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Swedish Radiation Safety Authority

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Research

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Geochemical Constraints on
Buffer Pore Water Evolution
and Implications for Erosion

SSM perspective

Background

The pore water composition of a KBS-3 bentonite buffer may gradually change as a result of reaction between groundwater and buffer minerals. The performance implication of such chemical reactions is that radionuclide solubility and sorption depend on the buffer chemical conditions. Moreover, pore fluid composition at the interface between the buffer and the surrounding bedrock is important for the modelling and assessment of potential buffer loss scenarios. Any process with the potential to affect this composition, such as interaction of the buffer with site groundwater needs to be identified and analysed.

Purpose of the Project

The purpose of this project is to assess to buffer reactivity in Forsmark site groundwater as a potential contribution to long-term geochemical processes in a KBS-3 bentonite buffer.

Results

Mineralogical data from the Forsmark Site show that smectite and calcite occur at all depths in Forsmark fractures, with no evidence for removal/dissolution by previous glacial episodes. This natural analogue information implies that these minerals may not have been eroded/dissolved during previous glacial episodes.

Available thermodynamic data suggest that repository-depth Forsmark groundwaters are in equilibrium (steady-state) with montmorillonite and saponite and these minerals may control pH, PCO_2 , $SiO_{2(aq)}$ and Na/Ca in groundwaters (and any future intruding glacial meltwaters) in the near-field at the site. This conclusion would not be evident from modelling approaches using mixing only.

Modelling of the reaction of montmorillonite in the buffer with Forsmark groundwater shows a trend towards conversion of montmorillonite to saponite, suggesting that the buffer may be partially altered prior to glacial meltwater intrusion.

Future work

Further work is desirable to examine the effects of the introduction of the kinetics of growth of secondary minerals on bentonite-groundwater equilibration times.

Project Information

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This report concerns a study which has been conducted for the Swedish Radiation Safety Authority, SSM. The conclusions and viewpoints presented in the report are those of the author/authors and do not necessarily coincide with those of the SSM.

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1. Introduction

Geological disposal of radioactive wastes relies upon the operation of a multi-barrier concept, namely the geological, or ‘natural’ barrier itself, together with a series of man-made, or ‘engineered’ barriers (e.g. [1]). For spent fuel/high-level waste, the latter usually consists of swelling clay(s) for the waste package buffer and tunnel backfill, a metal canister (copper in the KBS-3 concept) and spent fuel as the wasteform itself (e.g. [2]). It is desirable that juxtaposition of these barriers does not lead to interactions that would be deleterious to long-term performance.

With specific regard to the clay buffer, not only are there physicochemical interfaces with the canister and host rock to consider, but there are also chemical interactions with the saturating groundwater. The rock-groundwater system will impose geochemical constraints on the clay buffer, such as partial pressure of carbon dioxide (PCO_2), and activities of major ions, such as Na^+ , Ca^{2+} , K^+ , Mg^{2+} and $SiO_{2(aq)}$ which will affect clay mineral stability and potential long-term alteration/transformation.

Most safety assessments usually consider illite as the principal long-term alteration product of the interaction of bentonite with groundwater (e.g. [3]), but it is conceivable that transformation of montmorillonite (the main swelling clay mineral in bentonite) to other clay minerals such as beidellite or saponite, and/or to sheet silicates such as chlorite, or to framework silicates, such as zeolites and/or feldspars, could also occur, depending upon the precise composition of the ambient groundwater. However, such potential transformations are usually ignored in the modelling of long-term near-field interactions, because of the slow dissolution rate of montmorillonite (e.g. [4], [5], [6]).

Recent work carried out for SSM has shown that the above modelling approach is inadequate in describing long-term behaviour, since kinetic silicate mineral hydrolysis and growth can produce clay mineral transformations ([7], [8]). This previous work focused on interactions of bentonite with pure water and hyperalkaline fluids. In the report presented here, attention is directed at the interactions of bentonite with the groundwater at the Forsmark site in Sweden.

Goals for the project were to:

- identify possible water-rock reactions and define mineral stability using published SKB data for:
 - mineral assemblages in fractures at Forsmark.
 - Forsmark groundwaters.
- Carry out reaction path modelling of bentonite with Forsmark groundwater to evaluate the potential for alteration.

Work presented in this report is organised in the following sections:

- Section 2 reviews the available data from SKB for groundwater chemical evolution and mineral stability in fractures at Forsmark with reference to implications for long-term erosion of the buffer in the EBS.
- Section 3 examines potential water-rock interaction processes at Forsmark, evaluating possible controls on long-term water composition and mineral stabilities in the water-rock system.
- Section 4 presents the results of simple reaction-path modelling of bentonite-groundwater interaction.

2. Evidence for Clay Mineral Stability at Forsmark

SKB has produced a site descriptive model (SDM) for hydrochemical and geochemical data at the Forsmark site in preparation for the SR-Site licence application which is documented in a number of reports describing both hydrochemical and mineralogical properties of the site (e.g. [9]; [10]; [11]; [12]; [13]; [14]; [15]; [16]). It is relevant to summarise relevant portions of this work here as background to considerations of the stability of montmorillonite in the buffer and backfill of a KBS-3 type repository at Forsmark.

Several groundwater types which are now present in the bedrock can be associated with past climatic events in the late Pleistocene, including interglaciations, glaciations, deglaciations, and associated shore level displacements in connection with marine/non-marine transgressions and regressions. In particular, SKB's description has involved the development of models for groundwaters in relation to rock domains, fracture domains and deformation zones at Forsmark. To facilitate site description and modelling work, SKB has divided the bedrock in between deformation zones into several fracture domains, based on geological criteria, such as frequency of open fractures and, in the case of one fracture domain (FFM06), character of rock type (Figure 1). These zones essentially divide the candidate volume into a 'hanging wall' bedrock segment to the south-east, and a 'footwall' bedrock segment to the north-west. The hanging wall bedrock contains an increased number of gently dipping deformation zones, many of which extend down to at least 1 000 m depth.

2.1 Groundwater chemistry

Several groundwater types have been identified (Figure 2), with the following descriptions derived from [9]:

- **Near-surface freshwaters (0-20 m; $Cl^- < 200$ mg/L; < 1 g/L TDS):** these groundwaters, with $Cl^- < 200$ mg/L, comprise the most recent recharge compositions and their hydrogeochemical evolution is mainly determined by rock weathering reactions. The extensive presence of limestone blocks in the Quaternary overburden at Forsmark, promotes an overall distinctive character to these groundwaters. Properties include variable but higher pH values (usually higher than 7), and variable but higher calcium concentrations (mostly between 50 and 200 mg/L) depending on the biogenic carbon dioxide input. This contributes to the higher bicarbonate values observed (200–900 mg/L). Redox conditions are oxidising/reducing in character.

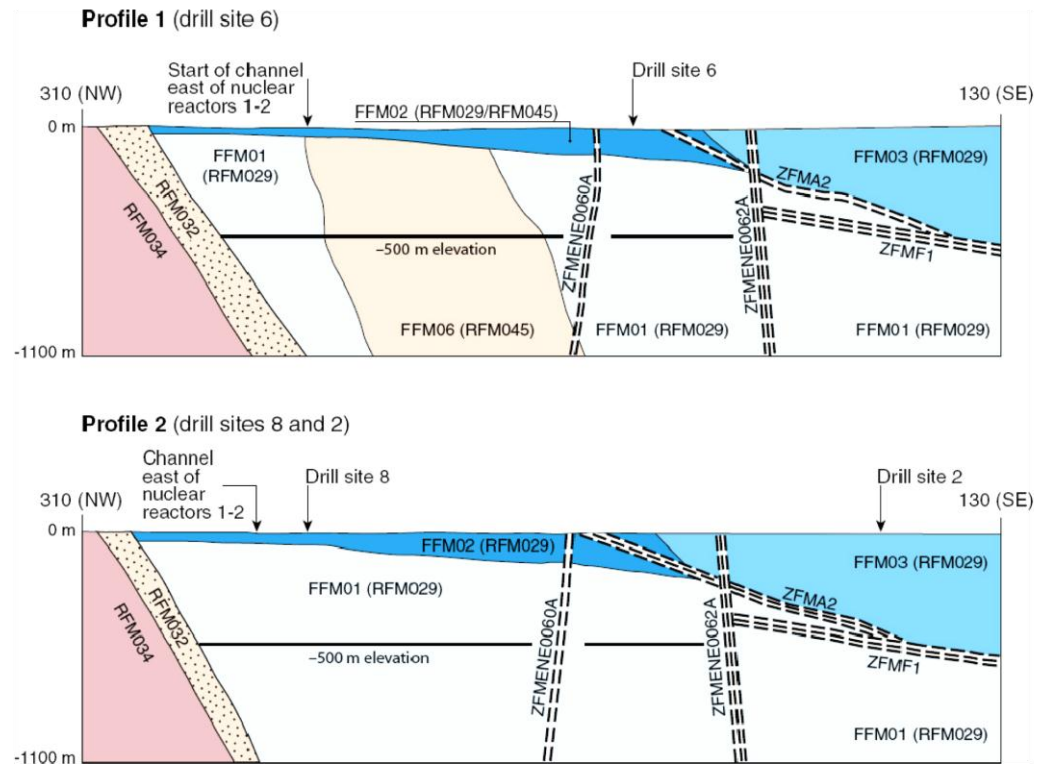


Figure 1 Simplified NW-SE profiles across the target volume that intersect drill sites 2 and 8 and drill site 6 at Forsmark. Note the major gently dipping deformation zones, which divide the candidate area into FFM03 (hanging wall) and fracture domains FFM01, 02 and 06 (footwall). The target volume is inside the footwall bedrock segment. The repository depth is shown by the black line at 500 m depth. From Laaksoharju et al. [9]

- **Shallow groundwaters (20-200 m):** This depth interval in the upper part of the footwall bedrock (i.e. repository target volume) includes effectively a shallow bedrock aquifer which facilitates the rapid transport of recharged meteoric groundwaters laterally towards the north-east and limits further recharge to deeper levels. These shallow groundwaters consist of a large percentage of fresh groundwater which has persisted to the depths of the shallow bedrock aquifer. This uppermost 20–200 m is also characterised by brackish groundwaters, referred to as ‘Mixed Brackish groundwaters’, comprising varying proportions of fresh and brackish waters with a chloride range of 200–2 000 mg/L. Redox measurements suggest the existence of a generalised anoxic state with possible episodic inputs of oxidising waters. Evidence from drillcore material from 0–100 m depth interval suggests that these oxidising episodes have not been intense enough to exhaust the reducing capacity of fracture filling minerals which are still present in the shallow system (e.g. through reduced iron dissolved from ferrous iron-bearing chlorite or pyrite - [13]).
- **Intermediate depth groundwaters (200–600 m):** During the Littorina Sea transgression, the Forsmark bedrock was under water with no active hydraulic gradient such that the seawater penetrated downwards by density intrusion flow. The bulk of the Littorina Sea waters, i.e. Brackish Marine groundwaters (2 000–6 000 mg/L Cl), preferentially entered the bedrock in the hanging wall along the gently dipping, highly transmissive deformation zones. The average depth of penetration at the present time along the gently dipping deformation zones is approximately 600–700 m. Littorina Sea water components are still present down to 250–300 m depth in the footwall. The chemical compositions here are thought to be controlled by mixing and depend on the proportion of each end-member. pH is thought to be mainly controlled by calcite dissolution-precipitation reactions and of secondary importance is the influence of other common chemical processes, such as aluminosilicate dissolution or cation exchange. The dissolved ferrous iron contents are generally lower than in the shallow groundwater system.
- Dissolved sulphide concentrations are systematically low and may be locally controlled by the precipitation of amorphous Fe(II)-monosulphides, linked to the activity of SRB. From approximately 300–650 m in the footwall bedrock, there is greater disparity between the porewater (from the rock matrix) chemistry and the adjacent groundwater compositions, the former being significantly more dilute. This depth interval represents transient conditions where the porewater has retained a very old, dilute and warm-climate water signature, much older than the surrounding fracture groundwaters which have been dated to at least 1.5 Ma. In the hanging wall, an overall transient state also is established down to about 650 m, where the porewater stores a dilute water signature with a probable cold-climate origin.

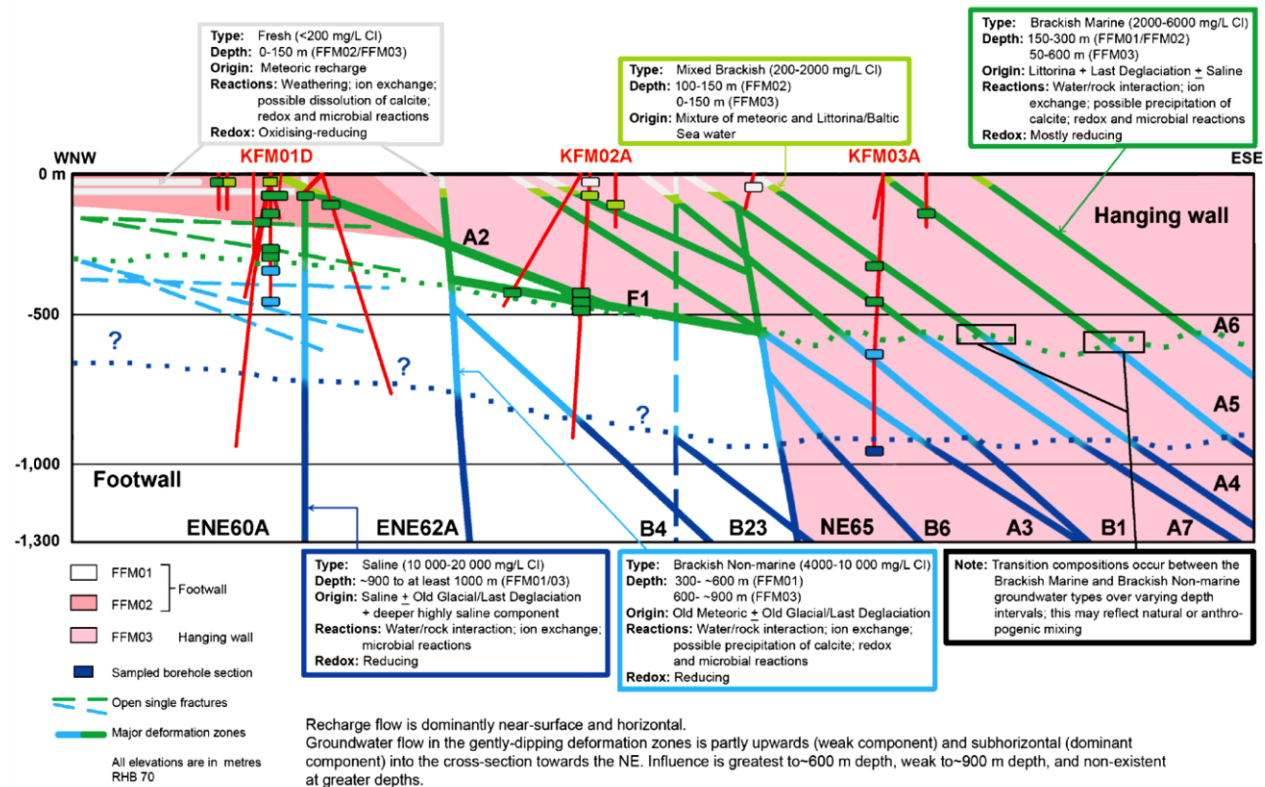


Figure 2 WNW-ESE cross-section through the repository candidate area showing the groundwater types (salinity, origin, major reactions, redox). The footwall (FFM01 and FFM02) and hanging wall (FFM03) segments are separated by the deformation zones A2 and F1. Dotted lines represent the extent of the groundwater types along fracture zones. From Laaksoharju et al. [9].

- **Deep groundwaters (> 600 m):** include Brackish Non-Marine groundwaters and the Saline groundwaters previously referred to as potential mixing components with the brackish marine (Littorina) groundwater at shallower levels. In the hanging wall bedrock, the transition from brackish marine (Littorina) type groundwaters to the brackish non-marine groundwaters is quite sharp and occurs at around 550–600 m depth. From 600–930 m depth, the chloride content increases steadily from 5 500–8 500 mg/L before levelling out at just under 10 000 mg/L at 1 000 m depth. With respect to redox conditions, the dissolved sulphide concentrations increase at depths greater than 600 m, which is consistent with the occurrence of sulphate-reducing bacteria (SRB) and with the active precipitation of Fe(II)-monosulphides. The iron system seems to be limited by crystalline oxides (mainly hematite) reflecting the pristine conditions of the geochemical system. The most saline groundwater in Forsmark deviates from the saline groundwater at Laxemar/ Simpevarp in having higher Br/Cl ratios and much lower SO₄ contents. In addition, element ratios like Sr/Cl and Li/Br are quite different and overall there is a suggestion of a different evolution trend. Unfortunately, the most saline groundwaters sampled at Forsmark only reach 15,000 mg/L Cl⁻, making comparisons with the saline water at Laxemar (45,000 mg/L Cl⁻) more uncertain.

From a perspective of clay stability and buffer erosion, there are a number of relevant features regarding the availability of divalent ions:

- Calcium concentration in groundwaters (Figure 3) increase with depth and are in the range 1000-2500 mg/L at repository depth (-500 m elevation), and reach 4 000 mg/L at -1000 m elevation. This implies a large resource of calcium ions at depths both at and beneath the potential repository horizon. The latter could be brought nearer the repository depth if groundwater up-coning occurs during repository operation.
- Mg concentrations are 0-250 mg/L at repository depth (Figure 4), but are uniformly low (< 25 mg/L) at depths below -700 m. Magnesium can also contribute to ion exchange reactions with montmorillonite to inhibit colloid formation.
- Groundwaters are saturated with calcite across all depth ranges studied (Figure 5), which together with mineralogical data (summarised below) indicates that calcite can provide a buffer for calcium ions in solution to mitigate against smectite colloid formation.

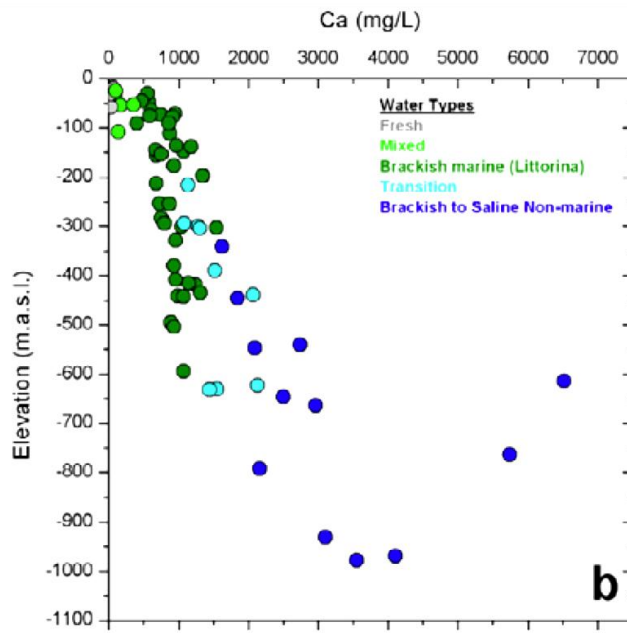


Figure 3 Distribution of calcium concentration with depth at Forsmark. From Laaksoharju et al. [9].

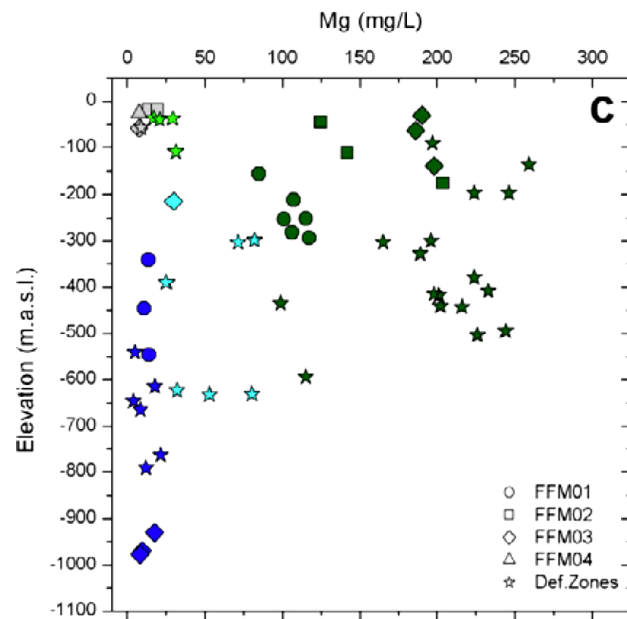


Figure 4 Distribution of magnesium concentration with depth at Forsmark. From Laaksoharju et al. [9].

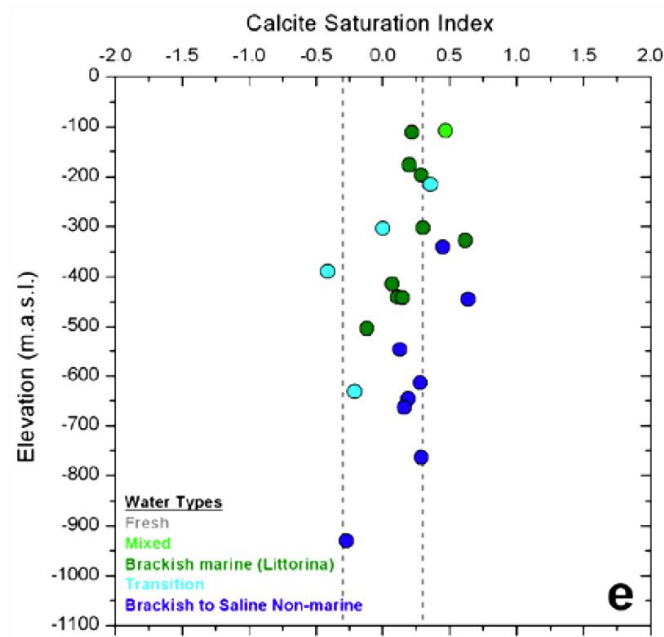


Figure 5 Variation of calcite saturation index with depth in groundwaters at Forsmark. From Laaksoharju et al. [9].

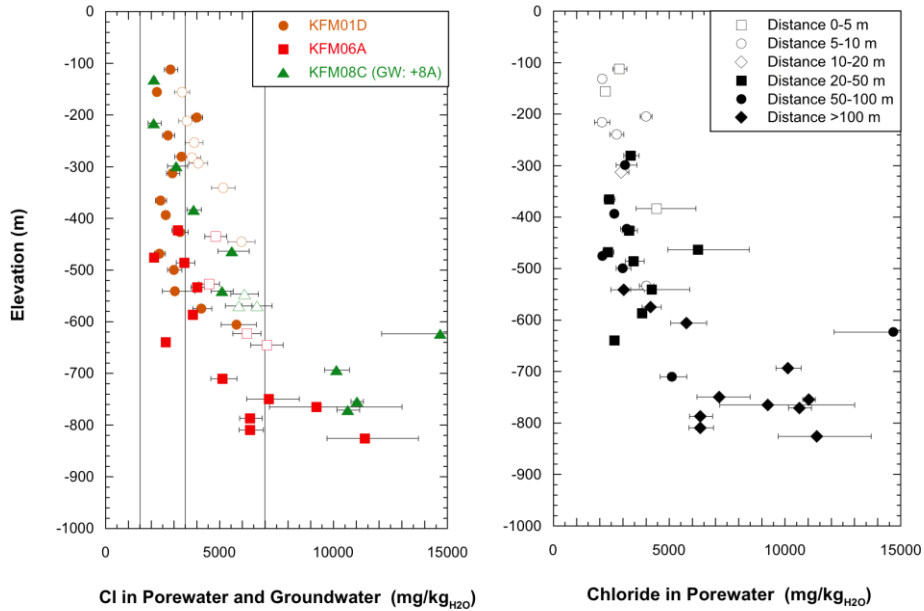


Figure 6 Chloride concentration in pore water (closed symbols) and related fracture groundwater (open symbols) on the left, compared with the distance of the pore water samples to the next water- conducting fracture on the right for boreholes representing mainly low transmissive, low fracture frequency conditions (KFM01D, KFM08C and the deeper part of KFM06A). From Laaksoharju et al. [9].

2.2 Pore water chemistry

An interesting feature of SKB's study is their investigation of *pore water* in the matrix of the bedrock ([9]; [12]; [17]), which has been carried out using large samples of rock core with in- and out-diffusion experiments to characterise chloride contents of entrained pore water.

Laaksoharju et al. [9] show that pore water from the footwall bedrock generally has lower chloride contents and is enriched in $\delta^{18}\text{O}$ compared with the fracture groundwaters, indicating a transient state between the pore water and groundwater down to at least 650 m depth at Forsmark. A signature with low chloride, low magnesium and enriched in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ has been preserved far away from water-conducting fractures, suggesting that these pore waters have evolved from an earlier, very long lasting circulation of old dilute groundwaters in a few fractures. According to Laaksoharju et al. [9], this is also consistent with the still prevailing transient state between this pore water and fracture groundwater from equivalent depths. South-east of the target volume in the hanging wall bedrock, a situation close to steady-state is suggested between pore water and fracture groundwater down to about 200 m depth, reflecting the high frequency of water-conducting, gently-dipping deformation zones, and the rapid circulation of significant volumes of water in this area (Figure 6). At greater depths, the pore water has a lower chloride content than the fracture groundwater, indicating a transient state down to about 650 m depth.

The implication of these studies is that the chemical composition of water sampled in fractures or higher-permeability zones need not correspond to that preserved in the rock matrix at similar depths away from the fracture zones. Indeed, given potential permeability contrasts in fractured hard rocks, it is likely that such a condition is the norm rather than the exception. Potentially therefore, matrix pore water could also be a source of divalent cations to counter the invasion of low ionic strength groundwaters during glacial periods. Concentration gradients between the rock matrix and fractures can drive diffusion of these cations into fracture groundwaters under appropriate circumstances. Currently, there are no analyses of cation concentrations in the pore waters.

2.3 Groundwater evolution

Because of the importance of the concentration of divalent cations for buffer erosion, SKB has modelled the potential evolution of groundwater chemistry at Forsmark ([18]).

For example, calcium participates in water-rock interactions, being released by the weathering of feldspar and being removed from solution by the precipitation of solid carbonates. At Forsmark, the deep saline groundwaters are rich in calcium, and modelling shows that groundwaters at depths greater

than ≈ 100 m may be simulated by mixing of component waters and that the relative effects of chemical reactions are minor.

The results of the modelling show the spreading of concentrations at repository depth, where most of the groundwaters that were present at repository closure have been replaced by waters of meteoric origin (Figure 7).

SKB concludes from these modelling results that for the whole temperate period following repository closure, Ca concentrations at repository depth at Forsmark will decrease with time and they will reach values that, in general, will remain close to 0.001 mol/L, that is, near to the limit where montmorillonite colloids start to become unstable ([18]).

2.4 Fracture minerals

In addition to groundwater chemistry, SKB has carried out extensive work to describe the nature and abundances of minerals lining fractures within the bedrock at Forsmark (e.g. as summarised by [13]; [14], with additional detail in: [19]; [20]; [21]; [22]; [23]). The abundance of fracture minerals is ([13]): chlorite/corrensite and calcite \gg laumontite > quartz, adularia (K-feldspar), albite, clay minerals > prehnite, epidote > hematite and pyrite. Minerals found as minor occurrences include asphaltite, analcime, and goethite.

Clay minerals have been identified using XRD analyses and the most common varieties are corrensite > illite > mixed layer clays > smectite > kaolinite, vermiculite and other swelling clays. No carbonates other than calcite have been identified and gypsum has not been identified in any of the fractures studies. Pyrite makes up more than 99 % of the identified sulphides, together with small amounts of galena, chalcopyrite and sphalerite.

Corrensite is the most common clay mineral, often forming with chlorite or as a replacement of earlier aluminosilicates (Figure 8). The FeO content in chlorite/corrensite is reported to be between 20 and 30 % and the MgO content between 3 and 24 % [24]. Smectite is not common at Forsmark, but occurs throughout the drilled section of rock (Figure 9). Laumontite is less common in the uppermost 100 m due to later reactivation and alteration [13]. Calcite-coated fractures are most common in the upper 350 m, along with fractures lacking any filling (Figure 10). Sandström et al. [13] note that when only fractures which are hydraulically conductive are considered, the most striking feature is the small number of fractures containing laumontite. The dominant fracture assemblages in the hydraulically conductive fractures are chlorite + calcite \pm other, and calcite \pm quartz \pm pyrite. These fractures are predominantly sub-horizontal to gently dipping.

Minerals such as chlorite show little or no variation with depth. Clay minerals are found more abundantly in fractures in the upper part of the bedrock but also at greater depths. The calcite \pm quartz \pm pyrite assemblage is most common in the upper 350 m of the bedrock, but occurs also abundantly at greater depths.

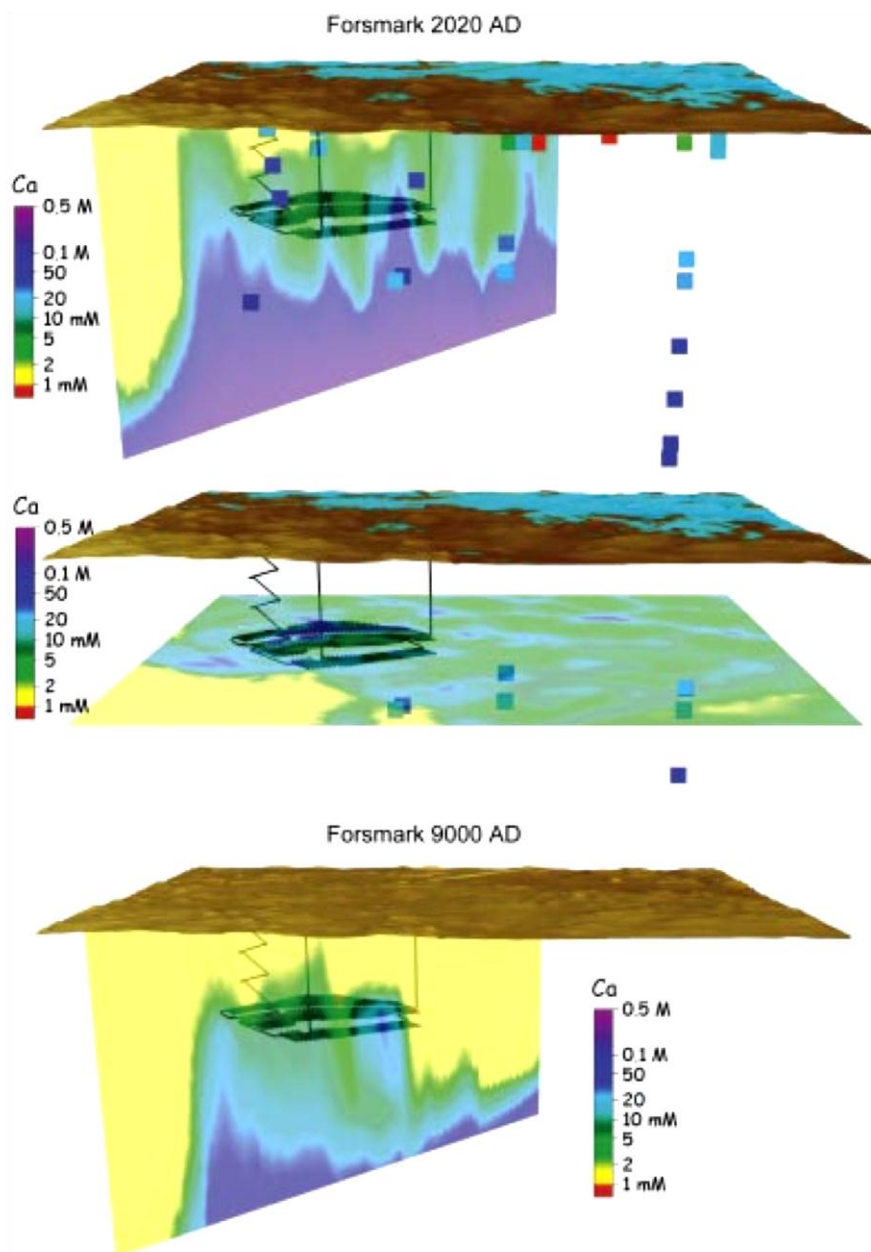


Figure 7 Calculated Ca concentrations at the Forsmark site (from [18]). **Top:** present-day groundwaters and a calculated vertical cut approximately perpendicular to the general coastal direction (upper picture) and horizontal cut at 400 m depth (lower picture). The top surface shows land and Baltic Sea areas. The repository layout is also shown. The vertical scale is exaggerated three times. **Bottom:** expected evolution of the groundwaters at the end of the temperate period, i.e. at year 9,000 AD. The coast has moved away from the site due to isostatic uplift and groundwaters have become diluted due to the increased infiltration of meteoric waters. From Auqué et al. [18].

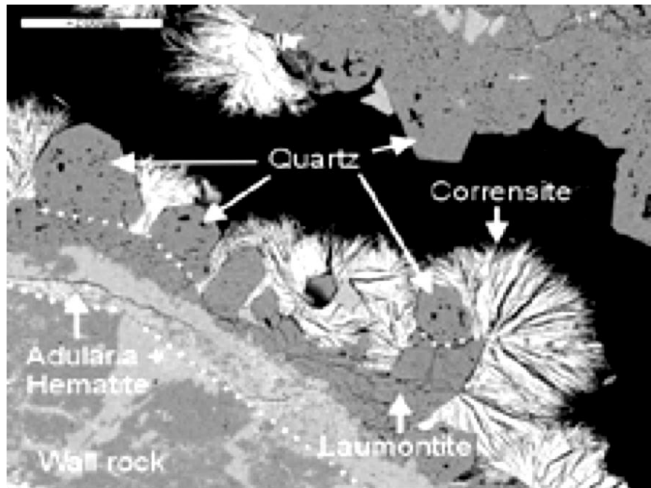


Figure 8 BSEM image of euhedral quartz and corrensite from borehole KFM05A 938.00–938.18 m, growing on hematite-stained adularia and laumontite. Scale bar is 200 μm . From Sandström et al. [13].

Potential differences in fracture mineralogy between the different fracture domains have been studied and it has been concluded that:

- With the exception of asphaltite and goethite, which almost exclusively are found in open fractures within the footwall (i.e. fracture domain FFM02) and probably in the upper part of the hanging wall (in fracture domain FFM03), the same fracture mineralogy is found in fracture domains FFM01, FFM02, FFM03 and FFM06, although the proportion of the different minerals may vary.
- Clay minerals also occur most abundantly in open fractures in the upper part of the footwall (fracture domain FFM02) but are found in all other fracture domains within the target volume as well.

The calcite \pm quartz \pm pyrite assemblage (i.e. generation 3; see below) is most common in the upper 350 m of the bedrock, but in the near-surface environment there is no evidence that calcite and pyrite have decreased in frequency due to surface related oxidation or dissolution of calcite.

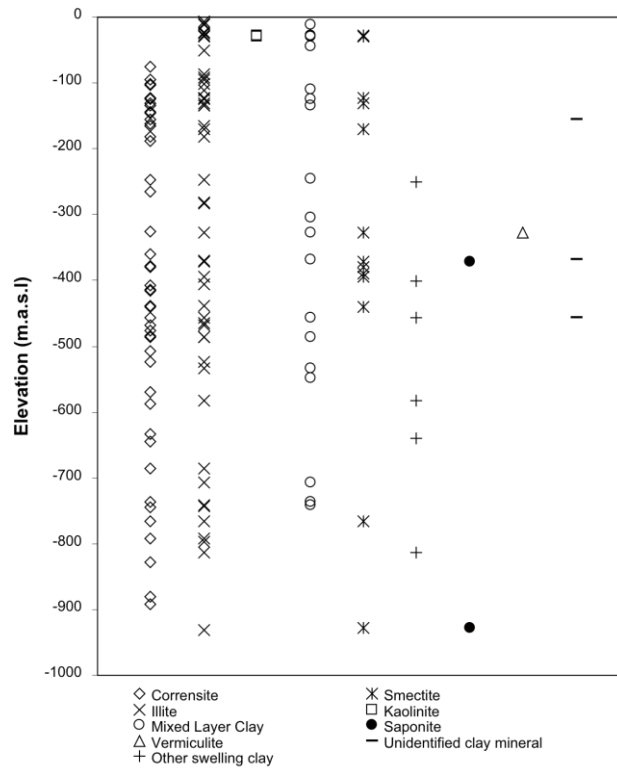


Figure 9 Depth distribution of different clay minerals identified by XRD. From Sandström et al. [13]. Note the presence of smectite throughout the section.



Figure 10 Calcite and pyrite crystals on top of a quartz coated fracture surface. Length of photograph is 2.5 cm (KFM01A 267.0 m). From Sandström et al. [20].

The dominant fracture assemblage in the hydraulically-conductive fractures is chlorite + calcite ± others, and calcite ± quartz ± pyrite ('Generation 4'), but the sequence of alteration is [9]:

- **Generation 1** (Pre-Sveconorwegian) is dominated by epidote, quartz and Fe-rich chlorite precipitated under hydrothermal conditions at temperatures higher than 150–250 °C.
- **Generation 2** (Sveconorwegian) consists of a sequence of fracture minerals precipitated during hydrothermal conditions at temperatures approximately 150–280 °C, and comprising mainly adularia, albite, prehnite, laumontite, calcite, chlorite and hematite. Dissolution of these fracture minerals occurred prior to the formation of Generation 3 minerals.
- **Generation 3** (Palaeozoic) consists of minerals precipitated under low temperature conditions during the Palaeozoic. The most abundant minerals are calcite, quartz, pyrite, corrensite (mixed layer smectite-chlorite) and asphaltite (derived from the brine-type formation fluid emanating from an overlying organic-rich sedimentary cover). The formation temperature was around 60–100°C, although higher temperatures (160–190°C) may have been reached locally in the fracture system. Precipitation of Generation 3 minerals has been demonstrated during the Late Palaeozoic (Permian), but fracture mineral formation probably occurred at several periods during the Palaeozoic
- **Generation 4** (Late Palaeozoic-Present) is dominated by clay minerals (chlorite/corrensite) and thin precipitates of calcite, but also minor amounts of goethite and pyrite mainly associated with hydraulically conductive fractures and fracture zones. Precipitation of these minerals may have occurred over a long period of time (since the Late Palaeozoic?), and during different events and at different times. Fractures without any visible mineral filling are also interpreted to belong to generation 4 and are possibly young in origin.

SKB report that the presence of goethite in hydraulically conductive zones suggests an input of oxidising waters associated mainly with sub-horizontal zones during some occasions in the past. However, consideration of an Eh-pH diagram for the iron-sulphur system for Forsmark groundwater conditions shows that goethite can coexist with pyrite under reducing conditions (Figure 11), thus questioning the validity of this assumption.

According to SKB, the pH buffer capacity in the Forsmark groundwaters at depths greater than 100 m appears to be controlled by the calcite system, and modelling indicates that this water is in equilibrium with calcite. Investigations of fracture minerals show that calcite in fractures is abundant and that no extensive leaching has occurred in response to past glaciation-deglaciation events.

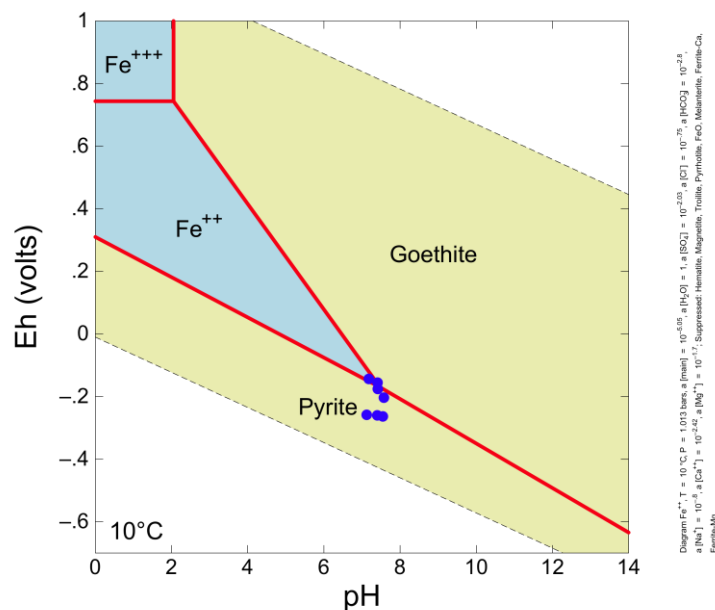


Figure 11 Eh-pH diagram for the iron-sulphur system, calculated using Geochemists Workbench and EQ3/6 database 'thermo.com.V8.R6.230'. The coexistence of pyrite, goethite and aqueous Fe²⁺ occurs at pH = 7.5; Eh = - 0.15 V. Fe = 10⁻⁵ mol/L; ΣS = 9 10⁻³ mol/L; Cl⁻ = 0.2 mol/L; ΣC = 2 10⁻³ mol/L; Na = 0.2 mol/L; Ca = 4 10⁻³ mol/L; Mg = 0.02 mol/L. Groundwater data from repository depths at Forsmark are shown as blue dots (data courtesy of Adrian Bath).

SKB report that no significant decrease in the frequency of calcite-coated fractures in the uppermost part of the bedrock can be seen, indicating that no extensive calcite leaching has occurred in response to Quaternary glaciation/deglaciation events ([9]). Auqué et al. ([18]) present a summary figure for the distribution of calcite in Swedish basement rocks (Figure 12).

2.5 Clay Mineral Compositions and Cation exchange data

It was not possible to find any compositional data for the clay minerals identified by SKB in fractures at Forsmark. Byegård et al. [25] refer to broad cation exchange properties of different rock types and fracture fillings at Forsmark and determined CECs of 15 and 18 cmole kg⁻¹ for 'fracture type B' (chlorite + clay ± epidote ± prehnite ± calcite) and 'fracture type C' (chlorite + hematite ± other), respectively. Cations desorbed (quoted to be Ca²⁺) for these fractures were 43 and 16 cmole kg⁻¹, respectively. Kalinowski ([26]) present some cation exchange capacity data for bulk rocks and fracture mineral assemblages from Forsmark (shown here in Figure 13), but not occupancies of individual cations.

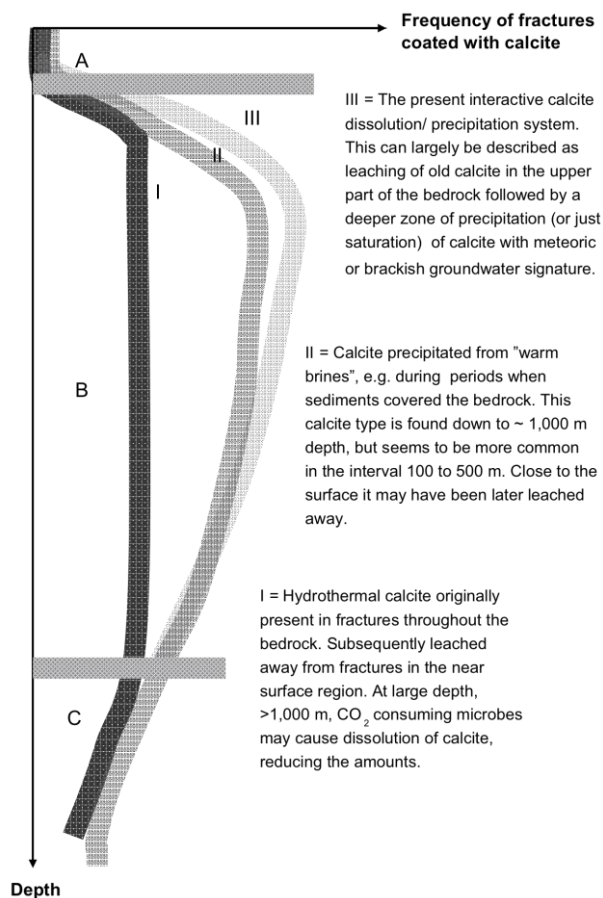


Figure 12 Simplified sketch showing the general view of calcites present in crystalline bedrock based on experiences from Swedish sites. **Zone A** is the upper 0 to 100 metres characterised by a dynamic situation including dissolution/precipitation of calcite. **Zone B** is from ~ 100 m down to ~ 500–600 m, where mainly precipitation of calcite is detected. **Zone C** (> 1,000 m) shows recent calcite precipitation is rare. From Auqué et al. [18].

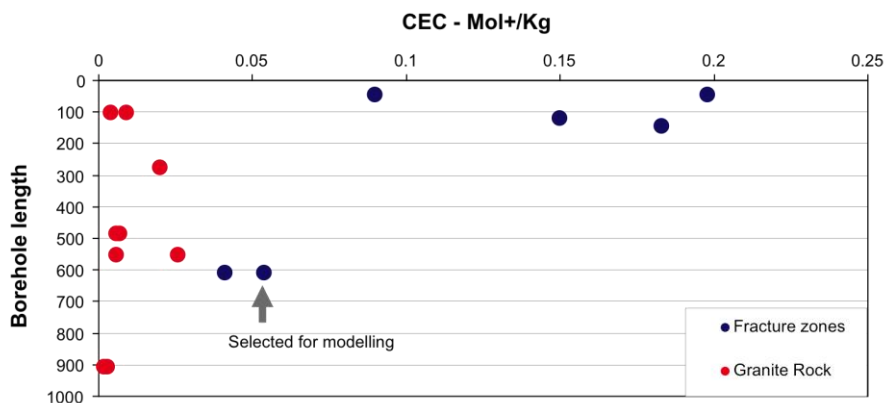


Figure 13 Cation exchange data from Forsmark rocks (red dots) and fracture mineral assemblages (blue dots). From [26].

3. Water-rock interaction processes

SKB's study of the Forsmark groundwaters, as described in Section 2 has confirmed the existence of at least four component waters: an old brine; a marine component (ancient Littorina Sea); a modern meteoric water; and an old glacial meltwater. SKB considers that mixing is the prime irreversible process responsible for the chemical evolution of the Forsmark groundwater system (e.g. [18]), so that the successive disequilibrium states resulting from mixing has conditioned the subsequent water-rock interaction processes and hence the re-equilibration pathways of the mixed groundwaters.

However, studies of fracture mineral assemblages carried out by SKB has highlighted the importance of the solid products of water-rock interaction in not only governing the mineralogical and physical properties of groundwater pathways (e.g. [25]), but also chemical properties of the groundwater, such as redox and pH (e.g. [18]; [27]). For redox, SKB considers that Fe-bearing minerals such as pyrite, biotite, chlorite, corrensite and goethite will be important, whereas for pH, calcite is the most significant ([9]).

Here, an independent investigation of potential controls on water chemistry has been carried out using mineral stability (activity) diagrams. Such diagrams are an important tool in establishing potential controls on water compositions (e.g. [28], [29]). A number of thermodynamic activity diagrams have been constructed to evaluate the possible control of key aqueous species (pH, PCO_2 , Na/Ca) by water-rock reactions.

3.1 Activity diagrams

Reactions involving calcium aluminosilicate minerals and $CO_{2(aq)}$ can be particularly important in controlling pH and PCO_2 in water-rock systems ([30]). PCO_2 can be critical in determining near-field pH because:

- in bentonite models that involve exchange reactions and calcite equilibrium (e.g. [4]), it is the most important parameter ([7]);
- strong evidence suggests that geosphere PCO_2 is 'set' by mineral fluid reactions, and is distinctly different in 'clay' and fractured hard rock environments (e.g. [31]).

Activity diagrams for the following systems have been constructed:

- CaO-MgO-K₂O-Al₂O₃-SiO₂-H₂O-CO₂ in Figure 14, Figure 16; and Figure 17.
- Na₂O-CaO-Al₂O₃-SiO₂-H₂O-CO₂ in Figure 15.

Cation activity ratio plots are particularly useful in this regard in that they increase the number of variables which can be represented on a 2-D plot, and moreover avoid inclusion of H^+ (pH) which can be prone to sampling/analytical errors due to CO_2 outgassing/absorption.

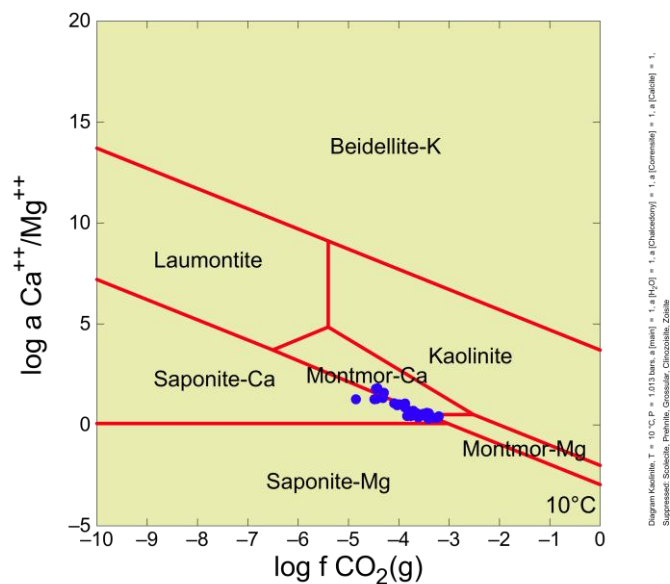


Figure 14 Mineral stabilities in the system CaO-MgO-K₂O-Al₂O₃-SiO₂-H₂O-CO₂ at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A.H. Bath, pers. comm.). Data suggest control of Ca/Mg, PCO₂ (and pH), by montmorillonite-saponite coexistence.

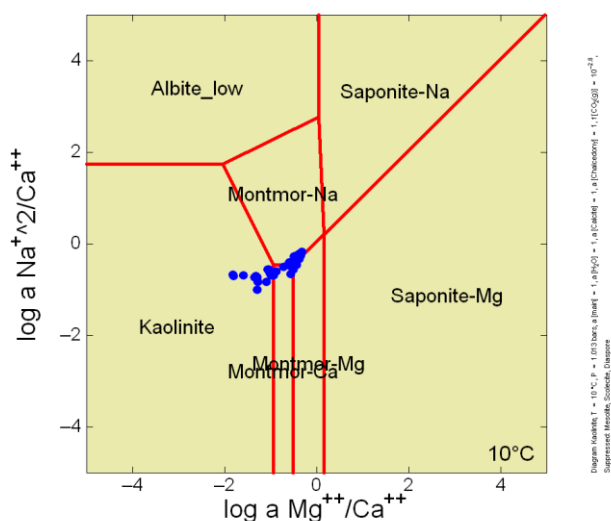


Figure 15 Mineral stabilities in the system Na₂O-CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A.H. Bath, pers. comm.). This suggests control of Na/Ca ratios by montmorillonite-saponite coexistence. This reaction could buffer Na/Ca in glacial meltwaters during intrusion to depth.

Figure 14 shows variations in log Ca/Mg activity ratio with log $f\text{CO}_{2(g)}$ (equivalent to log PCO_2). There are stability fields for beidellite, laumontite, saponites, montmorillonite and kaolinite. Beidellite, saponite and montmorillonite are all swelling clays (smectites), kaolinite is a non-swelling clay and laumontite is a calcium zeolite. Ca^{2+} , Al^{3+} and $SiO_{2(aq)}$ activities are buffered by calcite, kaolinite and chalcedony, respectively. Data for Forsmark groundwaters (blue dots) plot along, and with the same NW-SE trend, as the Ca-montmorillonite:Ca-saponite boundary. This implies control of Ca/Mg ratios, pH and PCO_2 by the following reaction (conserving Mg^{2+} and Al^{3+}):

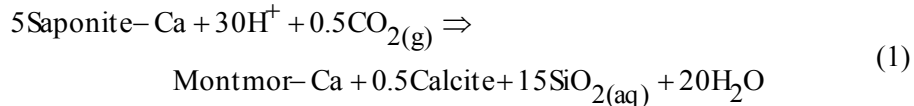


Figure 15 shows variations in log $(Na^+)^2/Ca^{2+}$ activity ratio with log Mg^{2+}/Ca^{2+} activity ratio. There are stability fields for albite, kaolinite, saponites, and montmorillonites. Albite is a sodium aluminosilicate framework mineral (plagioclase feldspar). Ca^{2+} , Al^{3+} , Mg^{2+} and $SiO_{2(aq)}$ activities are buffered by calcite, kaolinite, corrensite (Mg end-member) and chalcedony, respectively. Thermodynamic data for corrensite from [32] were employed. Again, it can be seen that Forsmark groundwater data plot along the montmorillonite-saponite boundary, providing additional evidence for the relevance of equation (1) above in controlling not only Mg^{2+}/Ca^{2+} activity ratios, but also $(Na^+)^2/Ca^{2+}$ activity ratios. This implies that regardless of Na/Ca ratios of intruding glacial meltwaters, the Forsmark rock will buffer this ratio in accord with saponite and montmorillonite coexistence.

Figure 16 shows variations in log activity Ca^{2+}/Mg^{2+} ratio versus activity of $SiO_{2(aq)}$. There are stability fields for clinocllore (Mg-chlorite), boehmite, kaolinite, saponites, and montmorillonites. Solubility limits for quartz and chalcedony are also shown. It may be seen from this figure that $SiO_{2(aq)}$ activities are in excess of those both for quartz and chalcedony solubilities at 10 °C and suggest buffering by the clay minerals saponite and montmorillonite.

Figure 17 shows variations in log $(K^+)^2/Ca^{2+}$ activity ratio with log Mg^{2+}/Ca^{2+} activity ratio. There are stability fields for microcline (K-feldspar), kaolinite, muscovite, corrensite (Mg end-member), saponites, and montmorillonites. Microcline is a potassium aluminosilicate framework mineral. Ca^{2+} , Al^{3+} , and $SiO_{2(aq)}$ activities are buffered by calcite, kaolinite, and chalcedony, respectively. Thermodynamic data for corrensite from [32] were employed. It can be seen that Forsmark groundwater data plot along the microcline-corrensite boundary, adjacent to stability fields for saponite clays. This suggests that K^+ and Mg^{2+} activities are controlled by reactions involving microcline (K-feldspar), corrensite and saponite clays.

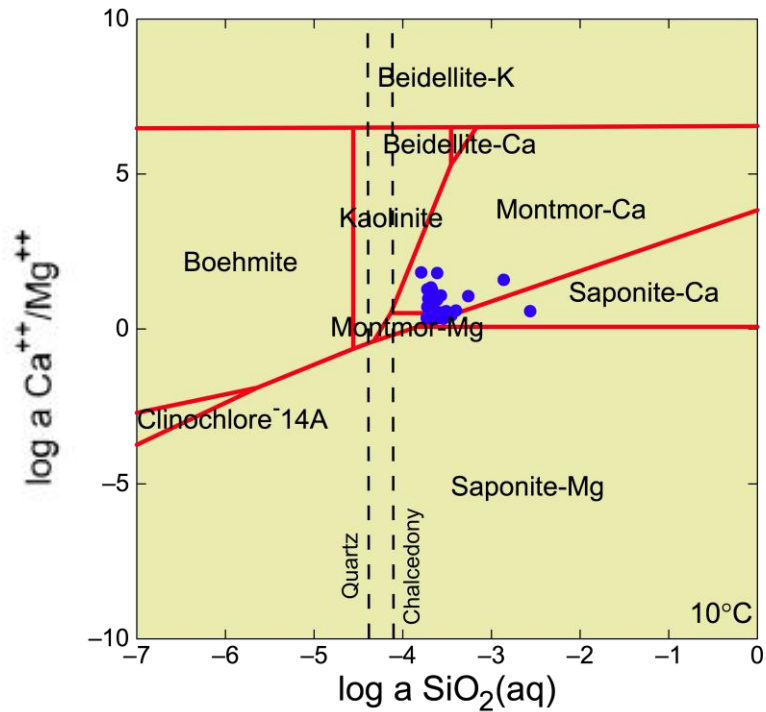


Figure 16 Mineral stabilities in the system $\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A.H. Bath, pers. comm.). Solubilities of quartz and chalcedony are indicated by dashed lines. The distribution of the groundwater data suggests control of $\text{SiO}_{2(\text{aq})}$ by montmorillonite-saponite coexistence.

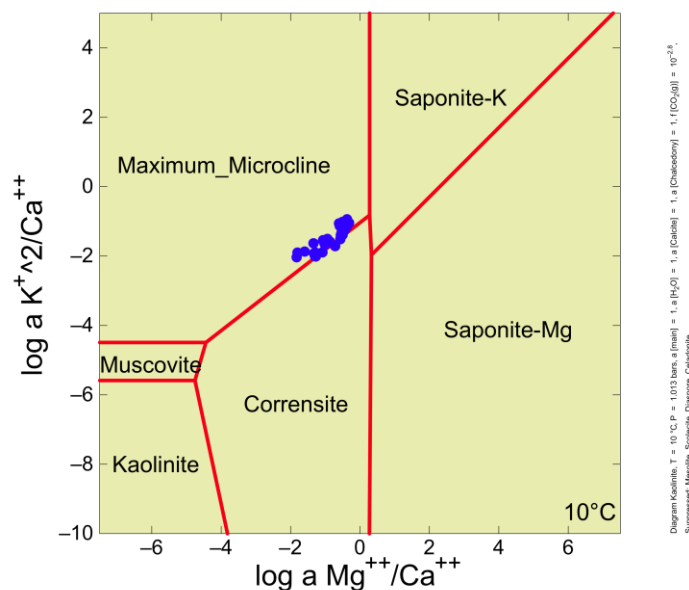


Figure 17 Mineral stabilities in the system K₂O-CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A.H. Bath, pers. comm.). This suggests control of K/Mg ratios by microcline-corrrensite-saponite coexistence.

These figures show that minerals present in Forsmark fractures (montmorillonite, saponite, calcite, corrensite, chalcedony) could be important controls of the activities of major cations in groundwater (Na, Ca, K, Mg), as well as other important parameters, such as pH, PCO₂, and SiO_{2(aq)}. These controls may also be extended to future periods of glacial meltwater intrusion, such that the compositions of these waters could be buffered by mineral-fluid reactions during migration from the surface.

3.2 Na/Ca activity ratios and clay sol stability

Arthur [33] has shown that the development of clay colloids (and hence potential for erosion) is dependent upon the (Na⁺)²/Ca²⁺ activity ratio and the Ca²⁺ content of the groundwater. For the reaction:



and the Gaines-Thomas convention for ion exchange:

$$K_{GT} = \frac{X_{\text{Ca}(\text{clay})} a_{\text{Na}^+}^2}{X_{\text{Na}(\text{clay})}^2 a_{\text{Ca}^{2+}}} \quad (3)$$

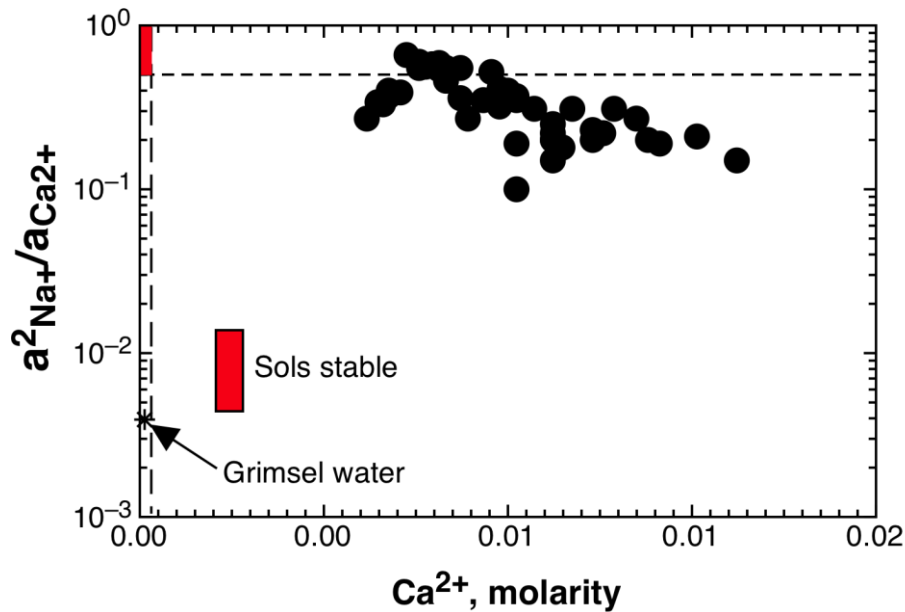


Figure 18 Plot of $(\text{Na}^+)^2/\text{Ca}^{2+}$ ratio versus Ca^{2+} for Forsmark groundwaters from repository depth. The region of sol stability is indicated in red. The composition of the Grimsel water used by SKB as being typical of glacial meltwaters is also shown (data from [2]). Diagram after Arthur [33]. Forsmark data from A.H. Bath.

Assuming $X_{\text{Ca}(\text{clay})} \approx 1 - X_{\text{Na}(\text{clay})}$, then [33] has shown that:

$$\square \quad 2 + \frac{a_{\text{Na}^+}^2}{K_{GT} a_{\text{Ca}^{2+}}} = X_{\text{Ca}(\text{clay})} + \frac{1}{X_{\text{Ca}(\text{clay})}} \quad (4)$$

Consequently, for $X_{\text{Ca}(\text{clay})} \geq 0.9$ (and hence absence of sol formation), then

$\square \quad \left(\frac{a_{\text{Na}^+}}{a_{\text{Ca}^{2+}}}\right)^2 \leq 0.05$, assuming that $K_{GT} = 4.5$ [34]. If this cation activity ratio is plotted against concentration of free Ca^{2+} for Forsmark groundwaters (Figure 18), then it can be seen that none of these waters plot in the area where clay sols are stable, and most plot at $(\text{Na}^+)^2/\text{Ca}^{2+} < 0.05$ implying that the clay exchanger in the Forsmark rock-groundwater system is Ca-rich ($X_{\text{Ca}(\text{clay})} > 0.9$). Consequently, this ion exchanger in the rock will tend to mitigate against development of clay sols by buffering the $(\text{Na}^+)^2/\text{Ca}^{2+}$ activity ratio at values less than 0.05.

4. Potential reaction of MX-80 bentonite with Site groundwater

Work on this topic carried out in 2008-9 focused on modelling the experiments of Muurinen & Carlsson [35], reacting compacted bentonite in diffusion cells with pure water and a complex Na-Ca-OH-Cl fluid (pH = 12), using the computer codes Geochemists Workbench [36] and QPAC [37]. Results showed that in the absence of the precipitation of secondary minerals, montmorillonite ‘rapidly’ approached equilibrium (7 years for H₂O; 65 years for Na-Ca-OH-Cl). However, when precipitation was included, equilibrium was delayed by thousands of years. This suggests that mineral hydrolysis and secondary mineral growth should be included in models of long-term pore water evolution because of the potential impact upon buffer erosion *inter alia* [7], [8]. This year, similar reaction-path calculations have been carried out, but this time with a repository-depth groundwater composition from Forsmark.

4.1 Input data

The bentonite composition employed in the calculations was the same as that used previously and contains trace amounts of halite and gypsum (Table 1). The amount of these minerals in saturated bentonite compacted to a density of 2000 kg m⁻³ is shown in Table 2, along with the amounts used in GWB simulations (mineral masses normalised to 1 kg H₂O).

Simulations were conducted either in pure water or in Forsmark groundwater (Table 3). The groundwater composition is that from Table 2.1 in [18] and represents a sample from borehole KFM02A at 512 m depth.

Thermodynamic data for two types of montmorillonite were employed (**Table 4**), including that for MX-80 smectite estimated using the method described by Vieillard [38], and a more simplified composition, with data proposed by Wolery [39].

Simulations were conducted at 25 °C, either with ‘secondary mineral precipitation off’ or ‘secondary mineral precipitation on’. Mineral dissolution occurred kinetically, with data as shown in Table 5, according to:

$$rate = k \cdot (a_{H^+})^2 A \left(1 - \frac{Q}{K} \right) \quad (5)$$

where k is the reaction rate (mol m⁻² s⁻¹), A is the reactive surface area, Q is the ion activity product, and K is the equilibrium constant.

□

Table 1 MX-80 composition. From [5], [35], and [40], and as used in [7].

| | Measured wt % | Simplified wt % | Simplified vol % |
|---|------------------|--------------------|---------------------|
| Montmorillonite | 87 | 90 | 48.7 |
| Quartz, SiO ₂ | 5 | 8.6 | 4.9 |
| Feldspar and mica | 7 | - | - |
| Calcite, CaCO ₃ | 0 | 1 | 0.6 |
| Pyrite | 0.07 | - | - |
| Gypsum CaSO ₄ ·2H ₂ O | 0.7 | 0.4 | 0.3 |
| Halite, NaCl | - | 0.0079 | 0.0055 |
| Porosity | - | - | 45.6 |

Table 2 Masses of minerals and water in compacted bentonite of 2000 kg m⁻³ saturated density and as employed in GWB simulations.

| | Mass (kg) | g per kg H ₂ O |
|---|-------------|---------------------------|
| Montmorillonite | 1463 | 3576 |
| Quartz | 140 | 342 |
| Calcite, CaCO ₃ | 16.25 | 40 |
| Gypsum CaSO ₄ ·2H ₂ O | 6.5 | 16 |
| Halite, NaCl | 0.13 | 0.3 |
| Water | 409 | - |
| Totals | 2035 | 3974 |

Table 3 Composition of Forsmark groundwater at repository depth (mol/L), from Table 2.1 of Auqué et al. ([18]). The pH has been adjusted from 7.2 to 6.9 to maintain calcite at saturation.

| Groundwater | |
|------------------------|--------|
| pH | 6.9 |
| Na | 0.089 |
| K | 9e-4 |
| Ca | 0.023 |
| Mg | 0.0093 |
| Al | 1e-10 |
| Si | 2e-4 |
| Cl | 0.142 |
| SO₄ | 0.0052 |
| HCO₃ | 0.0022 |

Table 4 Log K (25 °C) values for smectite dissolution reactions using data for MX-80 smectite estimated using the Vieillard technique ([38]) and a simplified sodium montmorillonite composition reported by Wolery ([39]).

| Smectite Dissolution Reaction | Log K |
|--|--------|
| Na _{0.18} Ca _{0.1} (Al _{1.64} Mg _{0.36})(Si _{3.98} Al _{0.02})O ₁₀ (OH) ₂ + 6.08H ⁺ = 0.18 Na ⁺ + 0.1 Ca ²⁺ + 1.66 Al ³⁺ + 0.36 Mg ²⁺ + 3.98 SiO _{2(aq)} + 4.04 H ₂ O | 5.9941 |
| Na _{.33} Mg _{.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂ 6H ⁺ = .33Na ⁺ + .33Mg ²⁺ + 1.67Al ³⁺ + 4SiO _{2(aq)} + 4H ₂ O | 2.4844 |

Table 5 Kinetic data for mineral dissolution. The surface area for smectite assumes a total edge area of 8.5 m² per gram [41]. Surface area values for other minerals in bentonite assume spherical particle geometry and a grain diameter of 100 μm. *n* is the dependence of montmorillonite dissolution rate on [OH⁻].

| Mineral | Log <i>k</i> (mol m ⁻² s ⁻¹) | <i>A</i> m ² g ⁻¹ | <i>n</i> | Source |
|------------------------------------|--|--|----------|--------|
| Other minerals in bentonite | | | | |
| Montmorillonite | -14.37 | 3e4 | 0.27 | a |
| Halite | -0.21 | 0.03 | - | b |
| Calcite | -5.81 | 0.02 | - | c |
| Quartz | -13.40 | 0.03 | - | b |
| Gypsum | -2.79 | 0.03 | - | b |

^a[[42]; ^b[43]; ^c[44].

In the simulations, the log *K* for quartz solubility was increased in order to maintain dissolved silica concentrations to that appropriate for chalcedony solubility (most low temperature water-rock systems are in equilibrium with chalcedony and not quartz).

Processes of ion exchange and surface complexation were excluded in the interest of focusing on mineral hydrolysis reactions.

The porosity (water) available for reaction was assumed to be equal to total porosity (e.g. [45]).

Simulations were run until montmorillonite saturation was reached or to 10 000 years.

4.2 Results

Results of the simulations showed that in the absence of secondary mineral precipitation, montmorillonite approached equilibrium rapidly (over a period of tens of days), both for MX-80 smectite (Figure 19) and for Na-montmorillonite (Figure 20).

When (equilibrium) secondary mineral precipitation is included, then attainment of equilibrium is delayed for tens of years for Na-montmorillonite (Figure 21) and for over 10 000 years for MX-80 smectite (Figure 22).

Secondary minerals forming in the MX-80 smectite simulations include laumontite, kaolinite, albite and Ca-saponite (Figure 23). MX-80 smectite is removed progressively throughout the simulation. Secondary minerals in the Na-montmorillonite simulation are much reduced and include chalcedony and kaolinite (Figure 24). Chalcedony results mainly from the dissolution of quartz.

The effects of montmorillonite dissolution on the Na/Ca ratio of the fluid in the bentonite are shown in Figure 25. It can be seen from this figure that the Na/Ca ratio of the coexisting groundwater is considerably increased.

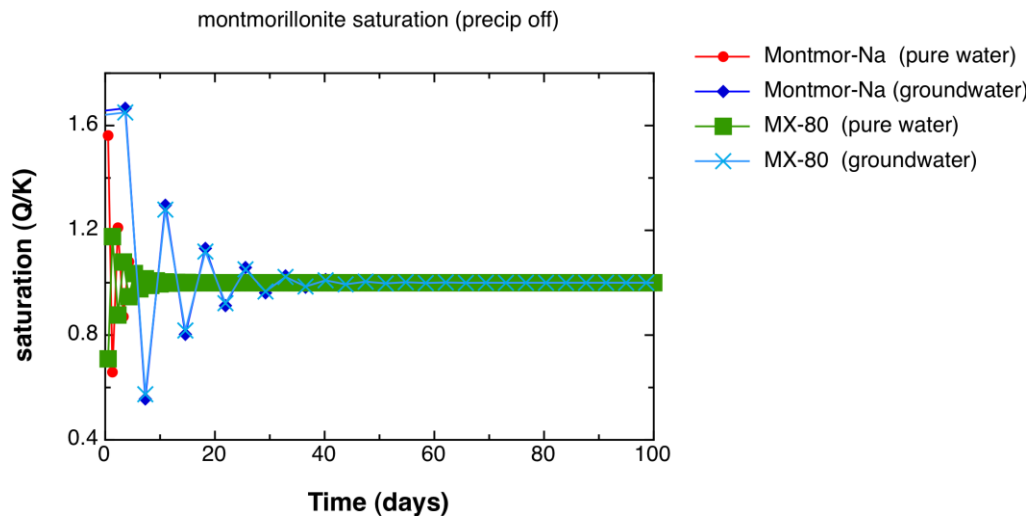


Figure 19 Degree of saturation of Na-montmorillonite and MX-80 smectite in simulations of reaction of bentonite with either pure water or Forsmark groundwater with precipitation of secondary minerals excluded.

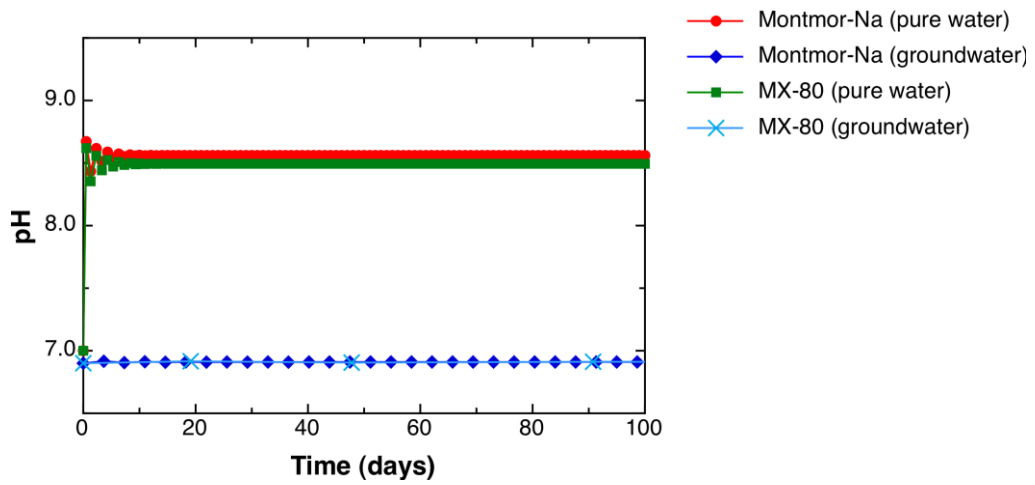


Figure 20 pH of fluids in simulations with bentonite in either pure water or Forsmark groundwater with precipitation of secondary minerals excluded.

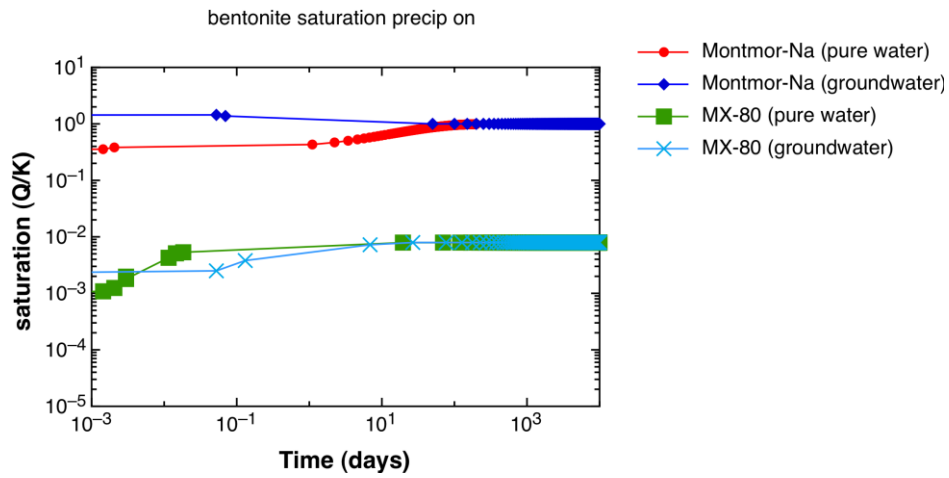


Figure 21 Degree of saturation of Na-montmorillonite and MX-80 smectite in simulations of reaction of bentonite in either pure water or Forsmark groundwater with precipitation of secondary minerals included.

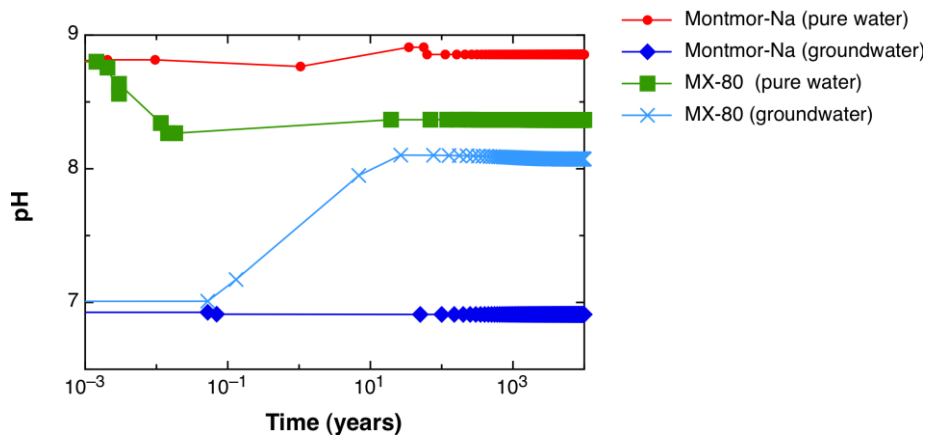


Figure 22 pH of fluids in simulations with bentonite in either pure water or Forsmark groundwater with precipitation of secondary minerals included.

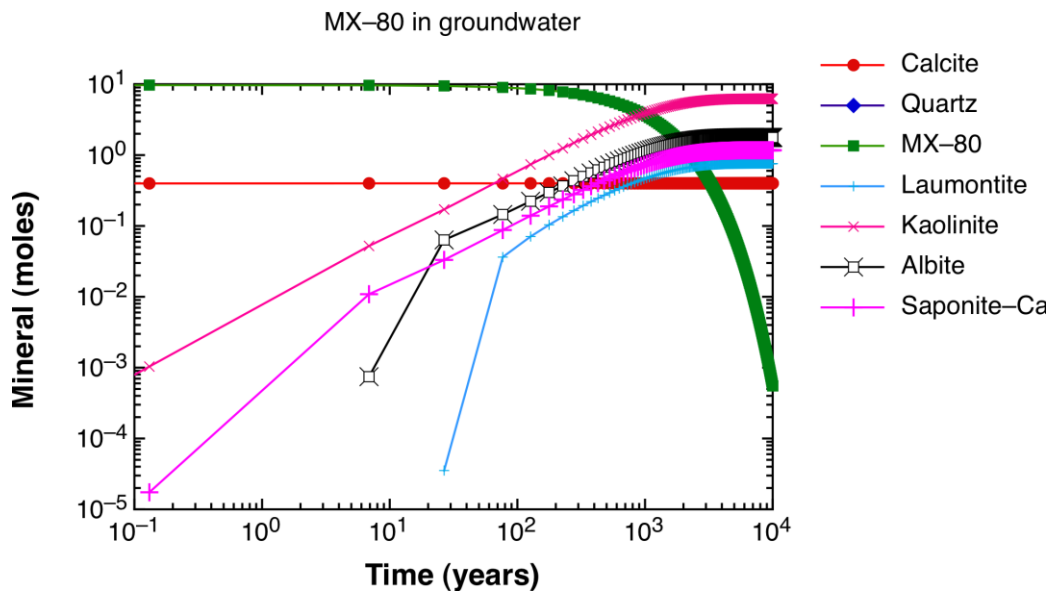


Figure 23 Secondary minerals precipitating in simulations with bentonite containing MX-80 smectite in Forsmark groundwater.

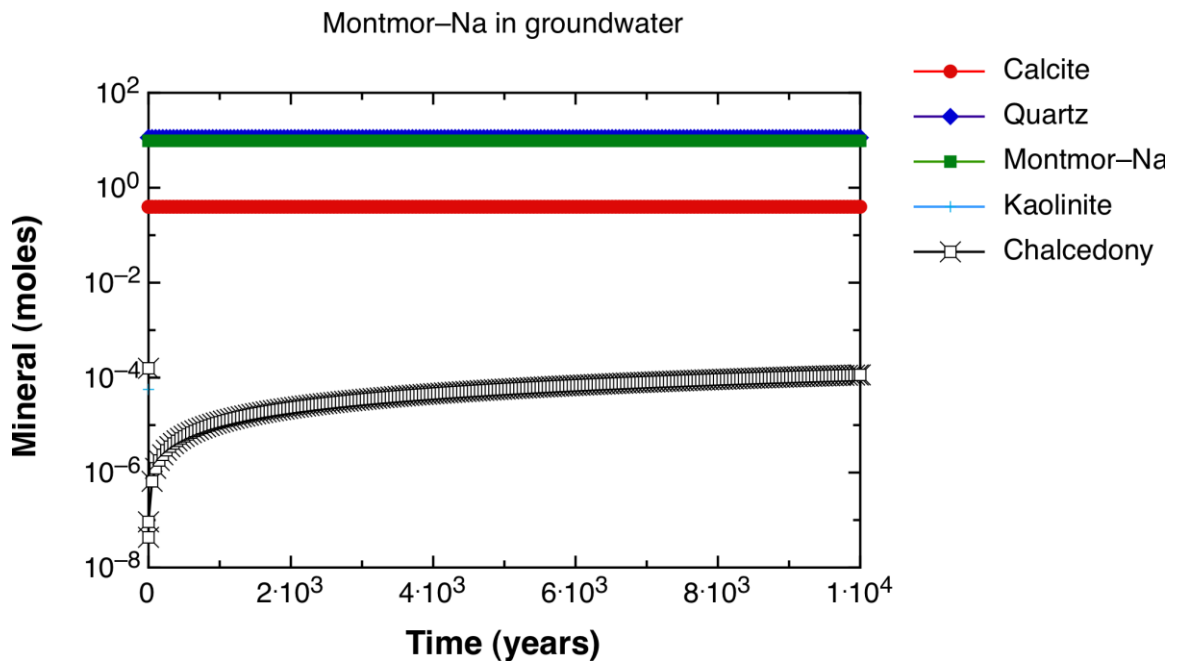


Figure 24 Secondary minerals precipitating in simulations with bentonite containing Na-montmorillonite in Forsmark groundwater.

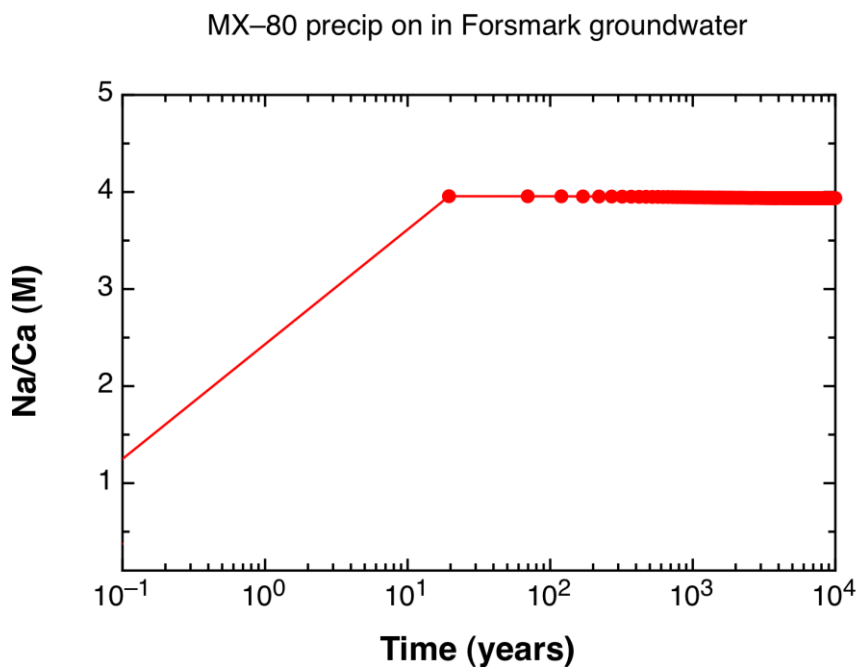


Figure 25 Effect of reaction of bentonite containing MX-80 smectite on Na/Ca ratio in the fluid in Forsmark groundwater.

4.3 Discussion

It can be seen from the above that time to equilibration and the alteration style of bentonite with Forsmark groundwater depends to a large degree upon the choice of thermodynamic data for montmorillonite:

- Data estimated using the ‘Vieillard Model’ [38] produced extensive alteration and postponement of equilibration until after 10 000 years.
- Data estimated by Wolery [39] showed rapid equilibration with Forsmark groundwater and minimal alteration of the initial bentonite.

Regardless of this issue, it seems that there is potential for the bentonite to be partially altered prior to onset of erosion and it should not be taken for granted that the initial Na-dominated condition of the montmorillonite will be preserved indefinitely.

5. Summary

Hydrochemical data obtained by SKB at Forsmark have been reviewed from a perspective of understanding the stability of smectite minerals under *in situ* (site) conditions. There are a number of relevant features:

- Calcium concentration in groundwaters increase with depth and are in the range 1000-2500 mg/L at repository depth (-500 m elevation), and reach 4 000 mg/L at -1000 m elevation. This implies a large resource of calcium ions at depths both at and beneath the potential repository horizon. The latter could be brought nearer the repository depth if groundwater up-coning occurs during repository operation.
- Mg concentrations are 0-250 mg/L at repository depth, but are uniformly low (< 25 mg/L) at depths below -700 m. Magnesium can also contribute to ion exchange reactions with montmorillonite to inhibit colloid formation.
- Groundwaters are saturated with calcite across all depth ranges studied, which together with mineralogical data indicates that calcite can provide a buffer for calcium ions in solution to mitigate against smectite colloid formation.
- Pore waters entrained in the rock matrix could be an additional source of divalent cations. However, data concerning cation concentrations and ratios are currently unavailable.

Mineralogical information for fracture fillings at depth at the Forsmark site has been reported in a series of SKB reports and papers. These data show a long history of water-rock reaction, from the Proterozoic to the present, in at least four discrete mineralisation events, ranging from temperatures as high as 250 °C for ‘Generations 1 and 2’, to less than 50 ° for late Palaeozoic to present minerals (‘Generation 4’). This latter generation is characterised by clay minerals and thin precipitates of calcite, but also minor amounts of goethite and pyrite, mainly associated with hydraulically-conductive fractures and fracture zones. Corrensite dominates and is a (Fe-Mg) mixed-layer chlorite-smectite mineral with some swelling properties. Although smectite is reported to occur at all depth levels at Forsmark, it is recorded as being ‘minor’ in abundance in comparison with corrensite, illite, saponite, and mixed-layer smectite-illite. Calcite is also present at all depth levels, but gypsum, dolomite, and siderite are absent throughout the system. Therefore, site mineralogical data show that smectite and calcite occur at all depths in Forsmark fractures, with no evidence for removal/dissolution by previous glacial episodes. This natural analogue implies that these minerals may not have been eroded/dissolved during previous glacial episodes.

Although SKB emphasise that groundwater compositions at Forsmark can be interpreted by simple mixing relationships alone, thermodynamic activity diagrams show that key parameters (pH, PCO_2 , Ca/Mg, Na/Ca, $SiO_{2(aq)}$) in Forsmark groundwaters may be controlled by reactions involving montmorillonite and saponite clays and calcite present in fracture infills. Therefore available thermodynamic data suggest that repository-depth Forsmark groundwaters are in equilibrium (steady-state) with montmorillonite and

saponite and these minerals may control pH, PCO_2 , Na/Ca and $SiO_{2(aq)}$ in groundwaters in the near-field. These reactions may thus buffer these parameters in any future intruding glacial meltwaters. This conclusion would not be evident from approaches assuming that mixing is the only process responsible for major element variations. $(Na^+)^2/Ca^{2+}$ activity ratios of most Forsmark groundwaters are < 0.05 , implying that any clay exchanger in equilibrium with these waters would be $> 90\%$ calcium end-member, and thus not in the stability field for sol formation.

The model analysis conducted in 2008-9, reacting MX-80 bentonite at high compaction density in 'batch' conditions has been repeated, extending the modelling to 2000 kg m^{-3} density, and introducing typical Forsmark groundwater as the reactant fluid. As demonstrated in a previous study [7], reaction of MX-80 both in pure water and in Forsmark groundwater proceeds to equilibrium extremely rapidly in the suppression of secondary mineral precipitation. However, the incorporation of (equilibrium) mineral growth in the simulations delays attainment of steady-state up to 10 000 years in the case of MX-80 smectite. Therefore modelling of the reaction of montmorillonite in the buffer with Forsmark groundwater shows a trend towards conversion of montmorillonite to saponite, suggesting that the buffer may be partially altered prior to glacial meltwater intrusion.

Further work is desirable to examine the effects of the introduction of the kinetics of growth of secondary minerals on these equilibration times.

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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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