissolution and oxidation of DOC. pH, though not reported in R-07-55, is assumed to evolve to slightly higher values during infiltration into shallow groundwaters where pH values are mostly in the range 6.8 to 7.6.

SKB have used the analysed composition of a dilute groundwater from shallow depth at Forsmark as the 'modified meteoric' end-member in multivariate calculations with the M3 model. The specific sample used for this purpose is that from the depth interval ca.17-50 metres in percussion borehole HFM09, sampled in 2004 (Table 1). However it is noted by SKB [17] that this water is anyway not so dilute and already has $Ca^{2+} + Mg^{2+}$ concentrations that exceed SKB's suitability criterion for alkali earth cations (>40 mg/L). This 'dilute' groundwater composition and the much more dilute composition of a typical rainwater sample have been used in modelling the combined processes of mixing in varying proportions with a brackish groundwater at repository depth (based on analysis of a water sample from borehole KFM01D at about 445 m depth that has 5800 mg/L Cl^-) and cation exchange (parameterised as described in section 1.6.1).

For SKB's M3 statistical analysis of groundwater compositions, in addition to the four predominant end-member waters (i.e. brine, Littorina, glacial and meteoric) and the additional 'modified meteoric' water, an additional end-member 'superficial granitic groundwater' from each site was identified. The shallow groundwater selected from the Forsmark data is that for percussion borehole HFM03 at about 20 m depth (Table 1, from Table 3-1 in [6]).

Table 1. *Compositions of selected shallow groundwaters at Forsmark.*

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	Charge bal
	mg/L								%
HFM09/17-50	7.91	274	5.6	41	8	181	85	465	0.8
HFM03/20	7.6	64.6	9.5	62	14	15.7	18.6	310	10.5

For consideration of hydrochemical conditions during a glacial period, SKB has assumed a reference water composition for the glacial melt water end-member. The reference compositions have been selected by SKB to meet the particular needs of various modelling studies. Two of the reference compositions are (i) an estimated composition for 'juvenile' melt water at the base of an ice sheet, prior to modification by reaction with underlying rock, taken from a melt water composition at the Josterdalsbreen glacier in Norway (from Table 2 in [5]), and (ii) a modelled composition for melt water after equilibration with calcite, chalcedony, kaolinite and $Fe(OH)_3$ (from Table 3-2 in [6]). These two 'glacial' water compositions are shown in Table 2; the only significant differences in the tabulated data are in pH, Ca^{2+} and HCO_3^- concentrations, reflecting the modelled degree of equilibration (saturation index = -1) with respect to calcite. The other solute data of primary interest in the equilibrated water are for Fe_{tot}, Si and Al: 0.045, 7.0, and 0.05 mg/L respectively.

Table 2. *Reference compositions for glacial melt waters.*

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
'Juvenile' glacial melt water	5.8	0.17	0.4	0.18	0.1	0.5	0.5	0.12
'Equilibrated' glacial melt water	9.25	0.17	0.39	3.0	0.1	0.5	0.5	5.43

A review for an SSM workshop of the chemistry of glacial meltwaters [18] has identified a new set of data for Arctic glacial run-off and melt waters from glacial till and ice streams associated with the Antarctic and Greenland ice sheets [19]. Compositions for five of these waters have been selected as illustrating a potential range of glacial melt water compositions (Table 3). The range of compositions incorporates the effects of biogeochemical rock weathering and perhaps also of evaporation in the water compositions. In particular, the relatively elevated SO_4 concentrations in some waters suggests that sulphide oxidation is occurring and may be driving the silicate mineral dissolution reactions as indicated by the relative changes in pH, HCO_3^-, Na^+, Ca^{2+} and Mg^{2+} concentrations.

Table 3. *Compositions for glacial melt waters from [19].*

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mmol/L							
Robertson Glacier, Canadian Rockies	8.3	0.02	0.01	1.7	0.5	0.01	1.0	2.6
John Evans Glacier, Canadian Arctic	8.3	0.3	0.04	1.3	0.3	0.1	1.5	0.4
Longyearbreen, Svalbard		3.4	0.08	4.5	4.9	0.08	10.0	2.2
Antarctic Ice Sheet, Casey Station	8.4	6.6	0.2	0.5	0.1	2.2	0.3	3.5
Bindschadler Ice Stream, Antarctica	6.5	35.0	0.7	9.0	8.6	2.0	31.0	7.5

5 Mineralogy of Forsmark Rocks

The host bedrock at Forsmark comprises various lithologies that collectively form a metagranite that has been deformed at amphibolite-facies metamorphic conditions. The lithologies include granite-to-granodiorite, tonalite, amphibolite, and pegmatitic granite [13, 20]. These lithologies mostly have high quartz contents, 20-50%. Rock matrix contains the major mineral components in proportions shown in Table 4.

Table 4. *Major mineral components in the lithologies at Forsmark (selected from [20]).*

Volume %	Quartz	Plagioclase	K-feldspar	Biotite	Epidote	Horblende	Calcite
Granite-granodiorite	27.8-45.8	24.0-63.8	0.2-36.0	0.8 - 8.2	0.1 - 3.2		
Tonalite-granodiorite	0.0-45.4	19.6-61.4	0.0-21.8	0.0-15.6	0.2 - 0.6	0.0-41.8	0.2
Granodiorite, tonalite, granite	15.4-35.4	29.4-67.0	0.0-38.0	1.8-19.4	0.4 - 1.8	0.0-25.2	
Granite	25.4-42.8	22.0-46.2	22.6-37.8	0.6 - 4.4	0.2 - 0.8		
Average for Forsmark granite	35.6 ± 4.2	35.6 ± 8.5	22.5 ± 8.6	5.1 ± 1.6	0.6 ± 0.7		

Fracture mineralisations have been categorised according to inferred relative ages into 4 generations, Generation 1 being the oldest and Generation 4 being the youngest (Table 5) [21]. About a half to a third of fractures in typical fracture domains have been logged as being ‘open or partly open’, i.e. potentially transmissive at greater or lesser degrees at the present time (Figure 4-19 in [21]). Pyrite traces have been identified in 55-83% of these open or partly open fractures. In addition to the minerals identified in the table, iron oxyhydroxides, goethite etc, have also been identified in Generation 4 fractures where they are interpreted to be primarily the product of oxidation of pyrite and other Fe^{II} minerals in the shallow subsurface.

Generation 4 is dominated by chlorite, clay minerals (corrensite, illite, mixed-layer clays, montmorillonite, kaolinite) and calcite with traces of pyrite and/or goethite. These are probably the most relevant minerals in relation to the evolution of dilute water infiltration because they are prominent in hydraulically conductive fractures and fracture zones including the sub-horizontal and gently-dipping fractures that are major pathways for potential water penetration to repository depth.

Table 5. *Fracture mineral occurrences according to mineralisation chronology, based on [17].*

	Quartz	Adularia	Epidote	Chlorite	Calcite	Prehnite	Laumontite	Analcime	Pyrite	Corrensite	Clays
Gen 1	✓		✓	✓							
Gen 2		✓		✓	✓	✓	✓				
Gen 3	✓	✓			✓			✓	✓	✓	
Gen 4				✓	✓				✓	✓	✓

6 Conceptual Hydrogeochemical Models

6.1 Hydrogeochemical processes

A conceptual model for hydrogeochemical evolution of dilute groundwaters from the zone of infiltration in the shallow subsurface to the vicinity of the engineered barrier system at repository depth has the following processes:

- Microbially-mediated oxidation of dissolved organic carbon (DOC) to CO_2.

- Assimilation of CO_2 in water by equilibration with the raised pCO_2 in the soil zone due to the above-mentioned biogeochemical oxidation of DOC.

- Oxidation of reduced species, in addition to DOC, in soil and bedrock. The most labile reduced mineral is likely to be pyrite existing as a secondary mineral in fractures in bedrock. On oxidation of pyrite by O_2 or other oxidised species, sulphate SO_4^{2-} will be released to groundwater. Oxidation of pyrite and other minerals containing ferrous iron Fe^{2+}, e.g. biotite and chlorite, will also result in precipitation of $Fe(OH)_3$. The slight depletion of OH^- in solution as the ferric oxyhydroxide is precipitated will cause a decrease of pH.

- Depletion and elimination of dissolved oxygen, O_2, due to consumption by the above-mentioned oxidation reactions, as a consequence of which the redox conditions change from oxidising to reducing (i.e. positive to negative Eh values versus standard hydrogen electrode potential.

- Dissolution of calcite $CaCO_3$, enhanced in relation to raised pCO_2.

- Dissolution/alteration of silicate minerals, release of alkali and alkali earth cations, enhancement of dissolved SiO_2, generation of alkalinity, and formation of secondary minerals such as calcite and clays.

- Ion exchange between cations in solution and cation populations on clays and other sorbing mineral surfaces.

- Biogeochemical homogeneous and heterogeneous redox reactions in which dissolved reducing ionic species undergo microbially-mediated interaction and approach to equilibration among themselves and also react with oxidised minerals, e.g. Fe^{3+}-containing minerals such as goethite/hematite and biotite, releasing reduced ionic species such as Fe^{2+} into solution.

- Continuous hydrodynamic mixing with pre-existing groundwater components from other sources and also diffusive mixing with pore waters held in the rock matrix.

As discussed above, redox reactions have been excluded from the present modeling study because they have already been considered elsewhere and inclusion of them would complicate the modelling and its interpretation. Hydrodynamic mixing has also been excluded because the focus of modelling is solely on the reactions of unmixed dilute infiltration water with silicate minerals and calcite, i.e. the non-redox alteration reactions that are common to hydrogeochemical evolution in this type of rock.

The following model calculations therefore are based on a conceptual model which comprises the three types of reactions in the above bulleted list: dissolution and precipitation of calcite, dissolution/alteration of silicate minerals (which may be primary minerals in the rock matrix or secondary minerals in fractures that have transmitted aqueous fluids in the past) and precipitation of other silicate minerals, and cation exchange between groundwater and surfaces of clays and other minerals.

6.2 Approaches to geochemical modelling

Two alternative approaches to model simulations of hydrogeochemical reactions have been tried in this study.

The first approach is ‘kinetic’ and has simulated the dissolution reactions of various aluminosilicate minerals in terms of the rates of each reaction. The overall potential for continued dissolution is governed by the calculated state of thermodynamic equilibrium for each mineral phase, but the progress of dissolution is calculated using empirical kinetics expressions.

The second approach is ‘local equilibrium’ and has assumed that reaction rates are fast relative to water movement through the system. Local equilibria are achieved between water and reactive minerals so that hydrochemical evolution is governed by a sequence of equilibria with different assemblages of minerals.

The aim of modelling with the alternative approaches is to study possible reactions between a dilute water and a representative assemblage of primary and secondary minerals and how the resulting groundwater compositions, specifically pH values and $[Ca^{2+}+Mg^{2+}]/[Na^{+}]$ ratios, vary depending on the model assumptions in terms of ‘kinetic’ or ‘local equilibrium’ and mineral assemblage.

In modelling a natural bedrock groundwater system, a kinetic approach is in principle more appropriate to a system in which reaction rates are low in relation to the flux of water. In other words, a system in which groundwater flow rate is so high and/or reaction rates are so low that water-mineral equilibria are not achieved over the flow path length of interest. A local equilibrium approach to modelling is more appropriate for groundwater systems in which the natural flow rate of water is so low that water-rock reactions approach equilibrium and the variability of water compositions reflect spatial variations of mineral assemblage and/or of incoming water compositions.

Rates of water-rock reactions depend strongly on the proximity to equilibrium (the ‘chemical affinity’), so that rates fall by many orders of magnitude as equilibrium is approached [22, 23]. Far-from equilibrium mineral dissolution rates for aluminosilicates are generally dependent on reacting mineral surface area and $[H^+]$ concentration, i.e. pH. Most of the experimental research into reaction mechanisms and kinetics has been carried out, for practical reasons, at far-from equilibrium conditions and thus kinetic parameters tend to represent these conditions. For example, dependences of reaction rates on pH have been widely studied but these studies have generally been in experimental set-ups with relatively fast flow rates and short path lengths that tend to maintain reactions at disequilibrium. Reaction kinetics closer to equilibrium are much less well quantified and anyway reaction mechanisms in this state are considerably more complex and dependent on local physical, geochemical and mineralogical properties of the system including precipitating secondary minerals, and on heterogeneities in all of these factors.

6.3 PHREEQC geochemical model and parameters

Hydrogeochemical reaction simulations were carried out with the PHREEQC computer program for speciation and reaction [16]. Version 2.13.2 of the program was used with the optional ‘llnl.dat’ file of thermodynamic data as supplied with version 2.10 of PHREEQC.

Thermodynamic data in the LLNL database have not been reviewed and quality controlled specifically for this study, but the provided database (version thermo.com.V8.R6.230) is in widespread use, both in its converted form for use with PHREEQC and also in its original form for use with the EQ3/6 program at Lawrence Livermore National Laboratory as well as with the Geochemists Workbench (GWB) program.

Reaction kinetics parameters used for the ‘kinetic dissolution’ approach to modelling (Section 7) were obtained from published data (see Table 8 in Section 7.1). Expressions for reaction rates require estimates for reactive surface areas of relevant minerals. In the absence of surface area measurements that are specific for each of the minerals in this geological setting, data were also taken from published literature, as shown in Table 9 in Section 7.1.

Cation exchange between the solution and solid mineral phases requires a set of model parameters that describe the exchange equilibrium. A subset of parameters specifies the proportions of alkali and alkali earth cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) occupying the exchange sites on mineral surfaces (usually understood to be predominantly clays). Cation exchange capacities (CEC) in the range 0 to 0.2 Mol kg^{-1} are reported for drillcore samples from Forsmark (Figure 4-5, [17]), with the bulk rock values being <0.03 Mol kg^{-1} and rock in fracture zones being between 0.04 and 0..2 Mol kg^{-1}, indicating the probable occurrence of clays in fracture zones. SKB selected a CEC value of 0.05 for their modelling, based on a measurement on drillcore from 600 m depth.

An empirical estimate of the exchange selectivity coefficients has been made by SKB, using analyses of coexisting groundwater and sorbed exchangeable cations (Table 6). The analysis of CEC and sorbed cation proportions was carried out on a crushed and sieved sample of drillcore from borehole KFM01B at depth of only 47.4 m but the co-existing groundwater is brackish (4370 mg/L Cl^-; see Table 4-10 in [17]). Therefore the sorbed cation distribution is assumed to be in equilibrium with that water composition.

Table 6. *Analysed cation concentrations on exchange sites in rock from 47.4 m depth in Forsmark borehole KFM01B (from Figure 4-11 in [17]).*

Sorbed species	Mol/kg
CaX_2	7.12×10^{-2}
NaX	0.97×10^{-2}
MgX_2	2.64×10^{-2}
KX	0.73×10^{-2}
CsX	6.7×10^{-7}
RbX	5.11×10^{-5}
CEC	19.8×10^{-2}

The resulting selectivity coefficients (using Gaines-Thompson convention for the equilibrium stoichiometry) are in Table 7.

Table 7. *Cation exchange reactions and computed selectivity coefficients for co-existing rock and groundwater in KFM01B at 47.4 m depth (from Table 4-2 in [17]).*

Exchange reaction	Log K
$Na^+ + \frac{1}{2} CaX_2 = \frac{1}{2} Ca^{2+} + NaX$	-1.706
$Mg^{2+} + CaX_2 = Ca^{2+} + MgX_2$	-0.007
$K^+ + \frac{1}{2} CaX_2 = \frac{1}{2} Ca^{2+} + KX$	-0.036

7 Hydrogeochemical Model with Kinetics

7.1 Model parameters

The hydrogeochemical model calculations of chemical evolution controlled by reaction rates are set up and conditioned by sets of kinetic parameters and reactive surface areas for mineral dissolution in the water-rock system (Tables 8 and 9).

Table 8. *Mineral dissolution rate expressions.*

Mineral	Rate expression	Reference
Biotite (based on empirical Mg^{2+} release rate)	$R = 10^{-4.93} [H^+]^{0.57} + 10^{-10.57} [H^+]^{-0.29}$ moles h^{-1} m^{-2}	[24]
Chlorite	$\log R = -9.79[H^+]^{0.49} -13.0 -16.79[H^+]^{-0.43}$ moles s^{-1} m^{-2}	[25]
Pyrite (oxidation by DO)	$R = 10^{-8.19} [DO^{0.54}]/[H^+]^{0.31}$ moles s^{-1} m^{-2}	[26]
Pyrite (oxidation by Fe^{3+})	$R = 10^{-8.58} [Fe^{3+}]^{0.301}/[Fe^{2+}]^{0.47}[H^+]^{0.32}$ moles s^{-1} m^{-2}	
Ca,Na-Plagioclase	$R = 2.4x10^{-15}$ moles s^{-1} cm^{-2}	[27]
K-feldspar	[$R = 2.4x10^{-15}$ moles s^{-1} cm^{-2}]	
Quartz	$R = 10^{-16.3} [H^+]^{-0.5}$ moles s^{-1} m^{-2}	[28]

Table 9. *Reactive surface areas for minerals.*

Mineral	Reactive surface area (cm^2/dm^3)	Reference
Biotite	1200	[24]
Chlorite		[25]
Pyrite		[26]
Ca,Na-Plagioclase	500	[27]
K-feldspar	500	
Quartz		[28]

These kinetic parameters are being used only for illustrative scoping modelling. The degree to which they could be considered to be representative of the system of interest cannot easily be assessed. Moreover, as discussed earlier, the rate expressions are valid only for reaction conditions that are far from equilibrium. It is evident from studies of groundwaters and of mineral changes in weathering profiles in shallow bedrock that equilibrium is approached in the first few metres of water infiltration in normal weathering conditions [29]. This approach to equilibrium is probably related to high surface areas of primary bedrock minerals and secondary alteration products in the soil and weathered zones.

Along with these parameter values, the model involves a number of assumptions about the geochemical system, specifically which mineral phases are reactive in terms of dissolution or precipitation. Choices for these assumptions are based on geochemical and mineralogical judgement, based on the broader scientific understanding from interpretative modelling of diverse water-rock systems.

7.2 Set-up of PHREEQC model

Batch-reaction calculations were carried out with a starting groundwater composition that was representative of dilute water infiltration at the top of the bedrock at Forsmark, as discussed above. Either the composition of soil pipe water SFM0009/2.7 or that of equilibrated glacial melt water was used as the starting composition. The reacting mineral assemblage comprised Na- and Ca-plagioclase (albite and anorthite), K-feldspar, biotite, calcite, chalcedony, chlorite, illite and kaolinite, though only dissolution reactions of plagioclase, feldspar, biotite and chlorite were allowed in the model. Cation exchange was included in the model, using the initial distribution of cations in exchange sites and the exchange coefficients shown in Tables 6 and 7. Reaction kinetics were applied for the dissolution reactions of Ca- and Na-plagioclase, K-feldspar (for which the reaction rate was assumed to be the same as for plagioclase) and biotite, using the rate expressions shown above. Note that, of these, only the reaction rate expression for biotite represents a dependence on pH. It is known that dissolution rates of plagioclase and feldspar are also dependent on pH and other factors [23], but these relationships and also the dependence on proximity to equilibrium are too complex to implement in the present modelling.

With unlimited forward reaction of these minerals, especially without pH-dependence being taken into account for the framework aluminosilicate minerals, H^+ is continually consumed and the pH of the resulting solution rises to unrealistic values that would obviously be buffered in reality by alkaline alteration and precipitation reactions. To counteract this artificial condition in the model, the partial pressure of CO_2, P_{CO2}, is held at a constant value in most of the model runs. This ‘device’ has the effect of buffering the pH at a lower value than if P_{CO2} were allowed to diminish in correlation with pH rise. The resulting pH values in the model, around 9-10, are similar to those higher values that have been observed in some ‘evolved’ dilute waters in groundwater systems in rocks dominated by silicate minerals.

A printout of a typical model run with PHREEQC is shown in Appendix A.

In each model run, four time periods were used with the kinetics expressions. Step 1 was 3.15×10^7 seconds, i.e. 1 year; step 2 was 10 years; step 3 was 1000 years; step 4 was 10000 years. Note that the time periods are not consecutive, i.e. they each start from time zero, so Step 4 includes the earlier evolution in Steps 1 to 3.

Details of the results of the model runs are in Appendix B.

7.3 Discussion of reaction kinetics modelling results

The PHREEQC model runs shown above attempt to investigate how a dilute water evolves as it reacts with typical rock minerals. The model makes a large number of assumptions and simplifications about the mineral assemblage and about the reactions that occur.

The most significant assumptions concern (a) the kinetics of key dissolution reactions and the relative values amongst the reacting minerals, (b) which solids, and their compositions, precipitate from solution as secondary minerals, and (c) the internal and external factors that control pH and the budget of inorganic C (with which P_{CO2} buffering is equivalent). It is apparent in the modelling that the assumptions in the latter are the most significant issue for control of cation concentrations and specifically control of the ratio of divalent alkali earth cations to univalent alkali cations, $(Ca^{2+}+Mg^{2+})/(Na^{+})$.

If P_{CO2} and pH are unbuffered in the model, H^+ is consumed and pH rises to high values that appear to be unrealistic when compared with observed alkaline pH values (around 9-10 as a generalised limit) in comparable natural systems.

In model run A4-Sim3_2-2-10, Ca^{2+} rises as anorthite dissolves and its concentration is not limited by calcite precipitation because of the very low P_{CO2} and correspondingly low CO_3^{2-} concentration. Na^+ and K^+ also rise due to dissolution of albite and K-feldspar. These increases in cation concentrations are balanced by high OH^- concentrations in the high pH solution. K^+ also derives from dissolution of biotite, from which Mg^{2+} also increases (but not in model run RunA2_29-1-10 where reacting biotite is absent).

In the modelled system here, only K^+ is buffered by a precipitating secondary mineral, i.e. by illite. In the longer timescale simulation, K^+ is seen to fall to a very low level which is unrealistic when compared with observations in natural systems.

Na^+, Ca^{2+} and Mg^{2+} concentrations are not similarly controlled in the model by secondary minerals (except Ca^{2+} by calcite which does not precipitate in this case as explained above). There is some adjustment of their concentrations because of cation exchange equilibration, but this effect is minor. In reality, Na^+, Ca^{2+} and Mg^{2+} are affected also by precipitation of montmorillonite and chlorite in the form of the mixed-layer mineral corrensite which is reported to be the most widespread clay mineral in fractures at Forsmark [21].

It is only in these high pH, freely-variable P_{CO2}, model runs that the (Ca+Mg)/Na molar ratio exceeds 1 in the longer timescale (Step 4) simulations. In the model runs in which P_{CO2} and pH are assumed to be buffered to realistic values, (Ca+Mg)/Na ratios are generally between 0.01 and 0.1; $[Ca^{2+}]$ is around 10^{-5} M and $[Mg^{2+}]$ is slightly higher at around 10^{-4} M, whilst $[Na^+]$ is between 10^{-3} to 10^{-2} M.

It is obvious that there are large uncertainties in these outcomes from geochemical modelling concerning the likely evolution of dilute waters during infiltration and circulation through Forsmark rock. There is also the evidence from comparison with observed groundwater compositions that the modelled water compositions, i.e. the high pH values and very low Ca^{2+} values, are unrealistic. SKB's archived data for deep (100 to 700 m) dilute water samples from historical boreholes at other Swedish locations have pH values mostly between 7 and 9.2, $[Ca^{2+}]$ between 10^{-4} and 10^{-3} M, $[Na^{+}]$ between 10^{-4} and 10^{-2} M, and (Ca+Mg)/Na molar ratios mostly between 0.1 and 5. But that does not totally discount the modelled direction of hydrochemical evolution. It has to be borne in mind that present-day groundwaters have been affected by mineral reactions over long timescales and by mixing with pre-existing groundwaters that would not be representative of the processes affecting relatively rapid and high fluxes of dilute water. However the geochemical consensus is that the modelled evolution could not occur because the tendency towards high pH solutions would be attenuated by alkaline alteration of the bedrock as is also forecast and modelled for the attenuation of alkaline water leaching from cementitious materials in tunnels and repository.

8 Hydrogeochemical Model with Local Equilibrium

8.1 Model parameters

One of the objectives of this modelling was to study the dependence of the evolved groundwater composition on the initial composition of dilute infiltration. For that purpose, the modelling was carried out with four of the dilute water compositions that are shown in Tables 2 and 3 in Section 4. In summary, these four alternative starting points for the hydrogeochemical modelling runs are:

- Norwegian glacial melt water, used by SKB as an end-member in M3 statistical analysis of mixed groundwater compositions and referred to as 'juvenile' glacial melt water. It is very dilute with very low Cl^- and SO_4^{2-}, has a relatively low pH (5.8) and very low alkalinity and is grossly undersaturated with respect to calcite; cations are at or below the 0.01 mM level, in the molar order $K^+ > Na^+ > Ca^{2+} \sim Mg^{2+}$.

- Glacial melt water from the Canadian Arctic (John Evans Glacier, JEG) as reported in Skidmore et al (2010). This is more mineralised in general than the 'juvenile' melt water and in particular has higher Ca^{2+}, HCO_3^- and SO_4^{2-} and higher pH (8.3), indicating that it has reacted with calcite and also has some mineralisation due to sulphide oxidation. The order of cation molar concentrations is more typical: $Ca^{2+} > Mg^{2+} \sim Na^+ > K^+$.

- Melt water from Antarctica (Bindschadler ice stream, BIS) as reported in Skidmore et al (2010). This has markedly high SO_4^{2-} (31 mM) indicating that it has a strong overprint of sulphide oxidation which would have created acidity and therefore driven silicate mineral dissolution reactions and increasing alkalinity. pH is below neutral (6.5) and HCO_3^- is high (7.5 mM). The order of cation molar concentrations clearly shows that considerable reaction with silicate and carbonate minerals has already occurred: $Na^+ >> Ca^{2+} \sim Mg^{2+} > K^+$. This is also supported by $Na^+ >> Cl^-$ although Cl^- is 2 mM suggesting that there is a minor source of salinity which probably has a marine source.

- Shallow groundwater from Forsmark, sampled at 20 m depth in borehole HFM03, used as the superficial granitic groundwater end-member in SKB's M3 statistical analysis. This has moderate Cl^- (0.4 mM) which may be typical of unmixed infiltration that has experienced evapotranspiration in the soil zone. Near-neutral pH (7.6) and HCO_3^- (5 mM) are typical for a groundwater that has already reacted with calcite and perhaps also fine-grained reactive silicate minerals in the soil zone. The order of cation molar concentrations is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$.

The exchangeable cation parameters for this model are the same as those used for the model with reaction kinetics (Tables 6 and 7). They are the best estimates for cation exchange selectivity coefficients specifically for secondary minerals in contact with groundwater in the Forsmark bedrock; the estimate is based on exchange involving present-day brackish groundwater at 47 m depth but it is a reasonable approximation to assume that the exchange parameters should be applicable to dilute water conditions.

8.2 Set-up of PHREEQC model

Sequential batch-reaction calculations were carried out in four groups corresponding to the different initial dilute water compositions as described above. The first stage calculation in each case comprised equilibration of that initial water with calcite, chalcedony and kaolinite. This initial equilibration aims to represent the likely rapid reactions and evolution that would occur when dilute water first enters the weathered and highly fractured upper zone of bedrock. In the second and third stage calculations, the water composition resulting from the previous stage was the starting water for equilibration with selected mineral assemblages. These mineral assemblages have been selected to represent secondary and primary minerals. The secondary minerals are selected from Na-montmorillonite, illite, chlorite, laumontite, saponite and prehnite. The specific compositions dissolution expressions and thermodynamic data (log K) are listed in Table 10.

Reversible equilibrium, i.e. allowing both dissolution and precipitation, is permitted in the model only for the secondary minerals. Dissolution but no precipitation is modelled for the primary aluminosilicate minerals: Na- and Ca-plagioclase and K-feldspar.

Cation exchange was included in the model, using the initial distribution of cations in exchange sites and the exchange coefficients shown above.

***Table 10.** Thermodynamic data for mineral dissolution in the llnl.dat thermodynamic database.*

Mineral	Composition	Equilibrium expression	Log K (25 degC)
Calcite	$CaCO_3$	CaCO3 +1.0000 H+ = + 1.0000 Ca++ + 1.0000 HCO3-	1.8487
Chalcedony	SiO_2	SiO2 = + 1.0000 SiO2	-3.7281
Kaolinite	$Al_2Si_2O_5(OH)_4$	Al2Si2O5(OH)4 +6.0000 H+ = + 2.0000 Al+++ + 2.0000 SiO2 + 5.0000 H2O	6.8101
Na-montmorillonite	$Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2$	Na.33Mg.33Al1.67Si4O10(OH)2 +6.0000 H+ = + 0.3300 Mg++ + 0.3300 Na+ + 1.6700 Al+++ + 4.0000 H2O + 4.0000 SiO2	2.4844
Illite	$K_{0.6}Mg_{0.25}Al_{1.8}Al_{0.5}Si_{3.5}O_{10}(OH)_2$	K0.6Mg0.25Al1.8Al0.5Si3.5 O10(OH)2 +8.0000 H+ = + 0.2500 Mg++ + 0.6000 K+ + 2.3000 Al+++ + 3.5000 SiO2 + 5.0000 H2O	9.0260
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	Mg5Al2Si3O10(OH)8 +16.0000 H+ = + 2.0000 Al+++ + 3.0000 SiO2 + 5.0000 Mg++ + 12.0000 H2O	67.2391
Laumontite	$CaAl_2Si_4O_{12}:4H_2O$	CaAl2Si4O12:4H2O +8.0000 H+ = + 1.0000 Ca++ + 2.0000 Al+++ + 4.0000 SiO2 + 8.0000 H2O	13.6667
Saponite	$Na_{.33}Mg_3Al_{.33}Si_{3.67}O_{10}(OH)_2$	Na.33Mg3Al.33Si3.67O10(OH)2 +7.3200 H+ = + 0.3300 Al+++ + 0.3300 Na+ + 3.0000 Mg++ + 3.6700 SiO2 + 4.6600 H2O	26.3459
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	Ca2Al2Si3O10(OH)2 +10.0000 H+ = + 2.0000 Al+++ + 2.0000 Ca++ + 3.0000 SiO2 + 6.0000 H2O	32.9305
Albite	$NaAlSi_3O_8$	NaAlSi3O8 +4.0000 H+ = + 1.0000 Al+++ + 1.0000 Na+ + 2.0000 H2O + 3.0000 SiO2	2.7645
Anorthite	$CaAl_2(SiO_4)_2$	CaAl2(SiO4)2 +8.0000 H+ = + 1.0000 Ca++ + 2.0000 Al+++ + 2.0000 SiO2 + 4.0000 H2O	26.5780
K-feldspar	$KAlSi_3O_8$	KAlSi3O8 +4.0000 H+ = + 1.0000 Al+++ + 1.0000 K+ + 2.0000 H2O + 3.0000 SiO2	-0.2753

Unlike the set-up for the model with reaction kinetics (Section 7.2), the partial pressure of CO_2, P_{CO2}, and pH are constrained only by the modelled reactions, i.e. they are internally controlled without any external control on P_{CO2} as was the case for many model runs with reaction kinetics.

A printout of a typical run of the hydrogeochemical model for the local equilibrium condition is shown in Appendix B.

The variations of the set-up used for the model runs carried out represent a limited range of all variability. Moreover the mineral compositions and parameters for cation exchange are fixed. Therefore the modelling can only be viewed as an illustration of the variability of modelled hydrogeochemical evolution in relation to the conceptual model and the chosen sequence of mineral dissolution and precipitation reactions and mineral equilibria, assuming that local equilibrium is appropriate.

8.3 Assumptions in the local equilibrium model

All modelling of geochemical reactions and equilibria has a substantial number of simplifications and assumptions that are inherent in the set-up and parameters that are used. In the present case, the main simplifications and assumptions are:

- Local equilibrium is valid, i.e. that reactions with minerals are sufficiently fast relative to the rate of groundwater flow and solute transport that equilibrium is achieved wherever reaction with that mineral is allowed in the model, as long as there is sufficient mineral available to react to equilibrium if dissolution is necessary.

- Minerals and their compositions in the thermodynamic database are representative of minerals that would react with infiltrating groundwater in bedrock at Forsmark. In particular, the mineral compositions used in the *llnl.dat* database are not pure end-members; specifically, montmorillonite, illite and saponite compositions have significant amounts of Mg. These may not be representative of mineral compositions at Forsmark, but this project does not have the scope to refine the database appropriately. Although the thermodynamic data may not be significantly different for this modelling, the effect on proportions of Na, K and Mg that are released by dissolution is significant.

- P_{CO2} is determined in a closed system and thus pH also is buffered by CO_2 and equilibria with calcite and silicate/aluminosilicate minerals.

- Waters react to equilibrium with various assemblages of minerals in a series of three stages, i.e. Stages 1, 2 and 3. These stages of the PHREEQC model simulations represent hypothetical variations in the reactive mineral assemblages encountered by water along a flowpath as it infiltrates to increasing depth. Thus Stage 1 of hydrogeochemical evolution is envisaged to take place in the soil and shallow weathered bedrock and in all model runs comprises equilibration with calcite, chalcedony and kaolinite. The main effects of this equilibration are seen in the Ca^{2+}, alkalinity and pH, Si and Al concentrations. Stage 2 of hydrogeochemical evolution in each model run is envisaged to comprise reactions with varying combinations of montmorillonite, illite and chlorite plus other secondary minerals laumontite, saponite or prehnite.

Stage 3 is envisaged to comprise dissolution of plagioclase or feldspar minerals.

- Equilibria with the low temperature secondary minerals, montmorillonite, illite and chlorite, are reversible, i.e. these minerals are allowed to dissolve and precipitate depending on the calculated saturation index. On the other hand, the secondary minerals that are generally interpreted to have originated from past hydrothermal mineralisation episodes, laumontite, saponite or prehnite, are allowed only to dissolve on the assumption that precipitation of these minerals in the low temperature condition is not feasible. These assumptions are adopted throughout this modelling.

- Thermodynamic data for the reacting minerals, i.e. the log K values given in the *llnl.dat* database are reliable for the conditions that are being simulated. This project has not had the scope to carry out a review of thermodynamic data so they have been used directly from the database. The *llnl.dat* database is supplied with the PHREEQC geochemical code and is therefore in widespread use. The provided log K values are defined for 25ºC whilst 5ºC is the temperature defined in the modelling. The log K values are adjusted for temperature in the model if a ΔH value has been provided in the database, otherwise the log K values for 25ºC are used.

- The parameters used in the cation exchange equilibria in the geochemical model are reasonable approximations for the system. The derivation of selectivity coefficients is explained in Section 6.3 and is the same as has been used by SKB.

8.4 Discussion of local equilibrium modelling results

The detailed results of model runs with local equilibrium are in Appendix D. The model runs using the Norwegian glacial melt water as the initial composition are identified as B5 to B12 and are in section D.1. The model runs using the shallow Forsmark groundwater are identified as B13 to B20 and are in section D.2. The model runs using the Canadian Arctic (JEG) melt water are identified as B21 to B26 and are in D.3. The model runs using the Antarctic ice stream (BIS) melt water are identified as B27 to B29 and are in D.4. Additionally, a single illustrative model run, identified as B30, with a deep brackish groundwater from Forsmark is in D.5.

8.4.1 General comments

The focus of the modelling is the possible hydrogeochemical evolution paths for dilute water reacting with the bedrock at Forsmark. In particular, the potential changes of the concentrations and the relative proportions of the major divalent and monovalent cations are considered in the light of the modelling results. It is evident that the modelled pH values are significant indicators of the validity of the modelling, so pH is also considered. Other aspects of hydrogeochemical evolution, such as changes of alkalinity and P_{CO2}, and evolution of redox (Eh) and of the redox-active systems of Fe and S species, are not included in Appendix D because they are outside the scope of this study and the PHREEQC model was not set up to study these variables.

There may be some inconsistencies and artefacts introduced by the modelling, such as minor changes in the concentrations of some ionic species that cannot be attributed to water-mineral reaction. Examples of this are found for example in variations of some reactive cations in model runs where the specified reacting minerals do not provide sources or sinks of those cations and the changes cannot be attributed fully to cation exchange. These discrepant results from the model are relatively minor and they do not substantially change the semi-quantitative value of the modelling. It can be suggested that they might indicate a general problem of hydrogeochemical modelling of waters with very low concentrations of solutes, perhaps due to numerical problems with achieving charge and mass balances in the reactive mass transfer calculations. These sources of error in quantitative accuracy of the modelling are not considered further here.

Taking those issues into account, it indicates that the hydrogeochemical modelling done in this project should be interpreted as being illustrative and indicative rather than as being a quantitatively accurate and internally consistent representation of possible hydrochemical evolution paths for dilute groundwater.

8.4.2 Evolution of cations and pH

Stage 1 of all model runs is the preliminary equilibration with calcite, chalcedony and kaolinite. It causes an increase of pH. Dissolution of calcite and equilibration with the cation exchanger in the model also raises dissolved concentrations of all four cations to a small extent. This initial evolution of a dilute water in Stage 1 is done in all runs of the model and the resulting compositions form the input for Stage 2 in each case.

The simplest model set-up for Stage 2 is equilibration with montmorillonite and illite. In Model B5 (see Appendix D.1), this results in a slight lowering of pH and further dissolution of calcite and increase of Ca^{2+}. Mg^{2+} concentration increases, along with Na^{+}, due to dissolution of montmorillonite (the montmorillonite composition in the thermodynamic database contains Mg^{2+}). The combination of mineral dissolution and cation exchange overall leads to an increase of the Ca+Mg/Na ratio. In Stage 3 of Model B5, laumontite is added to the assemblage of reactive equilibrated minerals and is constrained to dissolution only, resulting in higher pH and dissolution of laumontite. The resulting addition of Ca^{2+}, Al and Si to the system causes precipitation of both montmorillonite and illite and thus decreases of Na^{+} and K^{+} in solution. Consequently the Ca+Mg/Na ratio goes to a very high value.

If albite and K-feldspar are allowed to dissolve in Stage 3 of the model, a sharp and unrealistic increase of pH is output by the model (Model B6). A relatively large amount of albite dissolves and Na^+ increases whilst the other cations decrease, presumably due to cation exchange. The Ca+Mg/Na ratio therefore becomes very low.

There are differences in model outputs depending on whether laumontite and saponite are allowed to dissolve only or to dissolve and precipitate. These are studied in two variant models (Models B7 and B7a). The differences are substantial. In the case where these minerals are allowed to equilibrate by dissolution or precipitation (Model B7 Stage 3), Na^+ goes to an unrealistically very low concentration so that Ca+Mg/Na is very high. In Model B7a, Stage 2, dissolution only is allowed in accordance with the inference that laumontite and saponite are hydrothermal minerals from a much earlier stage of secondary mineral formation and are not reversibly equilibrated with present-day groundwaters. In this model run, pH goes to a higher value which is unrealistic but the cation concentrations are moderate and the Ca+Mg/Na ratio is just >1 (see Figure 1).

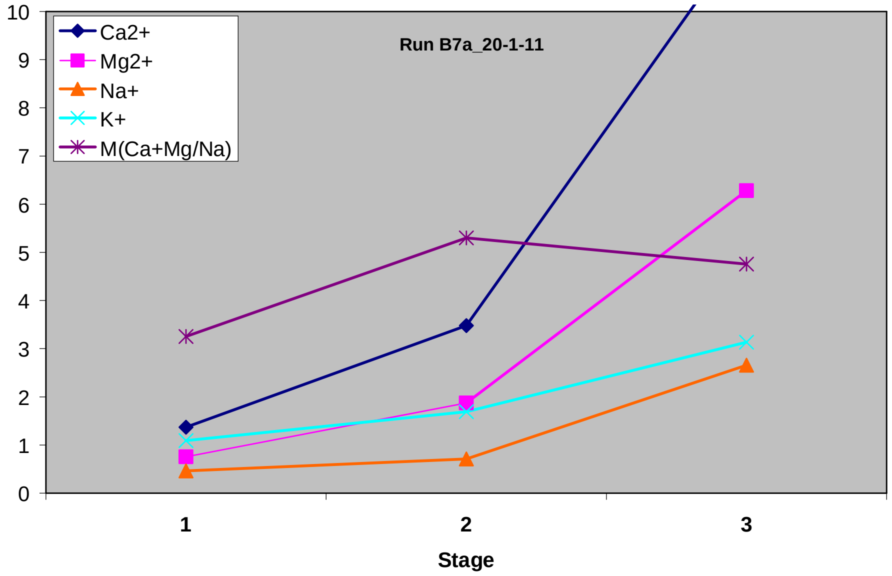

***Figure 1.** Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Model B7a. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flow-path of increasing depth from infiltration. Input water composition to Stage 1 is glacier melt water, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B7a, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds dissolution-only equilibration with laumontite and saponite; Stage 3 adds dissolution-only equilibration with albite and K-feldspar.*

Model B8 (see Appendix D.1) considers different behaviours of saponite and laumontite, whereby the former equilibrates reversibly whilst the latter is allowed only to dissolve. The results indicate that this is an unrealistic model. Precipitation of saponite leads to extremely low Na^+ (as in Model B7 Stage 2). Allowing only dissolution of saponite and laumontite does not give any change from the Stage 1 equilibration with calcite, chalcedony and kaolinite because saponite and laumontite are already saturated at that stage (Model B8a, similar to Model B7a Stage 2).

Model B9 simulates the reversible equilibration initially with montmorillonite in Stage 2 and additionally with illite and chlorite in Stage 3. This seems to be the most realistic hydrogeochemical evolution based on general understanding of water-rock reactions and on observed secondary mineral assemblages in these rocks. The model indicates that Ca^{2+} and Mg^{2+} concentrations are raised in both Stages 2 and 3 whilst Na^+ is kept low. Consequently, the Ca+Mg/Na ratio remains relatively high, as shown in Figure 2.

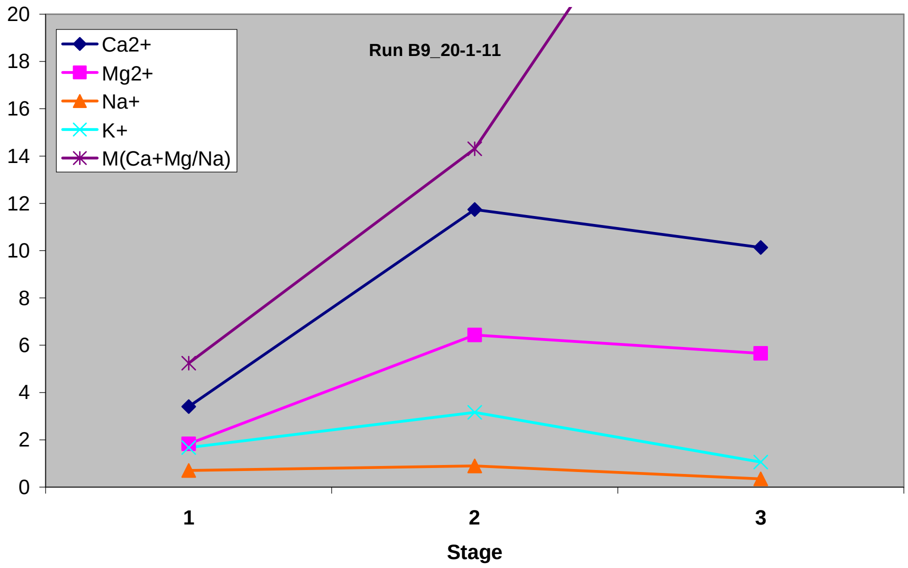

Figure 2. *Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Stages 1, 2 and 3 in Model B9. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flowpath of increasing depth from infiltration. Input water composition to Stage 1 is glacier melt water, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B9, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds reversible equilibration with montmorillonite; Stage 3 adds reversible equilibration with illite and chlorite.*

Model B10 (see Appendix D.1) removes illite and chlorite from the equilibrating mineral assemblage and replaces them with laumontite and albite + anorthite (both dissolving-only) in Stages 2 and 3 respectively. It results in a modelled evolution with swings of pH, Na^+, Ca^{2+} and Mg^{2+} concentrations. Although the model results are clearly unrealistic, they illustrate that if the reacting assemblage is limited in this way, the modelled Ca^{2+} and Mg^{2+} concentrations, depending on actual source mineral compositions, are kept moderate or high, whereas Na^+ is lowered. Thus the Ca+Mg/Na ratio would always be kept >1 and probably much higher.

In Model B11, laumontite dissolves to equilibrium in Stage 2, alongside equilibration with montmorillonite, and Stage 3 reverts to illite + chlorite equilibration without montmorillonite in the assemblage. In this model run, the very low Na^+ concentrations and correspondingly high Ca+Mg/Na ratios are maintained because montmorillonite precipitates in Stage 2 but is unavailable to re-dissolve in Stage 3. Both the alternating reacting mineral assemblages and the resulting Na^+ appear to be unrealistic in this case. If montmorillonite is retained with illite + chlorite in the reacting assemblage in Stage 3, then the Na^+ concentration rises slightly (though still relatively low) due to re-dissolution of montmorillonite in Stage 3 (Model B12; see Figure 3).

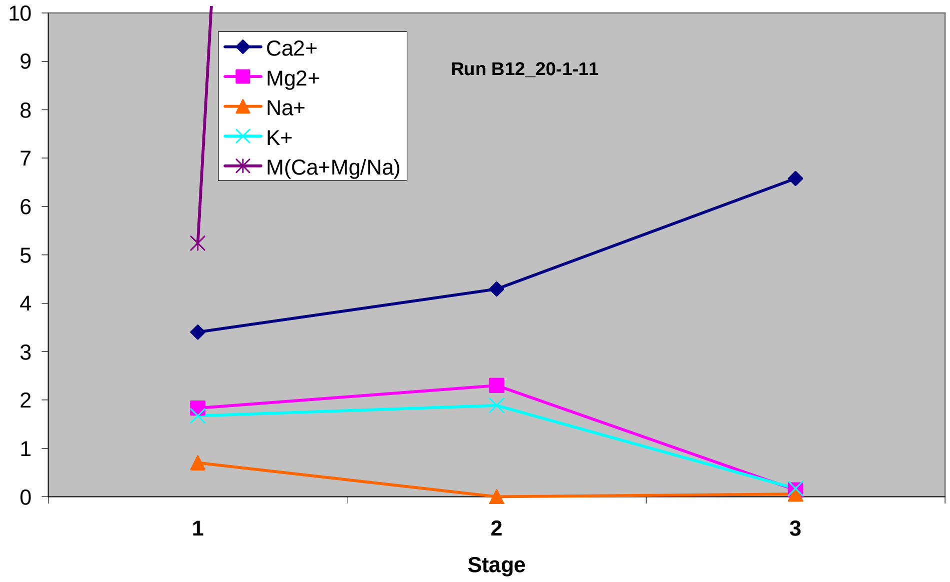

Figure 3. *Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Stages 1, 2 and 3 in Model B12. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flowpath of increasing depth from infiltration. Input water composition to Stage 1 is glacier melt water, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B12, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds reversible equilibration with montmorillonite and dissolution-only equilibration with laumontite; Stage 3 adds reversible equilibration with illite and chlorite.*

The model runs (B13 to B17) with shallow groundwater from Forsmark as the starting water composition investigate the hydrogeochemical evolution paths if the initial water were to be slightly more mineralised. Detailed model results for B13 to B17 are in Appendix D.2. Unlike the Norwegian glacial melt water considered in previous model runs (B5 to B12, Appendix D.1), Forsmark water sample HFM03/20 has pH just above neutral and cation and alkalinity concentrations that are already close to equilibrium with the mineral assemblage used for Stage 1 of all the model runs, i.e. calcite, chalcedony and kaolinite. Modelling equilibration in Stage 1 results in lower pH and lower Ca^{2+} indicating that HFM03/20 is slightly oversaturated with calcite.

The first observation from this set of model runs is that the more mineralised starting water composition has stronger buffering of pH. As is the case in model runs B5 to B12, dissolution of laumontite depresses Na^+ concentrations due to precipitation of montmorillonite (Model B13, Appendix D.2) whereas dissolution of albite raises Na^+ and depresses Ca^{2+} and Mg^{2+} (Model B14; Figure 4). It is noteworthy that equilibration with both albite (dissolving only) and montmorillonite results in a very low Ca+Mg/Na ratio which is therefore an interesting scenario in the context of potential near-field groundwater compositions (Model B14; Figure 4). In Stage 3 of Model B14, low Ca^{2+} is explained by the raised pH and calcite equilibrium, whereas very low Mg^{2+} is presumably due to the precipitation of montmorillonite which in the minerals database is attributed with a substantial Mg content.

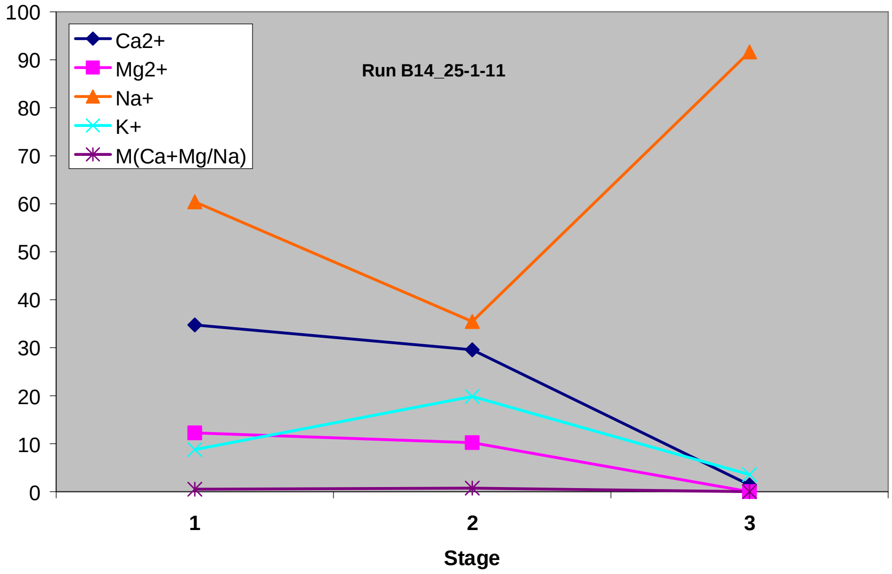

Figure 4. *Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Stages 1, 2 and 3 in Model B14. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flowpath of increasing depth from infiltration. Input water composition to Stage 1 is Forsmark shallow groundwater, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B14, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds reversible equilibration with montmorillonite and illite; Stage 3 adds dissolution-only equilibration with albite.*

A consequence of the more mineralised initial water composition (Forsmark shallow groundwater) is illustrated by Models B15 and B16 (Appendix D.2) in comparison with Model 7a. Model Run B15 simulates dissolution-only equilibration of laumontite and saponite without equilibration with montmorillonite and illite in both Stages 2 and 3. The relatively large increase of pH causes calcite precipitation and lowering of Ca^{2+} whereas Na^+ remains proportionately higher. The result is a low Ca+Mg/Na ratio, although the concentration of Ca^{2+} is still above 10 mg/L in this case. In contrast, if the system is equilibrated additionally with montmorillonite in Stage 3, the Na^+ falls sharply to a low value and the Ca+Mg/Na ratio becomes very high (Model B17, Appendix D.2).

Equilibrating with laumontite and montmorillonite in Stage 2 (Model B18, Appendix D.2) and then equilibrating with albite and anorthite (dissolution only) in Stage 3 raises pH to an unrealistic level (>12) and allows Ca^{2+} to rise due to dissolution of anorthite and precipitation of calcite. Due to the high pH, the modelled Si and Al concentrations are also unrealistically high. The increase of Mg^{2+} is presumably due to displacement of Mg^{2+} from cation exchange sites by Ca^{2+}. The result is that Ca+Mg/Na ratio is kept very high, as in Model B10 (Appendix D.1).

In Models B19 and B20 (Appendix D.2), laumontite is dissolved in Stage 2, prior to illite and chlorite equilibration in Stage 3. This results in low Na^+ concentrations and high Ca+Mg/Na ratios in both Stages 2 and 3.

Model runs B21 to B29 were carried out with alternative compositions for melt waters. Model runs B21 to B26 (Appendix D.3) use the relatively dilute Canadian Arctic glacier melt water ('JEG'). Model runs B27 to B29 (Appendix D.4) used a high-SO_4 melt water from an Antarctic ice stream ('BIS').

The Arctic melt water has pH above neutral and is moderately mineralised so is rather similar to the shallow Forsmark groundwater used in model runs B13 to B20. Consequently, dissolution of laumontite and equilibration with montmorillonite and illite (Model B21, Stage 3) shows high Ca+Mg/Na, a similar result to Models B19 and B20. Dissolution of albite and equilibration with montmorillonite and illite (Model B22, Stage 3) shows very low Ca+Mg/Na, a similar result to Model B14.

Models B23, B24 and B25 (Appendix D.3) simulate cases where various combinations of laumontite, saponite, prehnite, albite and anorthite dissolve in Stages 2 and 3, without equilibrating with montmorillonite, illite and chlorite. This scenario seems to be unlikely but is interesting as an alternative model. pH rises in both model stages. Ca^{2+} and Mg^{2+} increase proportionately more than Na^+ and K^+ when albite and K-feldspar react (Model B23) so that the Ca+Mg/Na ratio remains >1. It is noted that in this model run, laumontite dissolved to equilibrium whereas saponite remained oversaturated in Stage 2, and anorthite dissolved to equilibrium in Stage 3 with laumontite, saponite and albite all remaining oversaturated. Ca+Mg/Na is also high in the cases where only laumontite, saponite or prehnite are allowed to dissolve (Models B24 and B25).

The most realistic scenario is probably equilibration in Stages 2 and 3 with an assemblage of the low temperature secondary minerals, montmorillonite, illite and chlorite (Model B26, similar to Model B20). The modelled pH goes moderately high and Ca^{2+} increases slightly whilst Na^+ is substantially lowered; Mg^{2+} is also lowered relative to the initial melt water (see Figure 5).

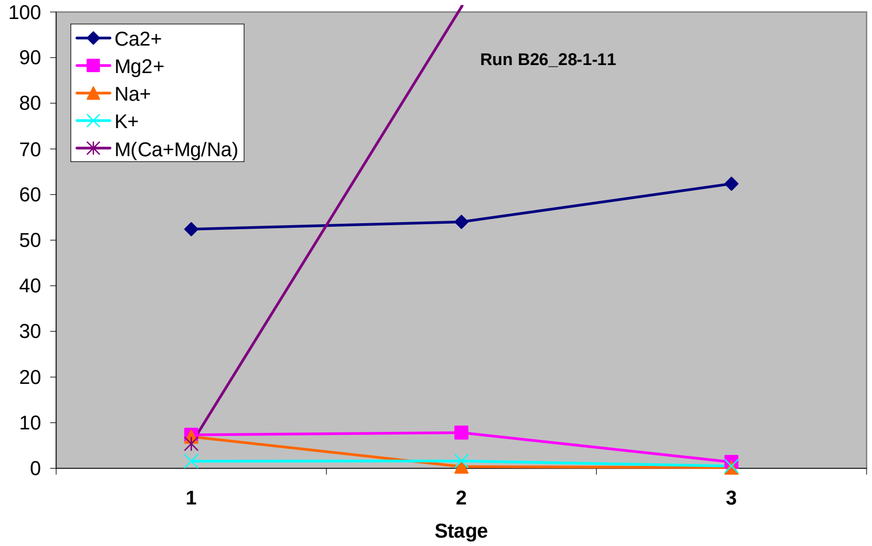

Figure 5. *Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Stages 1, 2 and 3 in Model B26. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flowpath of increasing depth from infiltration. Input water composition to Stage 1 is melt water from an Arctic glacier, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B26, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds reversible equilibration with montmorillonite and chlorite; Stage 3 adds reversible equilibration with illite and dissolution-only equilibration with laumontite.*

For the more mineralised Antarctic melt water, equilibration with montmorillonite and illite results in a moderate pH rise, slightly lowered Na^+ and increased Ca^{2+} and K^+ (Model B27, Stage 2; Appendix D.4). Ca+Mg/Na is low, <1, but the concentrations of divalent cations remain high. If laumontite also dissolves, Ca^{2+} increases further and Na^+ decreases, as also do K^+ and Mg^{2+} (Model B27, Stage 3). Consequently for this case the Ca+Mg/Na ratio increases slightly, >1.

Model B28 simulates an alternative case in which laumontite and saponite dissolve in Stage 2, and illite and chlorite equilibrate in Stage 3. Montmorillonite is not allowed to precipitate. Na^+ and Ca^{2+} concentrations remain high and K^+ and Mg^{2+} are lowered (Model B28; Appendix D.4). The Ca+Mg/Na ratio is <1 for both Stages 2 and 3 in this model.

In Model B29, montmorillonite, illite and chlorite are equilibrated in Stage 3 and laumontite is allowed to dissolve to equilibrium (see Figure 6). Na^+ is lowered due to montmorillonite precipitation which was not allowed in Model B28. The Ca+Mg/Na ratio is correspondingly higher than for Model B28, as is also the case in Models B9 and B20.

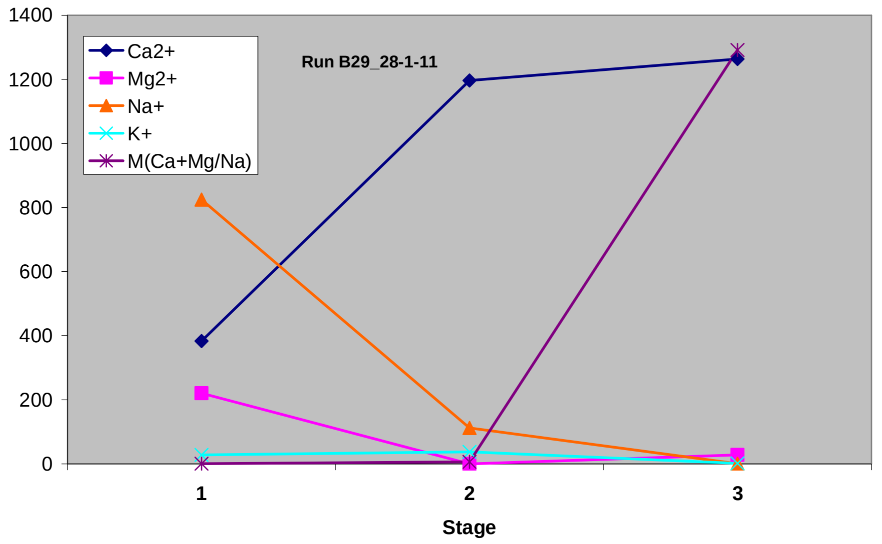

Figure 6. *Cation concentrations (mg/L) and Ca+Mg/Na ratio (molar) from Stages 1, 2 and 3 in Model B29. Stages 1, 2 and 3 are successive model simulations with different mineral assemblages, representing a hypothetical hydrogeochemical evolution along a flowpath of increasing depth from infiltration. Input water composition to Stage 1 is melt water from an Antarctic ice stream, output water composition from Stage 1 forms the input to Stage 2, output water composition from Stage 2 forms the input to Stage 3. In Model B29, Stage 1 is reversible equilibration with calcite, chalcedony and kaolinite; Stage 2 adds reversible equilibration with montmorillonite and dissolution-only equilibration with laumontite; Stage 3 adds reversible equilibration with illite and chlorite.*

A single model run (Model B31; Appendix D.5) has been carried out using a brackish groundwater from repository depth range (KFM02A/423) as the starting water composition. In Stage 2 of the model, the water is equilibrated with montmorillonite, illite and chlorite, then with illite and chlorite plus dissolving laumontite and saponite in Stage 3. As has been shown in the other model runs, Na^+ is lowered whilst Ca^{2+} is increased and Mg^{2+} is increased in Stage 2 but lowered in Stage 3. Overall, the Ca+Mg/Na ratio increases due to these reactions, from <1 to >100.

9 Summary and Conclusions

The following points summarise the modelling carried out and its results:

- The purpose of this study has been to simulate the hydrochemical evolution of dilute waters infiltrating into bedrock at Forsmark, with focus on the alkali and alkaline earth cation compositions which are of interest for the long-term development of the bentonite buffer in the Engineered Barrier System of the proposed deep geological repository.

- A geochemical model of batch reactions between dilute water and rock minerals has been constructed. Two approaches to simulating these hydrogeochemical reactions have been tried. Both approaches were implemented using the PHREEQC program for geochemical speciation, equilibrium and mass transfer. The first approach has been to simulate the dissolution reactions of various aluminosilicate minerals in terms of the rates of each reaction. The overall potential for continued dissolution is governed by the calculated state of thermodynamic equilibrium for each mineral phase, but the progress of dissolution is calculated using empirical kinetics expressions. The second approach has been to assume that local equilibria are achieved rapidly between water and reactive minerals so that hydrochemical evolution is governed by a sequence of equilibria with different assemblages of minerals. In this modelling, sequential equilibria with various permutations of mineral assemblages have been simulated to study how the resulting groundwater compositions, specifically the pH and the $[Ca^{2+}+Mg^{2+}]/[Na^{+}]$ ratio, depend on the selected mineral assemblages.

- Thermodynamic parameters used for the water-mineral and cation exchange equilibria have been derived from the standard phreeqc.dat (for equilibria in the reaction kinetics model) and llnl.dat (for the local equilibrium model) databases that are included with the PHREEQC package. Kinetic expressions for dissolution of minerals have been derived from various sources, some of which have also been used by SKB, though additional simplifications and assumptions are implicit in their use, for example that the plagioclase and feldspar framework silicate minerals that are sources of Na^{+}, K^{+} and Ca^{2+} all react at the same rate independent of pH. Cation exchange selectivity coefficients are those used by SKB in their modelling; they were estimated on the basis of analyses of sorbed cations in a rock sample from Forsmark and of a co-existing groundwater sample.

- Initial dilute water composition in the reaction kinetics model has been either from a water sample from a soil pipe at 2.7 m depth or a putative ‘typical’ composition of mineral-equilibrated glacial melt water that SKB have used in their modelling. Details of the initial water composition are found to have no significant effect on the outcome of the model. Initial water compositions in the local equilibrium model have been one of several varying compositions of glacial melt waters (including the dilute non-equilibrated glacier water that SKB has used in modelling) that range from very dilute to moderately mineralised. A fairly dilute shallow groundwater from Forsmark has also been used as alternative initial water.

- The equilibrating secondary minerals that are specified for both modelling approaches are calcite, chalcedony, kaolinite, illite and chlorite, plus montmorillonite in the local equilibrium model. The minerals selected for kinetic dissolution reactions in the first modelling approach are albite, anorthite, K-feldspar and biotite. The minerals selected for dissolution-only equilibration in the second modelling approach are laumontite, saponite, prehnite, albite, anorthite and K-feldspar. Model runs were constructed to represent various combinations of these minerals in three stages of local equilibrium.

- For most of the model runs for the reaction kinetics approach, an artificial constraint on evolving pH was applied by fixing P_{CO2} at finite low values, usually 10^{-4} atm. This has been necessary to prevent pH rising to unrealistically high alkaline values, above pH 10. It also has the effect of buffering inorganic C so that calcite precipitation is unconstrained by CO_3^{2-}. This artificial constraint introduces substantial uncertainty into the quantitative validity of modelled evolution of pH and Ca^{2+}, though the qualitative outcome appears to reflect reality in comparable natural systems.

- The general outcomes from the reaction kinetics modelling are:

  - (Ca+Mg)/Na molar ratio exceeds 1 in the longer timescale simulations of model runs with freely-variable P_{CO2} that go to unrealistically high pH;
  - (Ca+Mg)/Na ratios are generally between 0.01 and 0.1 in the model runs in which P_{CO2} and pH are assumed to be buffered to realistic values; in these models $[Ca^{2+}]$ is around 10^{-5} M and $[Mg^{2+}]$ is slightly higher at around 10^{-4} M, whilst $[Na^{+}]$ is between 10^{-3} to 10^{-2} M.
  - Caution is necessary when interpreting any possible significance in these model results; there are many assumptions, simplifications and parameter uncertainties that are implicit and explicit in the model.
  - There is not a straightforward single conceptual model for how pH, P_{CO2} and the relative proportions of the major cations will be determined in this type of water-rock system in the short term and long term geochemical evolution.

- The general outcomes from the local equilibrium modelling are:

  - Equilibration with calcite, chalcedony and kaolinite leads to increases of both the (Ca+Mg)/Na molar ratio and pH for dilute water compositions; (Ca+Mg)/Na ratio is strongly dependent on the initial value and cation exchange parameters but is probably between 1 and 10;
  - $[Ca^{2+}]$ increases proportionately more than $[Na^{+}]$ in very dilute melt water whilst these relative changes are smaller and less significant as mineralisation increases;

  - Equilibration with other low-temperature secondary minerals, montmorillonite, illite, chlorite leads to further increases of (Ca+Mg)/Na ratios for both dilute and more mineralised water compositions; pH rises or falls slightly depending on initial conditions and generally lies in the range 8.5 to 9.5;
  - $[Ca^{2+}]$ rises in most cases to between 10^{-4} and 10^{-3} M, whereas $[Na^{+}]$ falls sharply for the water compositions with high initial $[Na^{+}]$ for montmorillonite reaction only and then more markedly if illite and chlorite are added to the reacting assemblage;
  - $[Mg^{2+}]$ changes are dependent on the mineral compositions used in the model database but they are generally subsidiary to the changes of $[Ca^{2+}]$ and $[Na^{+}]$ so they do not have a dominant effect on (Ca+Mg)/Na ratios;
  - Dissolution-only equilibration with higher temperature secondary minerals and primary matrix minerals, laumontite, saponite, prehnite, albite, anorthite, K-feldspar, causes pH to rise and in many cases the modelled pH rises to unrealistic values >10, similar to the results in the reaction kinetics modelling;
  - In specific model runs where albite and K-feldspar are dissolved and montmorillonite plus illite are equilibrated, modelled (Ca+Mg)/Na are very low, <0.01, due to increases of $[Na^{+}]$ and decreases of $[Ca^{2+}]$ and $[Mg^{2+}]$.

- The conclusions to be drawn from this modelling study, referring to the results of the two different approaches based on reaction kinetics and local equilibrium, are:

  - The realistic and most likely scenarios for hydrogeochemical evolution would result in increases of $[Ca^{2+}]$ relative to $[Na^{+}]$, giving divalent cation concentrations and (Ca+Mg)/Na ratios that would not challenge the safety function indicator criterion, $\Sigma[M^{2+}] \geq 10^{-3}$ M, for groundwater compositions at repository depth in relation to limiting the stability and mobility of bentonite colloids derived from the engineered barrier system ([6] p46; [13] p187).
  - There are specific hydrogeochemical scenarios that in theory could result in groundwater compositions at repository depth that are depleted in Ca^{2+} and Mg^{2+} concentrations.
  - The first such scenario is the infiltration of very dilute melt water, typified by the Norwegian glacier water used in this modelling. In that case, hydrogeochemical evolution by mineral reaction and equilibration alone would not raise $\Sigma[Ca^{2+}+Mg^{2+}]$ above about $5x10^{-4}$ M.
  - The second such scenario would be the reaction of moderately dilute water with plagioclase, feldspar, montmorillonite and illite in the specific way illustrated by modelling that would result in increase of $[Na^{+}]$ and decreases of $[Ca^{2+}]$ and $[Mg^{2+}]$. The latter scenario is also associated with high pH values, >10, that are unrealistic for hydrogeochemical evolution in this type of setting, so appropriate caution is needed about drawing strong conclusions.

10 Comments for Safety Analysis Review

Consideration of the potential implications of groundwater compositions at repository depth in the reference evolution and variant scenarios for EBS performance will be a major element of SKB's safety case for a deep repository at Forsmark. Conceptual and modelling insights regarding the potential variability of groundwater compositions, combined with observational evidence for the actual variability of groundwater compositions, will be necessary to support review of the safety case. This modelling study provides some insights about the hydrogeochemical evolution of dilute infiltration water if it reaches repository depth without having mixed with pre-existing brackish or saline groundwaters. Such an influx of dilute water is perceived to be particularly possible due to melt water infiltration during a future glacial period. The displacement of brackish/saline groundwater in the near field by dilute water might affect EBS performance, specifically in relation to the potential erosion of bentonite buffer and the resulting generation and stability of bentonite colloids.

In that context, the following issues for the review of SKB's safety analysis are suggested by this study:

- The scientific basis and range of uncertainties for the safety function indicator criterion relating to bentonite erosion and colloid stability, i.e. currently $\Sigma[Ca^{2+}+Mg^{2+}] \geq 10^{-3}$ M, should be well established and supported by an appropriate depth of theoretical reasoning and experimental evidence. Additionally, its validity for the relevant ranges of ionic strengths (i.e. salinities) and $[Na^{+}]$ concentrations should be similarly established and supported.

- Hydrogeological scoping modelling should investigate the process of dilute water influx to the system, particularly for the glacial stage of normal long-term evolution. It should present a robust assessment of the possibility of dilute water invading the near field depending on the hydrogeological properties, surface boundary conditions and duration of such an episode.

- The issues, illustrated by this study, of reactions between minerals and dilute water should be further explored to better understand the hydrogeochemical aspects of the glacial meltwater intrusion scenario. The present study indicates potential issues but has not had the scope for a sensitivity analysis and an investigation of uncertainties.

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Appendix A: Example of PHREEQC input file for hydrogeochemical model with reaction kinetics

```
TITLE Reaction path model of SFM0009/2.7 dilute water,
RunA4_1-2-10
SOLUTION 1 SFM0009/2.7
    temp      8
    pH        7.3
    pe        4
    redox     pe
    units     mg/kgw
    density   1
    Na        5
    K         2.7
    Ca        88
    Mg        6
    Cl        6 charge
    S(6)      21
    Alkalinity 279 as HCO3
    Fe(2)     2
    Mn        0.2
    S(-2)     0.01
    Si        8.5
    Al        0.04
    -water    1 # kg
PHASES
Biotite
    KMg3AlSi3O10(OH)2 + 6H+ +4H2O = K+ + 3Mg+2 +
Al(OH)4- + 3H4SiO4
    log_k     0
RATES
    Albite
-start
10 rem M = current moles of albite
20 rem M0 = initial moles of albite
30 rem PARM(1) = A/V, cm^2/L
40 si_ab = SI("Albite")
50 if (M<=0 and si_ab<0) then goto 120
60 t=1
70 if M0>0 then t=M/M0
80 if t=0 then t=1
90 area = PARM(1)*t
100 rate=area*2.4*10^(-15)
110 moles=rate*TIME
120 SAVE moles
-end
    Anorthite
-start
10 rem M = current moles of anorthite
```

```
20 rem M0 = initial moles of anorthite
30 rem PARM(1) = A/V, cm^2/L
40 si_ab = SI("Anorthite")
50 if (M<=0 and si_ab<0) then goto 120
60 t=1
70 if M0>0 then t=M/M0
80 if t=0 then t=1
90 area = PARM(1)*t
100 rate=area*2.4*10^(-15)
110 moles=rate*TIME
120 SAVE moles
-end
    K-feldspar
-start
10 rem M = current moles of K-feldspar
20 rem M0 = initial moles of K-feldspar
30 rem PARM(1) = A/V, cm^2/L
40 si_ab = SI("K-feldspar")
50 if (M<=0 and si_ab<0) then goto 120
60 t=1
70 if M0>0 then t=M/M0
80 if t=0 then t=1
90 area = PARM(1)*t
100 rate=area*2.4*10^(-15)
110 moles=rate*TIME
120 SAVE moles
-end
    Biotite
-start
10 rem M = current moles of Biotite
20 rem M0 = initial moles of Biotite
30 rem PARM(1) = A/V, cm^2/L
40 si_ab = SI("Biotite")
50 if (M<=0 and si_ab<0) then goto 120
60 t=1
70 if M0>0 then t=M/M0
80 if t=0 then t=1
90 area = PARM(1)*t
100 rate=area*((10^(-4.93)*ACT("H+")^(0.57))+(10^(-
10.57)*ACT("H+")^(-0.29)))/36000000
110 moles=rate*TIME
120 SAVE moles
-end
KINETICS 1
Albite
    -formula  NaAlSi3O8  1
    -m        10
    -m0       10
    -parms    500
    -tol      1e-008
Anorthite
    -formula  CaAl2Si2O8  1
    -m        10
    -m0       10
```

```
    -parms    500
    -tol      1e-008
K-feldspar
    -formula  KAlSi3O8  1
    -m        10
    -m0       10
    -parms    500
    -tol      1e-008
Biotite
    -formula  KMg3AlSi3O10(OH)2  1
    -m        10
    -m0       10
    -parms    1200
    -tol      1e-008
-steps       31500000 3150000000 31500000000
315000000000
-step_divide 1
-runge_kutta 3
EQUILIBRIUM_PHASES 1
    Albite    0 0 dissolve_only
    Anorthite 0 0 dissolve_only
    Calcite   0 10
    Chalcedony 0 10
    Chlorite(14A) 0 10 dissolve_only
    CO2(g)    -4 1 dissolve_only
    Illite    0 10
    K-feldspar 0 0 dissolve_only
    Kaolinite 0 10
    Biotite   0 0 dissolve_only
EXCHANGE 1
    CaX2    0.66
    NaX     0.19
    MgX2    0.14
    KX      0.01
SELECTED_OUTPUT
    -file                 C:\Documents and Set-
tings\Adrian\My Docu-
ments\Intellisci\Projects\SSM\Geochem 2009\Dilute water
evolution modelling\Run A4Sim1_1-2-10.sel
    -selected_out         true
    -solution             false
    -distance             false
    -time                 false
    -step                 false
    -totals               Al  Ca  Cl  K  Fe(2)  Mg  Mn
                          Na  S(-2)  Si  C
    -molalities           CaX2  NaX  MgX2  KX
    -equilibrium_phases   Anorthite  Calcite  Chalcedony
Albite
                          Chlorite(14A)  Gibbsite  Kao-
linite  K-feldspar
                          Illite  Pyrite
USER_PUNCH
-headings Ca+2 Mg+2 Na+ K+ (Ca+Mg)/Na CaX2 NaX MgX2 KX
```

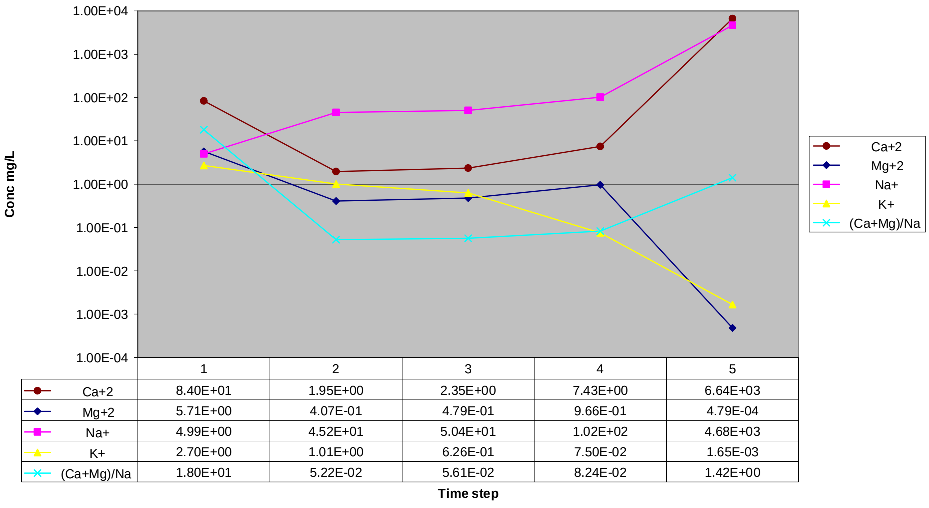
```
-start
10 REM convert to mg/L
20 PUNCH TOT("Ca")*40*1000
30 PUNCH TOT("Mg")*24.3*1000
40 PUNCH TOT("Na")*22.99*1000
50 PUNCH TOT("K")*39.1*1000
60
ratio=((TOT("Ca")*40)+(TOT("Mg")*24.3))/(TOT("Na")*22.99
)
70 PUNCH ratio
80 PUNCH MOL("CaX2")
90 PUNCH MOL("NaX")
100 PUNCH MOL("MgX2")
110 PUNCH MOL("KX")
-end
USER_PRINT
-start
10 REM convert to mg/L
20 PRINT "Ca2+ =   ", TOT("Ca")*40*1000
30 PRINT "Mg2+ =   ", TOT("Mg")*24.3*1000
40 PRINT "Na+ =    ", TOT("Na")*22.99*1000
50 PRINT "K+ =     ", TOT("K")*39.1*1000
60
ratio=((TOT("Ca")*40)+(TOT("Mg")*24.3))/(TOT("Na")*22.99
)
70 PRINT "Ca+Mg/Na = ", ratio
-end
PRINT
    -saturation_indices    false
    -solid_solutions       false
    -species               false
    -surface               false
    -warnings              -1
END
```

Appendix B: Results of model runs with reaction kinetics

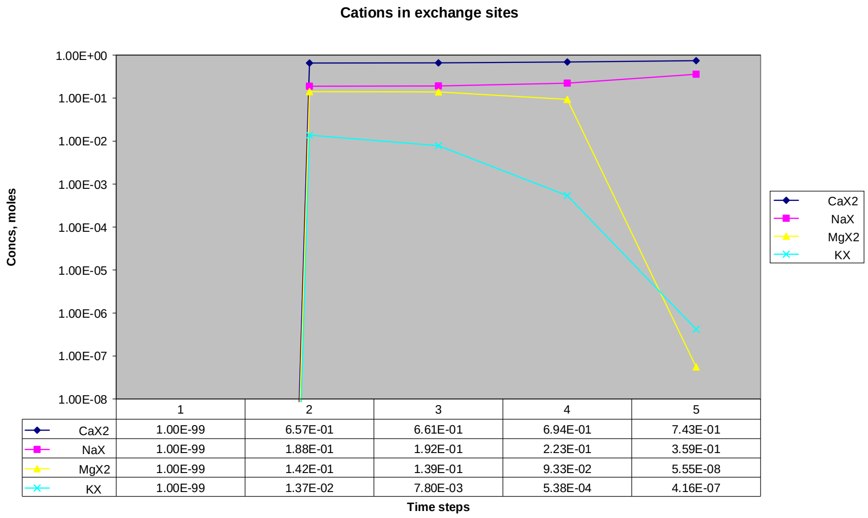
RunA2_29-1-10

Model run no	RunA2_29-1-10				
Starting water	SFM0009/2.7		$P(CO_2)$	variable	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite			
Initial amounts (M/L)	10	10			
Dissolved cations m	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	1.97E-03	2.58E-05	5.58E-05	1.88E-05	3.79E-02
Step 2 (10 y)	2.20E-03	1.60E-05	6.61E-05	2.21E-05	4.02E-02
Step 3 (1000 y)	4.44E-03	1.92E-06	2.01E-04	4.66E-05	5.57E-02
Step 4 (10000 y)	2.16E-01	4.35E-08	3.11E-01	1.09E-07	1.44E+00
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	6.57E-01	1.88E-01	1.42E-01	1.37E-02	10.84
Step 2 (10 y)	6.61E-01	1.92E-01	1.39E-01	7.80E-03	10.94
Step 3 (1000 y)	6.94E-01	2.23E-01	9.33E-02	5.38E-04	11.38
Step 4 (10000 y)	7.43E-01	3.59E-01	5.55E-08	4.16E-07	13.22
Comments: Calcite, chalcedony & illite show net precipitation in longer timescales to maintain equilibrium; K-feldspar shows not dissolution; kaolinite fluctuates between dissolution and precipitation.					

Dissolved cations versus time



	1	2	3	4	5
Ca+2	8.40E+01	1.95E+00	2.35E+00	7.43E+00	6.64E+03
Mg+2	5.71E+00	4.07E-01	4.79E-01	9.66E-01	4.79E-04
Na+	4.99E+00	4.52E+01	5.04E+01	1.02E+02	4.68E+03
K+	2.70E+00	1.01E+00	6.26E-01	7.50E-02	1.65E-03
(Ca+Mg)/Na	1.80E+01	5.22E-02	5.61E-02	8.24E-02	1.42E+00

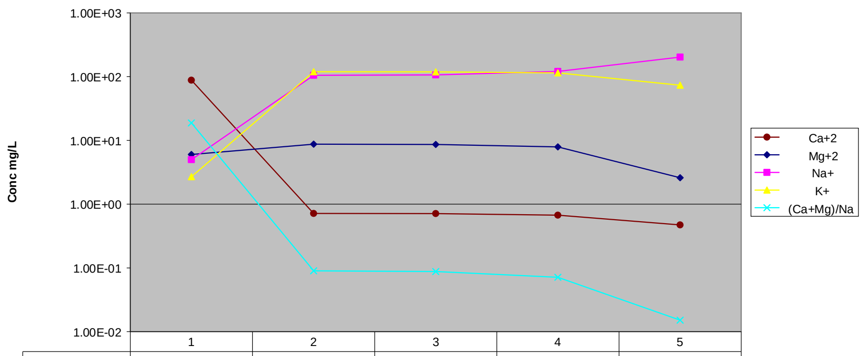


	1	2	3	4	5
CaX2	1.00E-99	6.57E-01	6.61E-01	6.94E-01	7.43E-01
NaX	1.00E-99	1.88E-01	1.92E-01	2.23E-01	3.59E-01
MgX2	1.00E-99	1.42E-01	1.39E-01	9.33E-02	5.55E-08
KX	1.00E-99	1.37E-02	7.80E-03	5.38E-04	4.16E-07

RunA3_1-2-10

Model run no	RunA3_1-2-10				
Starting water	SFM0009/2.7		P(CO_2)	fixed at 1E-04 atm, 1 mole	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar		
Initial amounts (M/L)	10	10	10		
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	4.55E-03	3.06E-03	1.79E-05	3.59E-04	8.27E-02
Step 2 (10 y)	4.63E-03	3.04E-03	1.78E-05	3.55E-04	8.07E-02
Step 3 (1000 y)	5.26E-03	2.93E-03	1.68E-05	3.26E-04	6.52E-02
Step 4 (10000 y)	8.82E-03	1.87E-03	1.18E-05	1.07E-04	1.35E-02
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	3.05E-02	1.91E-01	4.40E-01	7.18E-01	9.46
Step 2 (10 y)	3.04E-02	1.95E-01	4.38E-01	7.18E-01	9.46
Step 3 (1000 y)	2.99E-02	2.29E-01	4.23E-01	7.16E-01	9.48
Step 4 (10000 y)	3.76E-02	5.74E-01	2.67E-01	6.86E-01	9.72
Comments: Constant buffer of CO_2 maintains pH at a lower value, until Step 4 during which the CO_2 budget of 1 mole per litre solution is completely used up and the modelled final pH rises slightly. The amount of CO_2 consumed is equivalent to the amount of calcite precipitated, thus the very low Ca^{2+} concentration despite supply from anorthite is due to high pH and buffering of CO_3^{2-}.					

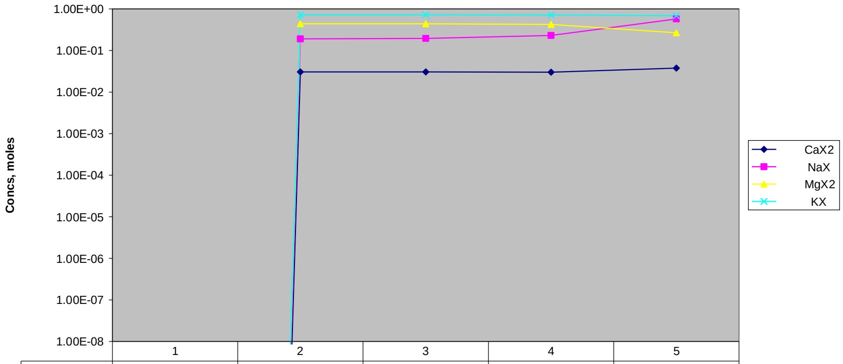
Dissolved cations versus time



	1	2	3	4	5
Ca+2	8.78E+01	7.16E-01	7.12E-01	6.72E-01	4.71E-01
Mg+2	6.00E+00	8.72E+00	8.64E+00	7.93E+00	2.60E+00
Na+	5.00E+00	1.05E+02	1.06E+02	1.21E+02	2.03E+02
K+	2.70E+00	1.20E+02	1.19E+02	1.15E+02	7.33E+01
(Ca+Mg)/Na	1.88E+01	9.01E-02	8.79E-02	7.11E-02	1.52E-02

Time step

Cations in exchange sites



	1	2	3	4	5
CaX2	1.00E-99	3.05E-02	3.04E-02	2.99E-02	3.76E-02
NaX	1.00E-99	1.91E-01	1.95E-01	2.29E-01	5.74E-01
MgX2	1.00E-99	4.40E-01	4.38E-01	4.23E-01	2.67E-01
KX	1.00E-99	7.18E-01	7.18E-01	7.16E-01	6.86E-01

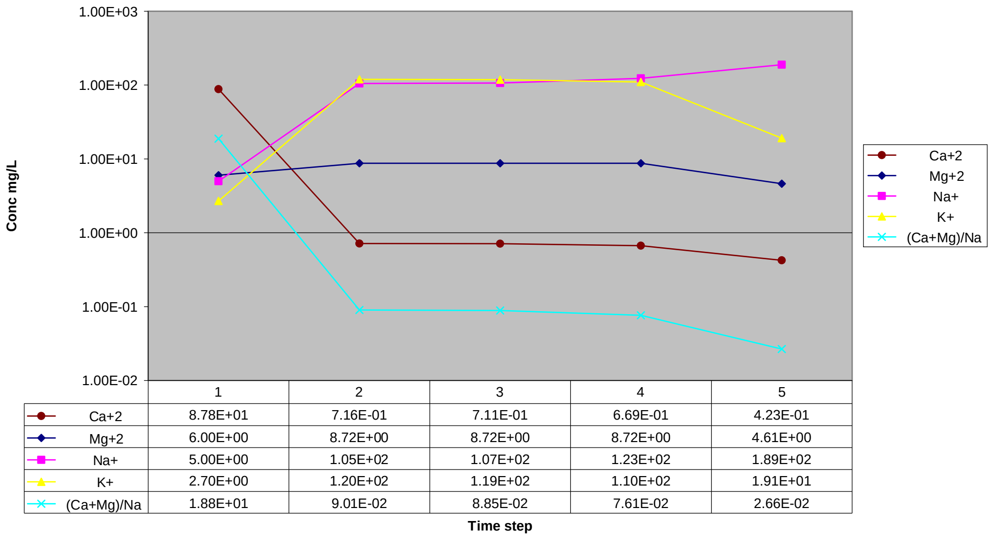
Time steps

RunA4-Sim1_1-2-10

Model run no	RunA4-Sim1_1-2-10				
Starting water	SFM0009/2.7		P(CO_2)	fixed at 1E-04 atm, 1 mole	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar	Biotite	
Initial amounts (M/L)	10	10	10	10	
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	4.56E-03	3.06E-03	1.79E-05	3.59E-04	8.27E-02
Step 2 (10 y)	4.64E-03	3.03E-03	1.78E-05	3.59E-04	8.12E-02
Step 3 (1000 y)	5.37E-03	2.81E-03	1.67E-05	3.59E-04	7.00E-02
Step 4 (10000 y)	8.22E-03	4.88E-04	1.06E-05	1.90E-04	2.44E-02
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	3.05E-02	1.91E-01	4.40E-01	7.18E-01	9.46
Step 2 (10 y)	3.03E-02	1.95E-01	4.41E-01	7.13E-01	9.46
Step 3 (1000 y)	2.85E-02	2.29E-01	4.46E-01	6.71E-01	9.48
Step 4 (10000 y)	3.46E-02	5.60E-01	5.03E-01	1.87E-01	9.98

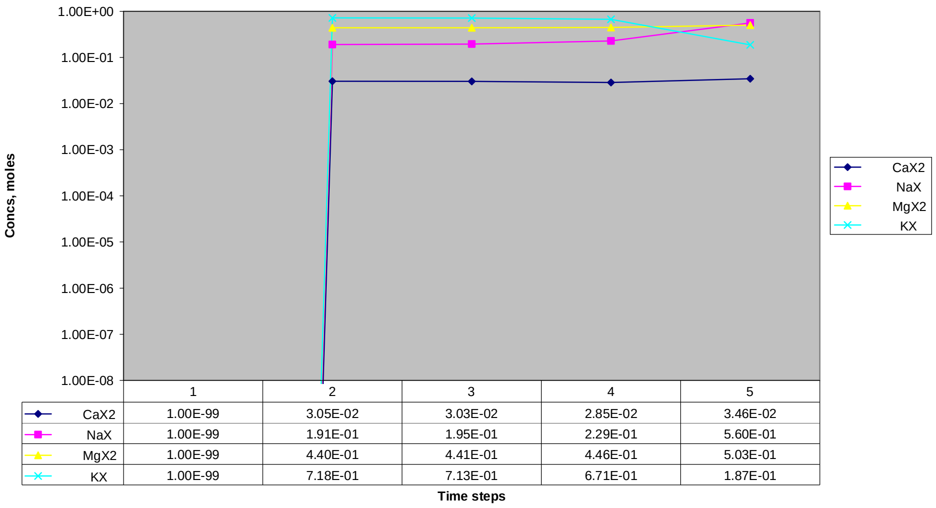
Comments: Biotite dissolution is a source of Mg^{2+} and K^+ additional to K^+ from K-feldspar. However biotite makes no difference to general outcome of model.

Dissolved cations versus time



	1	2	3	4	5
Ca+2	8.78E+01	7.16E-01	7.11E-01	6.69E-01	4.23E-01
Mg+2	6.00E+00	8.72E+00	8.72E+00	8.72E+00	4.61E+00
Na+	5.00E+00	1.05E+02	1.07E+02	1.23E+02	1.89E+02
K+	2.70E+00	1.20E+02	1.19E+02	1.10E+02	1.91E+01
(Ca+Mg)/Na	1.88E+01	9.01E-02	8.85E-02	7.61E-02	2.66E-02

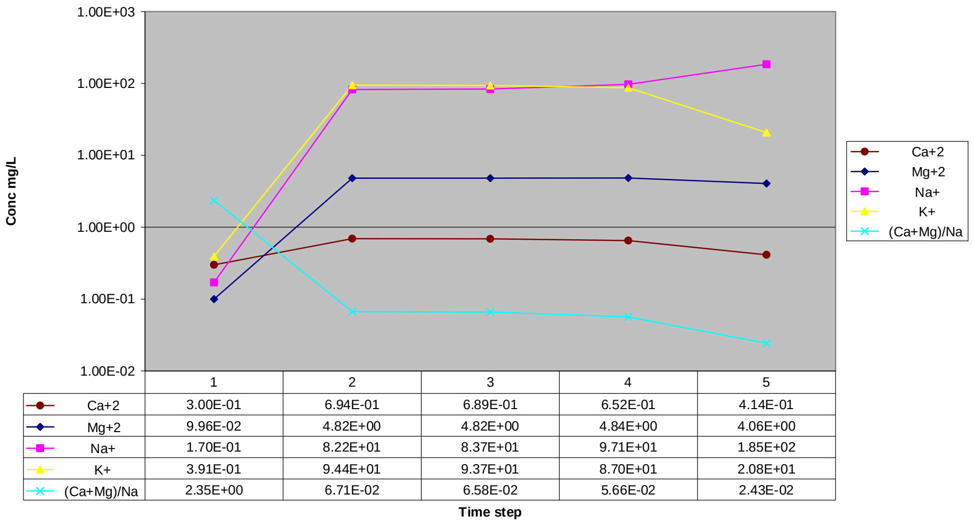
Cations in exchange sites



	1	2	3	4	5
CaX2	1.00E-99	3.05E-02	3.03E-02	2.85E-02	3.46E-02
NaX	1.00E-99	1.91E-01	1.95E-01	2.29E-01	5.60E-01
MgX2	1.00E-99	4.40E-01	4.41E-01	4.46E-01	5.03E-01
KX	1.00E-99	7.18E-01	7.13E-01	6.71E-01	1.87E-01

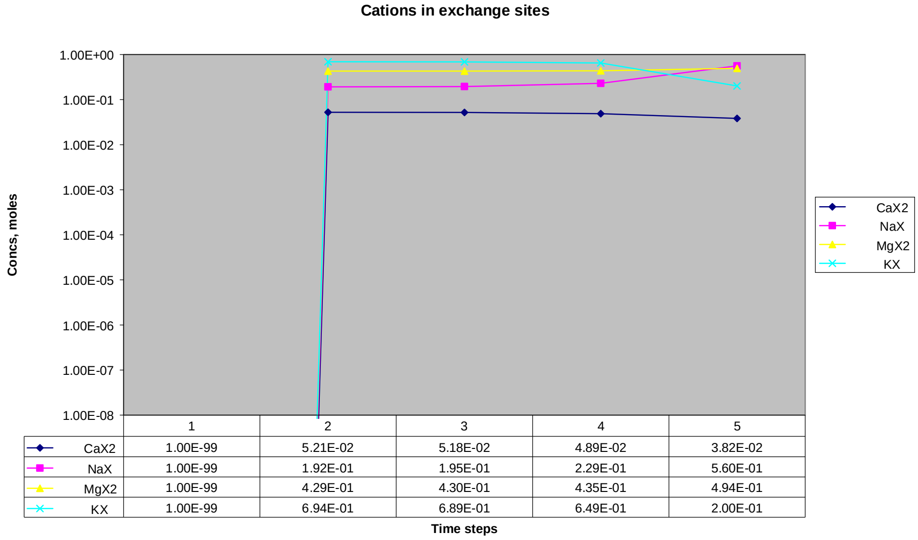
RunA4-Sim2_2-2-10

Model run no	RunA4-Sim2_2-2-10				
Starting water	SFM0009/2.7		P(CO_2)	fixed at 1E-02 atm, 1 mole	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar	Biotite	
Initial amounts (M/L)	10	10	10	10	
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	3.58E-03	2.42E-03	1.73E-05	1.98E-04	6.03E-02
Step 2 (10 y)	3.64E-03	2.40E-03	1.72E-05	1.98E-04	5.92E-02
Step 3 (1000 y)	4.22E-03	2.23E-03	1.63E-05	1.99E-04	5.10E-02
Step 4 (10000 y)	8.03E-03	5.31E-04	1.03E-05	1.67E-04	2.21E-02
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	5.21E-02	1.92E-01	4.29E-01	6.94E-01	9.42
Step 2 (10 y)	5.18E-02	1.95E-01	4.30E-01	6.89E-01	9.42
Step 3 (1000 y)	4.89E-02	2.29E-01	4.35E-01	6.49E-01	9.44
Step 4 (10000 y)	3.82E-02	5.60E-01	4.94E-01	2.00E-01	9.83
Comments: P_{CO2} is fixed at the higher value of 10^{-2} atm but is totally depleted during Step 4.					



Dissolved cations versus time

	1	2	3	4	5
● Ca+2	3.00E-01	6.94E-01	6.89E-01	6.52E-01	4.14E-01
◆ Mg+2	9.96E-02	4.82E+00	4.82E+00	4.84E+00	4.06E+00
■ Na+	1.70E-01	8.22E+01	8.37E+01	9.71E+01	1.85E+02
▲ K+	3.91E-01	9.44E+01	9.37E+01	8.70E+01	2.08E+01
✕ (Ca+Mg)/Na	2.35E+00	6.71E-02	6.58E-02	5.66E-02	2.43E-02

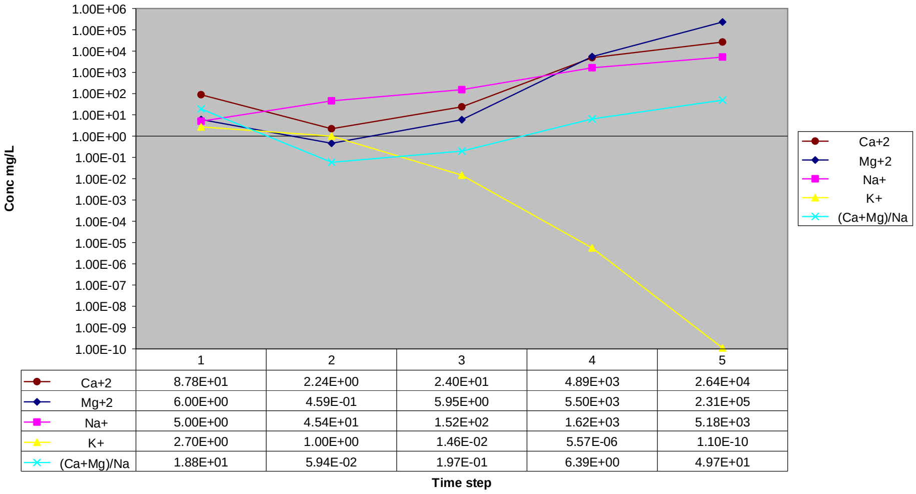


	1	2	3	4	5
CaX2	1.00E-99	5.21E-02	5.18E-02	4.89E-02	3.82E-02
NaX	1.00E-99	1.92E-01	1.95E-01	2.29E-01	5.60E-01
MgX2	1.00E-99	4.29E-01	4.30E-01	4.35E-01	4.94E-01
KX	1.00E-99	6.94E-01	6.89E-01	6.49E-01	2.00E-01

RunA4-Sim3_2-2-10

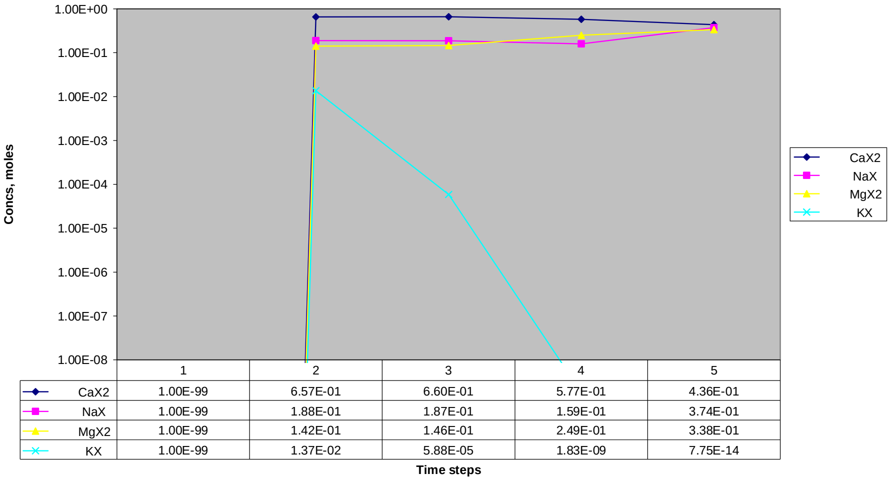
Model run no	RunA4-Sim3_2-2-10				
Starting water	SFM0009/2.7		$P(CO_2)$	variable	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar	Biotite	
Initial amounts (M/L)	10	10	10	10	
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	1.97E-03	2.57E-05	5.59E-05	1.89E-05	3.79E-02
Step 2 (10 y)	6.61E-03	3.72E-07	6.00E-04	2.45E-04	1.28E-01
Step 3 (1000 y)	7.07E-02	1.43E-10	1.22E-01	2.26E-01	4.93E+00
Step 4 (10000 y)	2.25E-01	2.80E-15	6.61E-01	9.52E+00	4.52E+01
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	6.57E-01	1.88E-01	1.42E-01	1.37E-02	10.84
Step 2 (10 y)	6.60E-01	1.87E-01	1.46E-01	5.88E-05	11.63
Step 3 (1000 y)	5.77E-01	1.59E-01	2.49E-01	1.83E-09	13.12
Step 4 (10000 y)	4.36E-01	3.74E-01	3.38E-01	7.75E-14	15.42
Comments: P_{CO2} is not buffered and therefore decreases as pH rises. Illite precipitates in Steps 2, 3 and 4 which accounts for the very low K^+ concentrations.					

Dissolved cations versus time



	1	2	3	4	5
Ca+2	8.78E+01	2.24E+00	2.40E+01	4.89E+03	2.64E+04
Mg+2	6.00E+00	4.59E-01	5.95E+00	5.50E+03	2.31E+05
Na+	5.00E+00	4.54E+01	1.52E+02	1.62E+03	5.18E+03
K+	2.70E+00	1.00E+00	1.46E-02	5.57E-06	1.10E-10
(Ca+Mg)/Na	1.88E+01	5.94E-02	1.97E-01	6.39E+00	4.97E+01

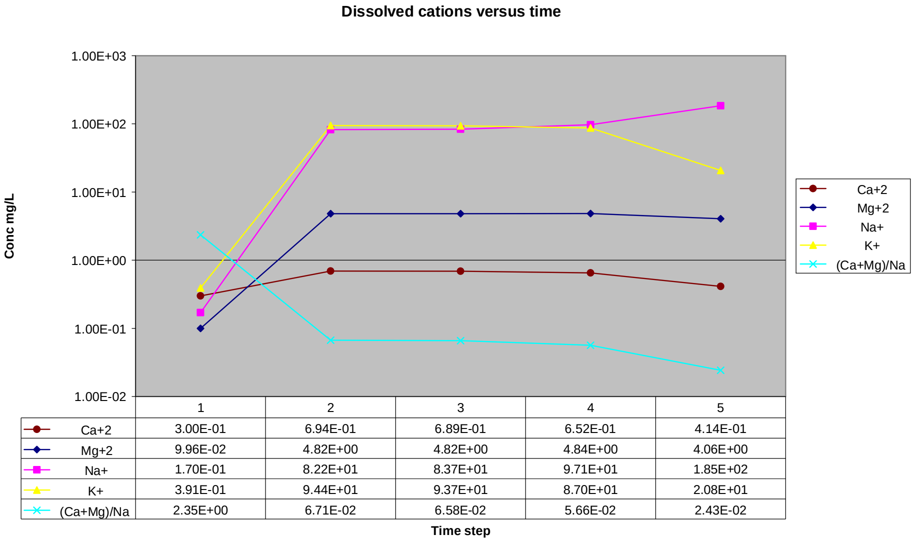
Cations in exchange sites



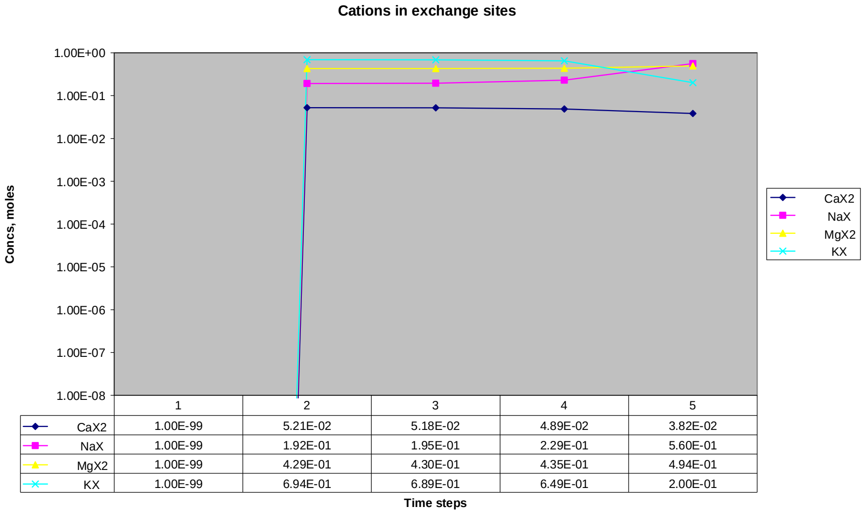
	1	2	3	4	5
CaX2	1.00E-99	6.57E-01	6.60E-01	5.77E-01	4.36E-01
NaX	1.00E-99	1.88E-01	1.87E-01	1.59E-01	3.74E-01
MgX2	1.00E-99	1.42E-01	1.46E-01	2.49E-01	3.38E-01
KX	1.00E-99	1.37E-02	5.88E-05	1.83E-09	7.75E-14

RunA5_2-2-10

Model run no	RunA5_2-2-10				
Starting water	Equilibrated glacial melt water		P(CO_2)	fixed at 1E-04 atm, 1 mole	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar	Biotite	
Initial amounts (M/L)	10	10	10	10	
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	3.58E-03	2.42E-03	1.73E-05	1.98E-04	6.03E-02
Step 2 (10 y)	3.64E-03	2.40E-03	1.72E-05	1.98E-04	5.92E-02
Step 3 (1000 y)	4.22E-03	2.23E-03	1.63E-05	1.99E-04	5.10E-02
Step 4 (10000 y)	8.03E-03	5.31E-04	1.03E-05	1.67E-04	2.21E-02
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	5.21E-02	1.92E-01	4.29E-01	6.94E-01	9.42
Step 2 (10 y)	5.18E-02	1.95E-01	4.30E-01	6.89E-01	9.42
Step 3 (1000 y)	4.89E-02	2.29E-01	4.35E-01	6.49E-01	9.44
Step 4 (10000 y)	3.82E-02	5.60E-01	4.94E-01	2.00E-01	9.83
Comments: This model run uses ‘equilibrated glacial melt water’ which is more dilute than SFM0009/2.7 and has a higher initial pH. The different initial composition makes little difference to the outcome of the model. CO_2 buffering controls pH and Ca^{2+}.					

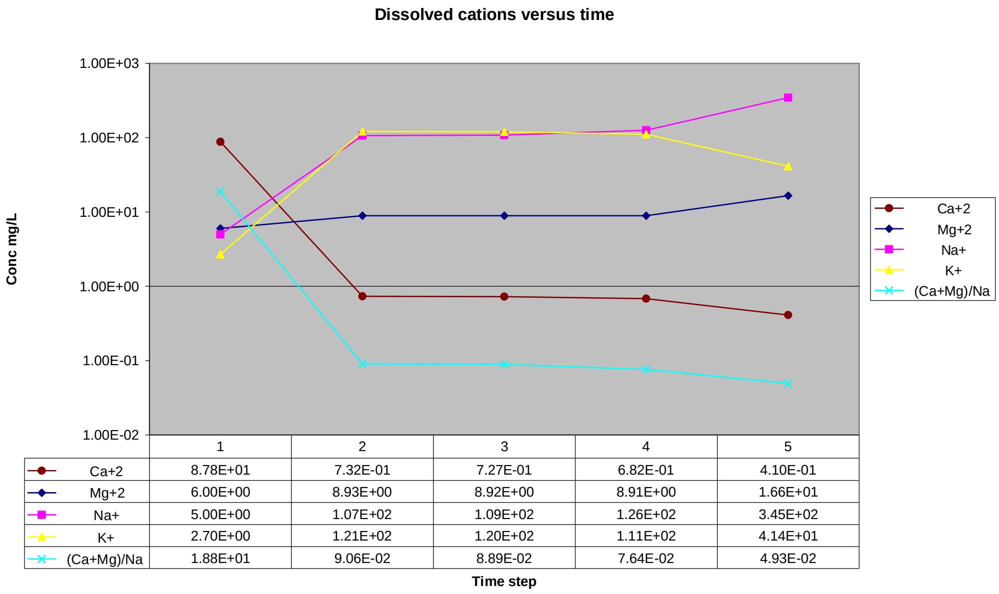


	1	2	3	4	5
Ca+2	3.00E-01	6.94E-01	6.89E-01	6.52E-01	4.14E-01
Mg+2	9.96E-02	4.82E+00	4.82E+00	4.84E+00	4.06E+00
Na+	1.70E-01	8.22E+01	8.37E+01	9.71E+01	1.85E+02
K+	3.91E-01	9.44E+01	9.37E+01	8.70E+01	2.08E+01
(Ca+Mg)/Na	2.35E+00	6.71E-02	6.58E-02	5.66E-02	2.43E-02

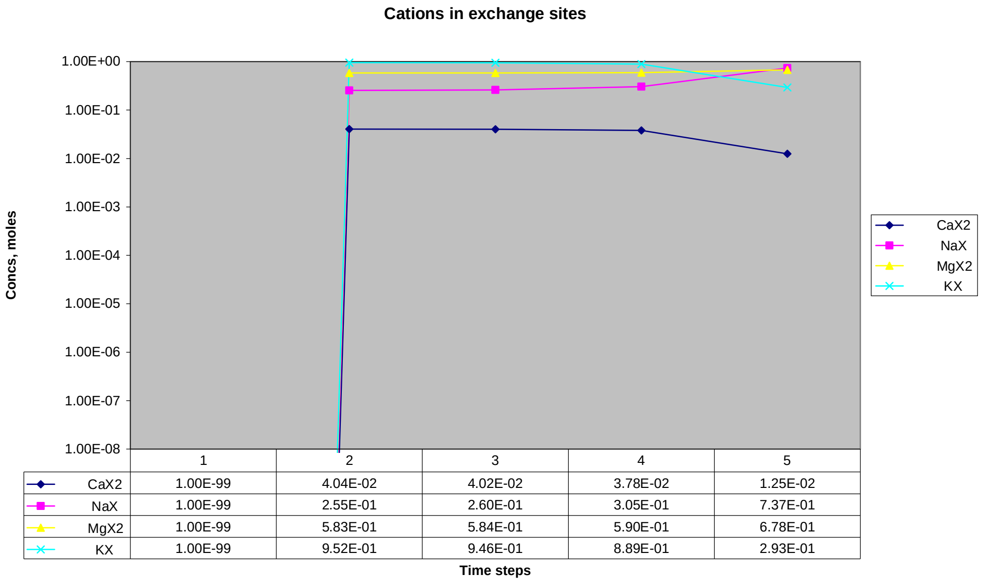


RunA6_2-2-10

Model run no	RunA6_2-2-10				
Starting water	Equilibrated glacial melt water		$P(CO_2)$	fixed at 1E-04 atm, 10 moles	
Equilibrium phase	Calcite	Chalcedony	Chlorite	Illite	Kaolinite
Initial amounts (M/L)	10	10	10 (diss only)	10	10
Kinetic phases (dissolving only)	Albite	Anorthite	K-feldspar	Biotite	
Initial amounts (M/L)	10	10	10	10	
Dissolved cations Moles per litre	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca+Mg/Na
Step 1 (1 y)	4.64E-03	3.10E-03	1.83E-05	3.67E-04	8.31E-02
Step 2 (10 y)	4.72E-03	3.07E-03	1.82E-05	3.67E-04	8.16E-02
Step 3 (1000 y)	5.46E-03	2.84E-03	1.71E-05	3.67E-04	7.02E-02
Step 4 (10000 y)	1.50E-02	1.06E-03	1.02E-05	6.84E-04	4.62E-02
Exchange cations M	CaX_2	NaX	MgX_2	KX	pH
Step 1 (1 y)	4.04E-02	2.55E-01	5.83E-01	9.52E-01	9.46
Step 2 (10 y)	4.02E-02	2.60E-01	5.84E-01	9.46E-01	9.46
Step 3 (1000 y)	3.78E-02	3.05E-01	5.90E-01	8.89E-01	9.48
Step 4 (10000 y)	1.25E-02	7.37E-01	6.78E-01	2.93E-01	9.70
Comments: Ca-montmorillonite added to Equilibrium Phases, but it undergoes no reaction.					


Dissolved cations versus time

	1	2	3	4	5
Ca+2	8.78E+01	7.32E-01	7.27E-01	6.82E-01	4.10E-01
Mg+2	6.00E+00	8.93E+00	8.92E+00	8.91E+00	1.66E+01
Na+	5.00E+00	1.07E+02	1.09E+02	1.26E+02	3.45E+02
K+	2.70E+00	1.21E+02	1.20E+02	1.11E+02	4.14E+01
(Ca+Mg)/Na	1.88E+01	9.06E-02	8.89E-02	7.64E-02	4.93E-02


Cations in exchange sites

	1	2	3	4	5
CaX2	1.00E-99	4.04E-02	4.02E-02	3.78E-02	1.25E-02
NaX	1.00E-99	2.55E-01	2.60E-01	3.05E-01	7.37E-01
MgX2	1.00E-99	5.83E-01	5.84E-01	5.90E-01	6.78E-01
KX	1.00E-99	9.52E-01	9.46E-01	8.89E-01	2.93E-01

Appendix C: Example of PHREEQC input file for hydrogeochemical model with local equilibrium

```
TITLE Equilibrate JEG glacial melt water with calcite,
chalcedony, kaolinite, RunB26Sim1_28-1-11
SOLUTION 1 JEG glacial melt water
    temp      5
    pH        8.3
    pe        4
    redox     pe
    units     mmol/kgw
    density   1
    Na        0.3
    K         0.04
    Ca        1.3
    Mg        0.3
    Cl(-1)    0.1
    S(6)      1.5 charge
    C(4)      0.4
    -water    1 # kg
EQUILIBRIUM_PHASES 1
    Calcite   0 10
    Chalcedony 0 10
    Kaolinite 0 10
EXCHANGE 1
    X       1
    -equilibrate with solution 1
PRINT
    -saturation_indices    true
    -solid_solutions       false
    -species               false
    -surface               false
    -warnings              -1
USER_PRINT
-start
10 REM convert to mg/L
20 PRINT "Ca2+ =   ", TOT("Ca")*40*1000
30 PRINT "Mg2+ =   ", TOT("Mg")*24.3*1000
40 PRINT "Na+ =    ", TOT("Na")*22.99*1000
50 PRINT "K+ =     ", TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PRINT "M(Ca+Mg/Na) = ", ratio
-end
SELECTED_OUTPUT
    -file                 C:\Documents and Set-
tings\Adrian\My Docu-
ments\Intellisci\Projects\SSM\Geochem 2010\Dilute water
evolution Stage 2\Run B26Sim1_28-1-11.sel
    -selected_out         true
```

```
    -solution             false
    -distance             false
    -time                 false
    -step                 false
    -totals               Na  K  Ca  Mg  Cl  S(6)  C
                          Al  Fe  Si
    -equilibrium_phases   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
    -saturation_indices   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
USER_PUNCH
-headings Ca+2mg/L Mg+2 Na+ K+ M(Ca+Mg)/Na
-start
10 REM convert to mg/L
20 PUNCH TOT("Ca")*40*1000
30 PUNCH TOT("Mg")*24.3*1000
40 PUNCH TOT("Na")*22.99*1000
50 PUNCH TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PUNCH ratio
-end
SAVE solution 1
SAVE exchange 1
END
TITLE Equilibrate JEG glacial melt water with calcite,
chalcedony, kaolinite, mont, chlorite RunB26Sim2_28-1-11
USE solution 1
EQUILIBRIUM_PHASES 2
    Calcite   0 10
    Chalcedony 0 10
    Clinochlore-14A 0 10
    Kaolinite 0 10
    Montmor-Na 0 10
USE exchange 1
PRINT
    -exchange              true
    -saturation_indices    true
    -solid_solutions       false
    -species               false
    -surface               false
    -warnings              -1
USER_PRINT
-start
10 REM convert to mg/L
20 PRINT "Ca2+ =   ", TOT("Ca")*40*1000
30 PRINT "Mg2+ =   ", TOT("Mg")*24.3*1000
```

```
40 PRINT "Na+ =    ", TOT("Na")*22.99*1000
50 PRINT "K+ =     ", TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PRINT "M(Ca+Mg/Na) = ", ratio
-end
SELECTED_OUTPUT
    -file                 C:\Documents and Set-
tings\Adrian\My Docu-
ments\Intellisci\Projects\SSM\Geochem 2010\Dilute water
evolution Stage 2\Run B26Sim2_28-1-11.sel
    -selected_out         true
    -solution             false
    -distance             false
    -time                 false
    -step                 false
    -totals               Na  K  Ca  Mg  Cl  S(6)  C
                          Al  Fe  Si
    -equilibrium_phases   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
    -saturation_indices   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
USER_PUNCH
-headings Ca+2mg/L Mg+2 Na+ K+ M(Ca+Mg)/Na
-start
10 REM convert to mg/L
20 PUNCH TOT("Ca")*40*1000
30 PUNCH TOT("Mg")*24.3*1000
40 PUNCH TOT("Na")*22.99*1000
50 PUNCH TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PUNCH ratio
-end
SAVE solution 1
SAVE exchange 1
END
TITLE Equilibrate JEG glacial melt water with calcite,
chalcedony, kaolinite, mont, chlorite, laum
RunB26Sim3_28-1-11
EQUILIBRIUM_PHASES 3
    Calcite   0 10
    Chalcedony 0 10
    Clinochlore-14A 0 10
    Illite    0 10
    Kaolinite 0 10
    Laumontite 0 10 dissolve_only
    Montmor-Na 0 10
```

```
USE exchange 1
USE solution 1
PRINT
    -exchange              true
    -saturation_indices    true
    -solid_solutions       false
    -species               true
    -surface               false
    -warnings              -1
USER_PRINT
-start
10 REM convert to mg/L
20 PRINT "Ca2+ =   ", TOT("Ca")*40*1000
30 PRINT "Mg2+ =   ", TOT("Mg")*24.3*1000
40 PRINT "Na+ =    ", TOT("Na")*22.99*1000
50 PRINT "K+ =     ", TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PRINT "M(Ca+Mg/Na) = ", ratio
-end
SELECTED_OUTPUT
    -file                 C:\Documents and Set-
tings\Adrian\My Docu-
ments\Intellisci\Projects\SSM\Geochem 2010\Dilute water
evolution Stage 2\Run B26Sim3_28-1-11.sel
    -selected_out         true
    -solution             false
    -distance             false
    -time                 false
    -step                 false
    -totals               Na  K  Ca  Mg  Cl  S(6)  C
                          Al  Fe  Si
    -equilibrium_phases   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
    -saturation_indices   Calcite  Chalcedony  Kaolinite
Montmor-Na
                          Illite  Clinochlore-14A  Al-
bite  K-Feldspar
                          Anorthite  Laumontite
Prehnite  Saponite-Na
USER_PUNCH
-headings Ca+2mg/L Mg+2 Na+ K+ M(Ca+Mg)/Na
-start
10 REM convert to mg/L
20 PUNCH TOT("Ca")*40*1000
30 PUNCH TOT("Mg")*24.3*1000
40 PUNCH TOT("Na")*22.99*1000
50 PUNCH TOT("K")*39.1*1000
60 ratio=((TOT("Ca"))+(TOT("Mg")))/(TOT("Na"))
70 PUNCH ratio
-end
```

```
SAVE solution 1
SAVE exchange 1
END
```

Appendix D: Results of model runs with local equilibrium

D.1 Initial water: 'Juvenile' Norwegian glacial melt water

The composition of the initial water is given below.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
Norwegian glacial melt water	5.8	0.17	0.4	0.18	0.1	0.5	0.5	0.12

Summary tables of model runs carried out using the 'juvenile' Norwegian melt water (as used in SKB's modelling) are given below. The top half of each summary table indicates the reacting mineral assemblage at each stage of the model equilibrium calculations (R indicates the minerals that are allowed to dissolve and precipitate, D indicates the minerals that are allowed to dissolve only). The lower half of each table shows the results of modelling of water compositions: pH, Na^+. K^+, Ca^{2+} and Mg^{2+} concentrations in mg/L, and $[Ca^{2+} + Mg^{2+}]/[Na^+]$ ratio of molar concentrations.

Model run no: B5												
Starting water: Norwegian glacier melt water												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R*	R	R									
Stage 2	R	R	R	R	R							
Stage 3	R	R	R	R	R		D					
	Modelled water compositions[2]											
	pH		Na^+ mg/L		K^+ mg/L		Ca^{2+} mg/L		Mg^{2+} mg/L		$\frac{[Ca+Mg]}{[Na]}$ (M)	
Stage 1	9.89		0.46		1.09		1.37		0.76		3.25	
Stage 2	8.63		1.70		2.93		13.2		7.26		8.50	
Stage 3	9.76		0.002		0.04		4.73		2.42		2620	
Comments: *Sat index (calcite) fixed at -1 in Stage 1												

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B6</td></tr>
<tr><td colspan="13">Starting water: Norwegian glacier melt water</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R*</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td>D</td><td></td><td>D</td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">9.89</td><td colspan="2">0.46</td><td colspan="2">1.09</td><td colspan="2">1.37</td><td colspan="2">0.76</td><td colspan="2">3.25</td></tr>
<tr><td>Stage 2</td><td colspan="2">8.63</td><td colspan="2">1.70</td><td colspan="2">2.93</td><td colspan="2">13.2</td><td colspan="2">7.26</td><td colspan="2">8.50</td></tr>
<tr><td>Stage 3</td><td colspan="2">11.54</td><td colspan="2">67.0</td><td colspan="2">0.045</td><td colspan="2">0.54</td><td colspan="2">3.9e-4</td><td colspan="2">4.6e-3</td></tr>
<tr><td colspan="13">Comments: *Sat index (calcite) fixed at -1 in Stage 1</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B7</td></tr>
<tr><td colspan="13">Starting water: Norwegian glacier melt water</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R*</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td>R</td><td>R</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td>R</td><td>R</td><td></td><td>D</td><td></td><td>D</td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">9.89</td><td colspan="2">0.46</td><td colspan="2">1.09</td><td colspan="2">1.37</td><td colspan="2">0.76</td><td colspan="2">3.25</td></tr>
<tr><td>Stage 2</td><td colspan="2">9.77</td><td colspan="2">1.4e-21</td><td colspan="2">1.89</td><td colspan="2">4.46</td><td colspan="2">2.19</td><td colspan="2">3.3e21</td></tr>
<tr><td>Stage 3</td><td colspan="2">10.18</td><td colspan="2">32.6</td><td colspan="2">0.022</td><td colspan="2">0.94</td><td colspan="2">1.3e-3</td><td colspan="2">0.017</td></tr>
<tr><td colspan="13">Comments: *Sat index (calcite) fixed at -1 in Stage 1</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B7a

Starting water: Norwegian glacier melt water

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R*	R	R									
Stage 2	R	R	R				D	D				
Stage 3	R	R	R				D	D		D		D

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	9.89	0.46	1.09	1.37	0.76	3.25
Stage 2	10.24	0.71	1.69	3.48	1.87	5.30
Stage 3	11.28	2.66	3.13	11.7	6.28	4.76

Comments: *Sat index (calcite) fixed at -1 in Stage 1. Note: Laumontite & saponite – dissolution only.

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B8

Starting water: Norwegian glacier melt water

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R					R				
Stage 3	R	R	R				D	R				

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	10.27	0.70	1.67	3.40	1.83	5.24
Stage 2	8.39	1.46	3.87	17.7	9.69	13.2
Stage 3	9.78	1.4e-21	1.88	4.39	2.16	3.3e21

Comments: Saponite allowed to dissolve & precipitate; laumontite – dissolution only allowed

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition.

Model run no: B8a												
Starting water: Norwegian glacier melt water												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R					D				
Stage 3	R	R	R				D	D				
	Modelled water compositions[2]											
	pH		Na^+ mg/L		K^+ mg/L		Ca^{2+} mg/L		Mg^{2+} mg/L		$\frac{[Ca+Mg]}{[Na]}$ (M)	
Stage 1	10.27		0.70		1.67		3.40		1.83		5.24	
Stage 2	10.27		0.70		1.67		3.40		1.83		5.24	
Stage 3	10.27		0.70		1.67		3.40		1.83		5.24	
Comments: Saponite & laumontite – dissolution only												

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B9												
Starting water: Norwegian glacier melt water												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R								
Stage 3	R	R	R	R	R	R						
	Modelled water compositions[2]											
	pH		Na^+ mg/L		K^+ mg/L		Ca^{2+} mg/L		Mg^{2+} mg/L		$\frac{[Ca+Mg]}{[Na]}$ (M)	
Stage 1	10.27		0.70		1.67		3.40		1.83		5.24	
Stage 2	8.74		0.90		3.16		11.7		6.43		14.3	
Stage 3	8.89		0.35		1.06		10.1		5.66		32.2	
Comments:												

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B10</td></tr>
<tr><td colspan="13">Starting water: Norwegian glacier melt water</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td>D</td><td>D</td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">10.27</td><td colspan="2">0.70</td><td colspan="2">1.67</td><td colspan="2">3.40</td><td colspan="2">1.83</td><td colspan="2">5.24</td></tr>
<tr><td>Stage 2</td><td colspan="2">9.78</td><td colspan="2">1.7e-3</td><td colspan="2">1.89</td><td colspan="2">4.29</td><td colspan="2">2.30</td><td colspan="2">2.7e3</td></tr>
<tr><td>Stage 3</td><td colspan="2">12.06</td><td colspan="2">0.72</td><td colspan="2">17.7</td><td colspan="2">581</td><td colspan="2">3.3e3</td><td colspan="2">4.7e3</td></tr>
<tr><td colspan="13">Comments:</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B11</td></tr>
<tr><td colspan="13">Starting water: Norwegian glacier melt water</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td></td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">10.27</td><td colspan="2">0.70</td><td colspan="2">1.67</td><td colspan="2">3.40</td><td colspan="2">1.83</td><td colspan="2">5.24</td></tr>
<tr><td>Stage 2</td><td colspan="2">9.78</td><td colspan="2">1.7e-3</td><td colspan="2">1.89</td><td colspan="2">4.29</td><td colspan="2">2.30</td><td colspan="2">2.7e3</td></tr>
<tr><td>Stage 3</td><td colspan="2">8.89</td><td colspan="2">2.7e-3</td><td colspan="2">1.06</td><td colspan="2">10.2</td><td colspan="2">5.63</td><td colspan="2">4.2e3</td></tr>
<tr><td colspan="13">Comments:</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B12</td></tr>
<tr><td colspan="13">Starting water: Norwegian glacier melt water</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+
mg/L</td><td colspan="2">K^+
mg/L</td><td colspan="2">Ca^{2+}
mg/L</td><td colspan="2">Mg^{2+}
mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">10.27</td><td colspan="2">0.70</td><td colspan="2">1.67</td><td colspan="2">3.40</td><td colspan="2">1.83</td><td colspan="2">5.24</td></tr>
<tr><td>Stage 2</td><td colspan="2">9.78</td><td colspan="2">1.7e-3</td><td colspan="2">1.89</td><td colspan="2">4.29</td><td colspan="2">2.30</td><td colspan="2">2.7e3</td></tr>
<tr><td>Stage 3</td><td colspan="2">9.68</td><td colspan="2">0.056</td><td colspan="2">0.17</td><td colspan="2">6.58</td><td colspan="2">0.14</td><td colspan="2">70.8</td></tr>
<tr><td colspan="13">Comments:</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

D.2 Initial water: Shallow groundwater at Forsmark

The composition of the initial water is given below.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
Forsmark shallow water HFM03/20	7.6	64.6	9.5	62	14	15.7	18.6	310

Summary tables of model runs carried out using the shallow groundwater composition for Forsmark are given below. The top half of each summary table indicates the reacting mineral assemblage at each stage of the model equilibrium calculations (R indicates the minerals that are allowed to dissolve and precipitate, D indicates the minerals that are allowed to dissolve only). The lower half of each table shows the results of modelling of water compositions: pH, Na^+. K^+, Ca^{2+} and Mg^{2+} concentrations in mg/L, and $[Ca^{2+} + Mg^{2+}]/[Na^+]$ ratio of molar concentrations.

<table>
<tr><td colspan="13">Model run no: B13</td></tr>
<tr><td colspan="13">Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R*</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td>R</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">6.90</td><td colspan="2">60.4</td><td colspan="2">8.78</td><td colspan="2">34.8</td><td colspan="2">12.3</td><td colspan="2">0.52</td></tr>
<tr><td>Stage 2</td><td colspan="2">8.16</td><td colspan="2">35.4</td><td colspan="2">19.8</td><td colspan="2">29.6</td><td colspan="2">10.2</td><td colspan="2">0.75</td></tr>
<tr><td>Stage 3</td><td colspan="2">9.33</td><td colspan="2">0.014</td><td colspan="2">0.16</td><td colspan="2">37.0</td><td colspan="2">7.27</td><td colspan="2">2.0e3</td></tr>
<tr><td colspan="13">Comments: *Sat index (calcite) fixed at -1 in Stage 1</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B14</td></tr>
<tr><td colspan="13">Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R*</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td>D</td><td></td><td>^1.8</td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">6.90</td><td colspan="2">60.4</td><td colspan="2">8.78</td><td colspan="2">34.8</td><td colspan="2">12.3</td><td colspan="2">0.52</td></tr>
<tr><td>Stage 2</td><td colspan="2">8.16</td><td colspan="2">35.4</td><td colspan="2">19.8</td><td colspan="2">29.6</td><td colspan="2">10.2</td><td colspan="2">0.75</td></tr>
<tr><td>Stage 3</td><td colspan="2">9.74</td><td colspan="2">91.6</td><td colspan="2">3.54</td><td colspan="2">1.40</td><td colspan="2">8E-5</td><td colspan="2">8.8e-3</td></tr>
<tr><td colspan="13">Comments: *Saturation index (calcite) fixed at -1 in Stage 1;
^ K-feldspar is oversaturated at the end of Stage 3, saturation index = 1.8</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B15

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

Reacting minerals[1]

	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R*	R	R									
Stage 2	R	R	R				D	D				
Stage 3	R	R	R				D	D				D

Modelled water compositions[2]

	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	6.90	60.4	8.78	34.8	12.3	0.52
Stage 2	9.59	35.7	5.08	11.4	4.03	0.29
Stage 3	9.59	35.7	5.08	11.4	4.03	0.29

Comments: *Sat index (calcite) fixed at -1 in Stage 1

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B16

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

Reacting minerals[1]

	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R					D				
Stage 3	R	R	R				D	D				

Modelled water compositions[2]

	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.59	71.2	10.4	50.2	17.6	0.64
Stage 2	8.37	48.8	6.98	21.7	7.79	0.41
Stage 3	9.59	35.7	5.08	11.4	4.03	0.29

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B17

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R								
Stage 3	R	R	R	R			R					

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.59	71.2	10.4	50.2	17.6	0.64
Stage 2	8.10	56.1	7.88	27.8	9.94	0.45
Stage 3	9.36	0.011	8.07	33.1	7.28	2.2e3

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B18

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R			R					
Stage 3	R	R	R							D	D	

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.59	71.2	10.4	50.2	17.6	0.64
Stage 2	9.36	0.011	8.07	33.1	7.28	2.2e3
Stage 3	12.13	0.57	21.6	282	652	1.4e3

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B19

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R			D					
Stage 3	R	R	R		R	R						

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.59	71.2	10.4	50.2	17.6	0.64
Stage 2	9.36	0.011	8.07	33.1	7.28	2.2e3
Stage 3	8.81	0.013	1.31	38.0	8.98	2.4e3

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B20

Starting water: Shallow groundwater at Forsmark, borehole HFM03, 20 m

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R			D					
Stage 3	R	R	R	R	R	R	D					

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.59	71.2	10.4	50.2	17.6	0.64
Stage 2	9.36	0.011	8.07	33.1	7.28	2.2e3
Stage 3	9.29	0.014	0.44	46.6	1.00	193

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

D.3 Initial water: Melt water from Canadian Arctic glacier

The composition of the initial water is given below.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
John Evans Glacier, Canadian Arctic	8.3	6.9	1.56	52	7.3	3.5	144	24.4

Summary tables of model runs carried out using the Canadian Arctic melt water as initial water composition are given below. The top half of each summary table indicates the reacting mineral assemblage at each stage of the model equilibrium calculations (R indicates the minerals that are allowed to dissolve and precipitate, D indicates the minerals that are allowed to dissolve only). The lower half of each table shows the results of modelling of water compositions: pH, Na^+. K^+, Ca^{2+} and Mg^{2+} concentrations in mg/L, and $[Ca^{2+} + Mg^{2+}]/[Na^+]$ ratio of molar concentrations.

<table>
<tr><td colspan="13">Model run no: B21</td></tr>
<tr><td colspan="13">Starting water: Melt water from Canadian Arctic glacier (JEG)</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">[Ca+Mg]
[Na] (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">8.65</td><td colspan="2">6.92</td><td colspan="2">1.57</td><td colspan="2">52.4</td><td colspan="2">7.34</td><td colspan="2">5.36</td></tr>
<tr><td>Stage 2</td><td colspan="2">8.59</td><td colspan="2">2.74</td><td colspan="2">3.87</td><td colspan="2">55.1</td><td colspan="2">7.62</td><td colspan="2">14.2</td></tr>
<tr><td>Stage 3</td><td colspan="2">9.28</td><td colspan="2">0.025</td><td colspan="2">0.22</td><td colspan="2">53.9</td><td colspan="2">6.84</td><td colspan="2">1.5e3</td></tr>
<tr><td colspan="13">Comments:</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B22

Starting water: Melt water from Canadian Arctic glacier (JEG)

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R	R							
Stage 3	R	R	R	R	R					D		^1.8

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	[Ca+Mg] [Na] (M)
Stage 1	8.65	6.92	1.57	52.4	7.34	5.36
Stage 2	8.59	2.74	3.87	55.1	7.62	14.2
Stage 3	9.84	72.7	2.82	6.04	5.1E-5	4.8E-2

Comments: ^ K-feldspar is oversaturated at the end of Stage 3, saturation index = 1.8

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B23

Starting water: Melt water from Canadian Arctic glacier (JEG)

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R				D	^5.3				
Stage 3	R	R	R				^6.1	^25		^1.5	D	

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	[Ca+Mg] [Na] (M)
Stage 1	8.65	6.92	1.57	52.4	7.34	5.36
Stage 2	9.31	6.63	1.50	47.9	6.71	5.11
Stage 3	12.10	16.7	3.34	260	132	16.5

Comments: ^ Saponite is oversaturated at the end of Stage 2, and laumontite, saponite and albite are oversaturated at the end of Stage 3

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition.

Model run no: B24

Starting water: Melt water from Canadian Arctic glacier (JEG)

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R				D					
Stage 3	R	R	R				D	^4.4				

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	8.65	6.92	1.57	52.4	7.34	5.36
Stage 2	9.31	6.63	1.50	47.9	6.71	5.11
Stage 3	9.28	0.025	1.57	53.1	6.89	1500

Comments: ^ Saponite is oversaturated at the end of Stage 3, saturation index 4.4

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B25

Starting water: Melt water from Canadian Arctic glacier (JEG)

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R						D			
Stage 3	R	R	R					^6.0	D			

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	8.65	6.92	1.57	52.4	7.34	5.36
Stage 2	9.59	3.1e-3	1.56	52.6	6.82	1.2e4
Stage 3	9.59	3.1e-3	1.56	52.6	6.82	1.2e4

Comments: ^ Saponite is oversaturated at the end of Stage 3, saturation index 6.0

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B26

Starting water: Melt water from Canadian Arctic glacier (JEG)

	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R		R						
Stage 3	R	R	R	R	R	R	D					

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	8.65	6.92	1.57	52.4	7.34	5.36
Stage 2	8.87	0.38	1.59	54.0	7.8	101
Stage 3	9.25	0.16	0.49	62.4	1.36	234

Comments:

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

D.4 Initial water: Melt water from Antarctic ice stream

The composition of the initial water is given below.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
Bindschadler Ice Stream, Antarctica	6.5	805	27.4	360	209	71	2976	458

Summary tables of model runs carried out using the Antarctic melt water as initial water composition are given below. This water composition is notably more mineralised than the other melt water compositions used in the modelling above. In particular the SO_4^{2-} concentration is high and the Na^+, Ca^{2+} and Mg^{2+} concentrations are also proportionately high.

The top half of each summary table indicates the reacting mineral assemblage at each stage of the model equilibrium calculations (R indicates the minerals that are allowed to dissolve and precipitate, D indicates the minerals that are allowed to dissolve only). The lower half of each table shows the results of modelling of water compositions: pH, Na^+. K^+, Ca^{2+} and Mg^{2+} concentrations in mg/L, and $[Ca^{2+} + Mg^{2+}]/[Na^+]$ ratio of molar concentrations.

Model run no: B27												
Starting water: Melt water from Antarctic ice stream (BIS)												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-montmorillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R	R							
Stage 3	R	R	R	R	R		D					
	Modelled water compositions[2]											
	pH		Na^+ mg/L		K^+ mg/L		Ca^{2+} mg/L		Mg^{2+} mg/L		$\frac{[Ca+Mg]}{[Na]}$ (M)	
Stage 1	7.00		825		28.1		383		220		0.52	
Stage 2	7.48		600		187		405		216		0.73	
Stage 3	8.79		133		17.2		1190		0.11		5.12	
Comments:												

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

Model run no: B28												
Starting water: Melt water from Antarctic ice stream (BIS)												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-montmorillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R				D	D				
Stage 3	R	R	R		R	R	D	D				
	Modelled water compositions[2]											
	pH		Na^+ mg/L		K^+ mg/L		Ca^{2+} mg/L		Mg^{2+} mg/L		$\frac{[Ca+Mg]}{[Na]}$ (M)	
Stage 1	7.00		825		28.1		383		220		0.52	
Stage 2	9.07		775		26.3		328		193		0.48	
Stage 3	8.95		823		1.23		587		13.1		0.43	
Comments:												

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

<table>
<tr><td colspan="13">Model run no: B29</td></tr>
<tr><td colspan="13">Starting water: Melt water from Antarctic ice stream (BIS)</td></tr>
<tr><td></td><td colspan="12">Reacting minerals[1]</td></tr>
<tr><td></td><td>Calcite</td><td>Chalcedony</td><td>Kaolinite</td><td>Na-mont-morillonite</td><td>Illite</td><td>Chlorite</td><td>Laumontite</td><td>Na-saponite</td><td>Prehnite</td><td>Albite</td><td>Anorthite</td><td>K-feldspar</td></tr>
<tr><td>Stage 1</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 2</td><td>R</td><td>R</td><td>R</td><td>R</td><td></td><td></td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Stage 3</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td>R</td><td>D</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="12">Modelled water compositions[2]</td></tr>
<tr><td></td><td colspan="2">pH</td><td colspan="2">Na^+ mg/L</td><td colspan="2">K^+ mg/L</td><td colspan="2">Ca^{2+} mg/L</td><td colspan="2">Mg^{2+} mg/L</td><td colspan="2">$\frac{[Ca+Mg]}{[Na]}$ (M)</td></tr>
<tr><td>Stage 1</td><td colspan="2">7.00</td><td colspan="2">825</td><td colspan="2">28.1</td><td colspan="2">383</td><td colspan="2">220</td><td colspan="2">0.52</td></tr>
<tr><td>Stage 2</td><td colspan="2">8.79</td><td colspan="2">112</td><td colspan="2">37.5</td><td colspan="2">1200</td><td colspan="2">0.13</td><td colspan="2">6.13</td></tr>
<tr><td>Stage 3</td><td colspan="2">8.77</td><td colspan="2">0.58</td><td colspan="2">1.83</td><td colspan="2">1260</td><td colspan="2">27.9</td><td colspan="2">1290</td></tr>
<tr><td colspan="13">Comments:</td></tr>
</table>

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

D.5 Initial water: Deep groundwater, KFM02A, 423 m

The composition of the initial water is given below.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
Forsmark ground-water KFM02A/423	7.11	1820	21.4	1140	198	5380	434	93

A summary table of the single model run to illustrate how equilibration with these mineral assemblages affects the water composition is given below. The top half of each summary table indicates the reacting mineral assemblage at each stage of the model equilibrium calculations (R indicates the minerals that are allowed to dissolve and precipitate, D indicates the minerals that are allowed to dissolve only). The lower half of each table shows the results of modelling of water compositions: pH, Na^+. K^+, Ca^{2+} and Mg^{2+} concentrations in mg/L, and $[Ca^{2+} + Mg^{2+}]/[Na^+]$ ratio of molar concentrations.

Model run no: B31												
Starting water: Deep groundwater, Forsmark borehole KFM02A, 423 m depth												
	Reacting minerals[1]											
	Calcite	Chalcedony	Kaolinite	Na-mont-morillonite	Illite	Chlorite	Laumontite	Na-saponite	Prehnite	Albite	Anorthite	K-feldspar
Stage 1	R	R	R									
Stage 2	R	R	R	R	R	R						
Stage 3	R	R	R		R	R	D	D				

	Modelled water compositions[2]					
	pH	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	$\frac{[Ca+Mg]}{[Na]}$ (M)
Stage 1	7.25	1820	21.4	1140	198	0.46
Stage 2	8.00	3.6	11.3	1650	815	478
Stage 3	8.58	3.8	2.95	2880	55.5	450
Comments:						

[1] Minerals react to equilibrium at each stage of the reaction model;
R = reversible equilibrium, i.e. dissolution & precipitation allowed;
D = dissolution only;
- = mineral not involved in this stage of the model run.

[2] Relevant features of equilibrated water composition

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The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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