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EFFECT OF CATION EXCHANGE ON MAJOR CATION CHEMISTRY IN THE LARGE SCALE REDOX EXPERIMENT AT ÄSPÖ

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ABSTRACT

Geochemical modeling was used to test the hypothesis that cation exchange with fracture-lining clays during fluid mixing in the Äspö Hard Rock Laboratory can significantly affect major element chemistry. Conservative mixing models do not adequately account for changes in Na, Ca and Mg concentrations during mixing. Mixing between relatively dilute shallow waters (e.g. HBH02) and more concentrated waters at depth (e.g. KA0483A) along fracture zones was modeled using the EQ3/6 geochemical modeling package. A cation exchange model was added to the code to describe simultaneously aqueous speciation, mineral precipitation/dissolution, and equilibration between a fluid and a cation exchanger. Fluid chemistries predicted to result from mixing were compared with those monitored from boreholes intersecting the fracture zone.

Modeling results suggest that less than 0.1 equivalent of a smectite exchanger per liter of groundwater is necessary to account for discrepancies between predictions from a conservative mixing model and measured Na and Ca concentrations. This quantity of exchanger equates to an effective fracture coating thickness of 20 μm or less given a fracture aperture width of 1000 μm or less. Trends in cation ratios in the fluid cannot be used to predict trends in cation ratios on the exchanger because of the influence of ionic strength on heterovalent exchange equilibrium. It is expected that Na for Ca exchange will dominate when shallow waters such as HBH02 are mixed with deeper waters. In contrast, Na for Mg exchange will dominate mixing between deeper waters.

1 INTRODUCTION

Predicting the chemical changes that result from excavating a repository below the groundwater table in granitic terrain is a major focus of the SKB geochemistry program. The modeling study presented here demonstrates that cation exchange can play a major role in controlling the fluid chemistry that results when groundwaters of differing composition mix due to flow induced by excavation of the HRL tunnel.

The major goal of this study was to assess whether an equilibrium cation exchange model could explain the composition of groundwater sampled from boreholes in the HRL tunnel. Given the consistency of the cation exchange hypothesis with observations, geochemical modeling was used to assess whether the quantity of exchanger necessary to match model results and observation was physically reasonable. The impact of mineral dissolution and precipitation on fluid chemistry was also evaluated. Finally, the compositions of exchanger phases expected to be in equilibrium with various Äspö groundwaters were predicted.

1.1 BACKGROUND

Äspö groundwaters can be divided into four groups based on major cation and anion chemistry and total chloride concentration /Laaksoharju, 1990/. In general, the groundwater becomes more saline with depth, varying from a Na-HCO_3 type with less than 300 mg/L Cl for near surface waters, to a Ca-Na-Cl type with greater than 6500 mg/L Cl for groundwaters from depths greater than 500 m.

Groundwater flow has been induced due to the intersection of the HRL tunnel with transmissive fracture zones. The predominantly downward movement of groundwater into the tunnel results in mixing between relatively dilute shallow waters and more concentrated waters found at the tunnel depth.

The Large Scale Redox Experiment /Banwart et al., 1992/ was designed to monitor the groundwater composition in a fracture zone before and during groundwater mixing. The primary objective of this experiment was to assess the changes in the groundwater composition and redox state that result from fluid mixing, and to test and develop models to describe the observed compositional variation.

Fluids were sampled for about 225 days from tunnel-based boreholes intersecting the transmissive fracture zone and from flow collected from fractures debouching into the tunnel at its roof. On the basis of this sampling period several observations germane to this report were noted /Banwart et al., 1992/:

- The concentrations of dissolved components reflect a large (>50%) input of shallow water.
- The concentrations of major dissolved ions reflect the dilution of deep older groundwater by shallow water.
- If a conservative mixing model involving two endmember fluids (shallow and native (pre-excavation)) is used to predict the composition of mixed groundwater, discrepancies between model predictions and observations are apparent for dissolved Ca, Mg, Na, and alkalinity (HCO_3^-). For Ca and Mg, predicted concentrations are significantly higher than measured concentrations; for Na and HCO_3^- the opposite is observed.

Three hypotheses have been put forward to explain the above discrepancies /Banwart et al., 1992/:

- During dilution of native groundwater by shallow water, Ca and Mg in the fluid exchanges for Na on exchange phases in the fractures of the transmissive zones.
- Dissolution of plagioclase feldspar causing an increase in alkalinity and precipitation of calcite occurs when shallow, dilute, CO_2-bearing groundwaters react with the rock during mobilization and mixing with groundwater at the tunnel level.
- A third groundwater source, anoxic marine sediment pore water, also contributes to the waters sampled at the tunnel level.

This paper describes testing of the hypothesis that cation exchange with fracture-lining clays during fluid mixing can account for discrepancies observed when using the conservative mixing model.

1.2 APPROACH

The approach taken to test and refine the cation exchange hypothesis involved the following steps.

- Following Banwart et al. /1992/, assume that groundwater sampled from the tunnel is derived from two sources; the native (tunnel depth) groundwater and a shallow groundwater.
- Simulate the mixing of the two groundwaters in the presence of a cation exchanger.
- Compare the simulation results with the observed compositions of groundwater sampled from the tunnel boreholes by assuming that Cl is conserved during mixing.
- If possible, adjust the quantity of cation exchanger in the simulation to give a good match between simulation results and observations.

The cation exchange model was then used to predict the composition of cation exchangers expected to coexist with various types of groundwaters from Äspö.

2 METHODS AND DATA

2.1 EQ3/6 MODELING

The geochemical modeling package EQ3/6 /Wolery et al., 1990; version 3245R116/, to which a cation-exchange model was added, was used with an associated thermodynamic data base (version DATA0R19) to simulate the mixing between two fluids (defined below). This version of EQ3/6 allows the simultaneous calculation of aqueous speciation in the fluid phase, mineral/fluid reactions (e.g. dissolution/precipitation), and equilibrium between a fluid and a cation exchanger. All reactions simulated were assumed to attain equilibrium instantaneously, i.e., no kinetic constraints were considered. Simulations were carried out assuming a groundwater temperature of 10 °C.

2.1.1 Simulating fluid mixing using EQ3/6

The limitations of EQ3/6 require the process of fluid mixing to be simplified. Mixing of shallow and native groundwaters was approximated by the following sequence:

a) x liters of shallow groundwater are added to y liters of native groundwater to form a mixed groundwater ($x+y=1$).

b) z equivalents of a cation exchanger whose composition is in equilibrium with the deep groundwater are added to the mixed groundwater.

c) Aqueous and exchange equilibria are allowed to occur; supersaturated phases are allowed to precipitate.

d) The compositions of the exchanger and resulting equilibrium fluid are noted.

e) Steps a to d are repeated for differing values of x and y so as to span the range in composition from shallow to deep groundwaters.

The above conceptual process translates into the following EQ3/6 modeling steps:

a) A preliminary EQ3 run is made to determine the composition of an exchanger that would be in equilibrium with the deep groundwater.

b) An EQ3 run is used to speciate the deep groundwater in the presence of z equivalents of exchanger (with composition defined in (a)) to define the starting equilibrium mixture.

c) An EQ6 run is made in which an increment of fluid with the composition of the shallow groundwater is added to the starting mixture while simultaneously removing an equal increment of fluid that has the composition of the deep groundwater. Following each incremental addition and removal, the fluid and the cation exchanger are re-equilibrated; if necessary, phases that may be supersaturated are "precipitated".

d) Steps b and c are repeated for each value of z considered.

The above conceptual model of fluid mixing is a simplified approximation of the actual process that is occurring at Äspö. Inherent to this simplification is the assumption that the shallow groundwater undergoes no compositional change (i.e., no reaction with its surroundings) prior to mixing with the native groundwater.

2.1.2 Cation exchange modeling using EQ3/6

A cation exchange model employing the Vanselow convention /Sposito, 1981/ was used for the simulations. According to the Vanselow convention, the thermodynamic activity of the exchanger component is numerically equal to the mole fraction of the exchange cation on the exchanger. A binary exchange reaction according to this convention can be written as

$$\text{Na-Z} + 1/2\ \text{Ca}^{2+} = 1/2\ \text{Ca-Z}_2 + \text{Na}^{+},$$

where Z signifies one equivalent of exchanger. Details of the implementation of this option in EQ3/6 and examples of its application may be found in Viani and Bruton / 1992a,b/.

The data required to simulate cation exchange using EQ3/6 are: 1) the quantity of exchanger (equiv/kg of water); 2) binary exchange energies for cation pairs of interest (kcal/equiv); and 3) the initial composition of the exchanger (mol-% or equiv-%).

To predict the composition of an exchanger phase that would be in equilibrium with a specific groundwater composition, an EQ3 simulation is run in which a trace quantity of exchanger (~ 10^{-14} equiv) is allowed to equilibrate with the fluid. This approach allows the equilibrium composition of the exchanger to be determined without significantly perturbing the composition of the fluid phase. Initial compositions of the exchangers used for the fluid mixing simulations and for predicting the variation in exchanger composition with depth for the KAS02 borehole were determined in this manner.

The exchanger phase used for the simulations was assumed to have the cation exchange properties of a smectite. Binary exchange energies (Table 2-1), defined for reactions as written above, were taken from Fletcher and Sposito /1989/.

Table 2-1. Cation exchange energies for smectite(1)

Exchange Reaction	Exchange Energy, kcal/equiv
Na --> 0.5 Ca(2)	-0.116
Na --> 0.5 Mg	-0.116
Na --> 0.5 Sr	-0.116
Na --> K	-0.348
Na --> Li	0.030
Na --> H	0.030

(1) Data from Fletcher and Sposito /1989/ except for Na --> H which was assumed to equal the value for Na --> Li. Note: this data is strictly accurate at 25 °C only. It was assumed that, for the purposes of this simulation, the variation of exchange energy with temperature is a second order effect.

(2) Na --> 0.5 Ca signifies the conversion of one equivalent of a Na-smectite to one equivalent of a Ca-smectite.

2.2 GROUNDWATER DATA

The groundwater composition data used to define endmembers used in the mixing model and to compare with simulation results were taken from Tables 1-5 in Appendix 1 of Banwart et al. /1992/. The shallow and native groundwaters used as the two components of the mixing model were the same as those used by Banwart et al. /1992/: samples HBH02-910912 and KA0483A-910312, respectively. Fluid compositions predicted from the mixing modeling runs were compared with compositions reported for groundwater samples collected from the three boreholes drilled into the fracture zone from the HRL side tunnel (KR0012B, KR0013B, and KR0015B) and for samples collected from the inflow from the tunnel roof (YA0513T). Only samples for which analyses of Cl, Na, K, Ca, and Mg were reported were used to compare with the simulation results.

Groundwater compositions used to predict exchanger compositions in equilibrium with groundwaters from borehole KAS02 were taken from data reported by Smellie and Laaksoharju /1992; Table 6.3/.

In order to simulate the mixing of the shallow and native endmember fluids using EQ3/6, several assumptions were made, as summarized in Table 2-2.

Table 2-2. Assumptions made in simulating mixing between shallow and native endmembers using EQ3/6.

Groundwater	Assumptions		
	Charge balance	Eh, mV	Other
HBH02 910912 (shallow)	An imbalance of 27% of the total charge was satisfied by increasing HCO_3^- from 114 to 238 mg/L.(1)	851(2)	The log K of the hydrolysis reaction for the strontianite endmember of the calcite solid-solution was augmented by 2.6 units.(3)
KA0483A 910312 (native)	An imbalance of -0.67% of the total charge was satisfied by reducing Cl^- from 4890 to 4827 mg/L.	-300(4)	The species CH_4(aq), $CH_3CO_2^-$, C, $S_2O_3^{--}$, $S_4O_6^{--}$, $S_5O_6^{--}$, and HS^- were suppressed.(5) Strontianite log K adjusted as above.

(1) Charge balance as calculated by EQ3/6. This sample probably lost CO_2 during the month-long period between sampling and analysis of dissolved inorganic carbon /Banwart et al., 1992/. The adjusted HCO_3^- value results in a log fCO_2 of -1.54 at this temperature which is in the range calculated for other shallow water samples from HBH01 and HBH02 /Banwart et al., 1992; Appendix 2/.

(2) It was assumed that the redox state of the shallow water was controlled by equilibrium with atmospheric oxygen (log fO_2 = -0.7) as assumed for modeling the breakthrough of dissolved oxygen /Banwart and Gustafsson, 1991/.

(3) In order to model the potential for Sr incorporation into a calcite solid solution, the log K of the hydrolysis reaction of strontianite in DATA0R19 was adjusted to make it consistent with the free energy of strontianite with a calcite structural type as given by Sverjensky / 1984/.

(4) This value was chosen because the Eh of deep groundwaters at Äspö are expected to range from -250 to -350 mV /Banwart et al., 1992/.

(5) The carbon species were suppressed because, although energetically favored at this Eh, the conversion of carbonate species to methane, acetate, and elemental carbon is kinetically inhibited. The reduced sulfur species were suppressed because, although the redox state is highly reducing, measurements have shown that the bulk of the dissolved sulfur is SO_4^{--}/Banwart et al., 1992/.

2.3 SIMULATION RUNS

The simulations that were made using EQ3/6 under the assumptions above are summarized in Table 2-3.

Table 2-3. Summary of simulations involving cation exchange.

Simulation	Calculation type	Exchanger amount, equiv/kg of H_2O	Precipitation considered(1)	Calcite dissolution considered
Exchanger composition (HBH02, KA0483A, KAS02)	EQ3	trace	no	no
Fluid mixing (HBH02 + KA0483A)	EQ3 -> EQ6	0.06	yes	no
		0.06	yes	yes(2)
	EQ3 -> EQ6	0.08	yes	no
	EQ3 -> EQ6	0.10	yes	no
		0.10	yes	yes

(1) Supersaturated solids (except graphite and dolomite) were allowed to precipitate.

(2) Runs in which a reservoir of calcite is allowed to maintain saturation with the groundwater during mixing, thus allowing dissolution of calcite to contribute to dissolved Ca and HCO_3.

3 RESULTS

3.1 PREDICTED EXCHANGER COMPOSITIONS

Results of simulations to predict the composition of an exchanger with the properties of a smectite in equilibrium with waters from HBH02, KA0483A and KAS02 are shown in Table 3-1. Two observations stand out. The "shallow" exchanger differs markedly from all of the other predictions, because it is almost completely Ca and Mg saturated. For the remainder of the waters considered, Ca shows relatively little variation, but Na and Mg exhibit opposite trends with depth. Exchangeable Mg is predicted to be almost absent at depth, but significant in the shallower zones. The difference between the predicted exchanger compositions for the 46 m separating the shallow and native waters (stippled rows) is much more dramatic than the change predicted for the next 800+ m. On the basis of these data one could infer that Na for Ca exchange might predominate during mixing of the upper two groundwaters, but that Na for Mg exchange might predominate for mixing between deeper waters.

Predictions of exchanger composition for the KAS02 waters make it clear that trends in cation ratios in the fluid may not follow trends in cation ratios on the exchanger (Figure 3-1). A major reason for this behavior is the strong influence of ionic strength on binary *heterovalent* exchange equilibria. In general, at a constant ratio of the ions in the solution phase, an increase in ionic strength will result in an increase in the lower valence ion on the exchanger /Sposito, 1981/. This effect will be most evident for mixing between very dilute fluids (ionic strength < 0.01 M) and concentrated

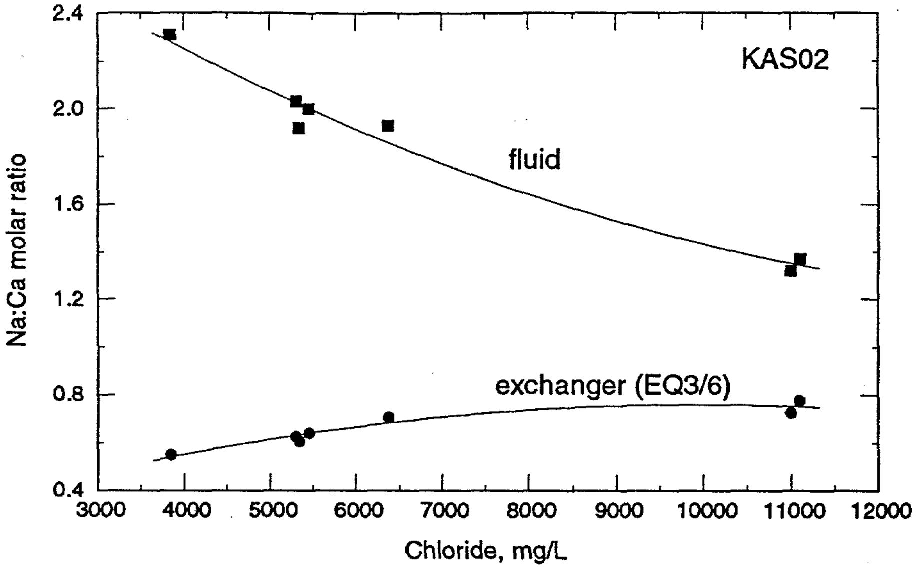

Figure 3-1. Variation in the Na:Ca ratio in groundwater sampled from KAS02 (solid squares) and ratios predicted for a coexisting exchanger (solid circles) versus chloride concentration.

Table 3-1. Composition of exchanger predicted to be in equilibrium with HBH02 (shallow), KA0483A (native), and KAS02 groundwaters.

Groundwater		Predicted exchanger composition, equiv-%			
Borehole	Depth, m	Na	Ca	Mg	Remainder[(1)]
HBH02-910912	24	0.58	88.11	11.05	0.26
KA0483A-910312	70	19.46	66.65	13.12	0.77
KAS02	202 - 214	19.33	70.53	9.01	1.13
KAS02	308 - 344	22.10	70.33	6.72	0.85
KAS02	314 - 319	21.51	71.14	6.53	0.82
KAS02	463 - 468	22.72	70.76	5.62	0.91
KAS02	530 - 535	25.11	70.98	3.02	0.89
KAS02	802 - 924	25.97	71.65	1.50	0.88
KAS02	860 - 924	27.49	70.58	1.10	0.83

(1) Sum of K, Li, Sr, and H.

fluids.

3.2 FLUID MIXING SIMULATIONS

3.2.1 Cation exchange and solution composition

An estimate of the quantity of exchanger necessary to account for the discrepancy between predictions using the conservative mixing model and measured Na and Ca concentrations was made using data for borehole KR0012B from Banwart et al. /1992/. Banwart et al. /1992/ used this data to illustrate the results of the conservative mixing model in their Figure 6-7. The data set spans about 81 to 86% shallow water input. The predicted exchanger compositions in Table 3-1 were used to make initial estimates of the required exchanger quantities used in the EQ3/6 simulations of fluid mixing.

Less than 0.1 equiv of exchanger per kg of water was necessary to match this set of data (Figure 3-2). A similar result was calculated for Mg (Figure 3-3). These figures

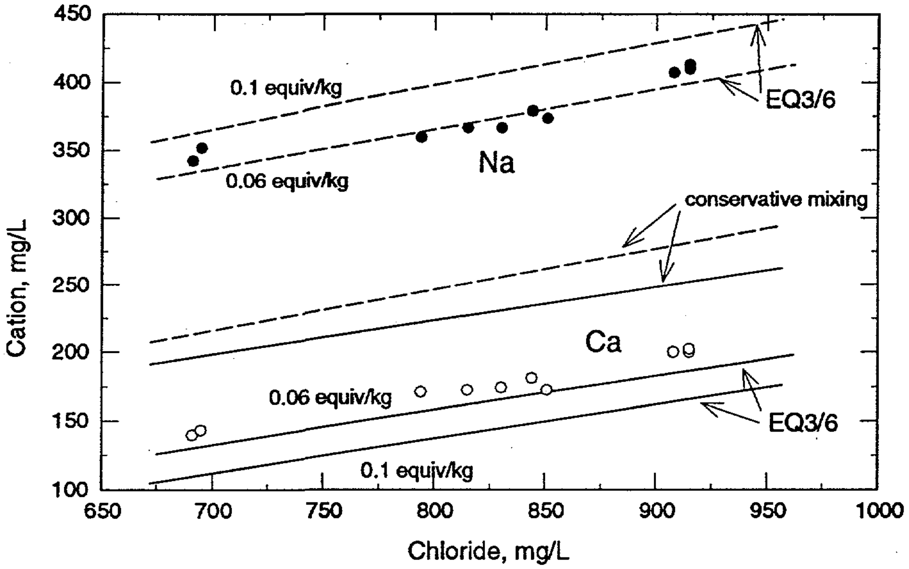

Figure 3-2. Measured concentrations of Na (solid circles) and Ca (open circles) in selected samples from KR0012B plotted against chloride concentration. Also shown are predictions (lines: Na - dashed, Ca - solid) made with a conservative mixing model and generated from EQ3/6 calculations that incorporate cation exchange equilibrium assuming 0.06 and 0.1 equiv exchanger/kg of H_2O.

show that the measured fluid compositions are consistent with the occurrence of simultaneous mixing and cation exchange. As the quantity of the exchanger in the simulation increases, the predicted concentrations of Ca and Mg decrease and that of Na increases because of increased Ca and Mg exchange for Na. This behavior, and

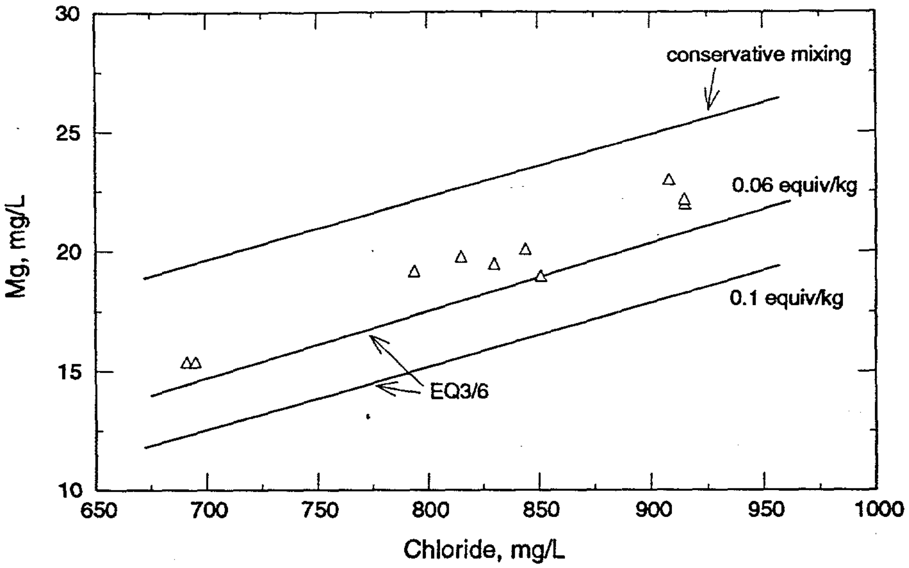

Figure 3-3. Measured concentrations of Mg (triangles) in selected samples from KR0012B plotted against chloride concentration. Also shown are predictions (lines) made with a conservative mixing model and generated from EQ3/6 calculations that incorporate cation exchange equilibrium assuming 0.06 and 0.1 equiv exchanger/kg of H_2O.

the fact that about the same quantity of exchanger is necessary to match the measured fluid concentrations for all three cations, suggest that the cation exchange hypothesis is consistent with the observations.

The EQ3/6 predictions are relatively sensitive to the amount of exchanger used in the simulation. A similar calculation for the entire data set reported by Banwart et al. /1992/ that encompasses a wider range in mixing and a longer time period (Figure 3-4), shows that the cation exchange model captures the trend of the measured data, but also suggests that although 0.06 equiv was a better match for the samples near 81-86% shallow water input (Figure 3-2), 0.1 equiv may be a better match for the data as a whole.

Inferences drawn from comparing measured ***fluid compositions*** with results of simulating fluid mixing that includes mass transfer between fluid and exchanger (i.e. an EQ6 calculation) can differ from what one would infer from the predicted equilibrium ***exchanger compositions*** (i.e. an EQ3 calculation; Table 3-1). Based on the predicted exchanger compositions for the shallow and native groundwaters in Table 3-1, one might expect fluid mixing to be accompanied by a increase in the concentration of Mg in the fluid phase, relative to conservative mixing. Instead, the opposite is predicted to occur when the fluids are allowed to react during mixing as simulated by an EQ6 calculation (Figure 3-3).

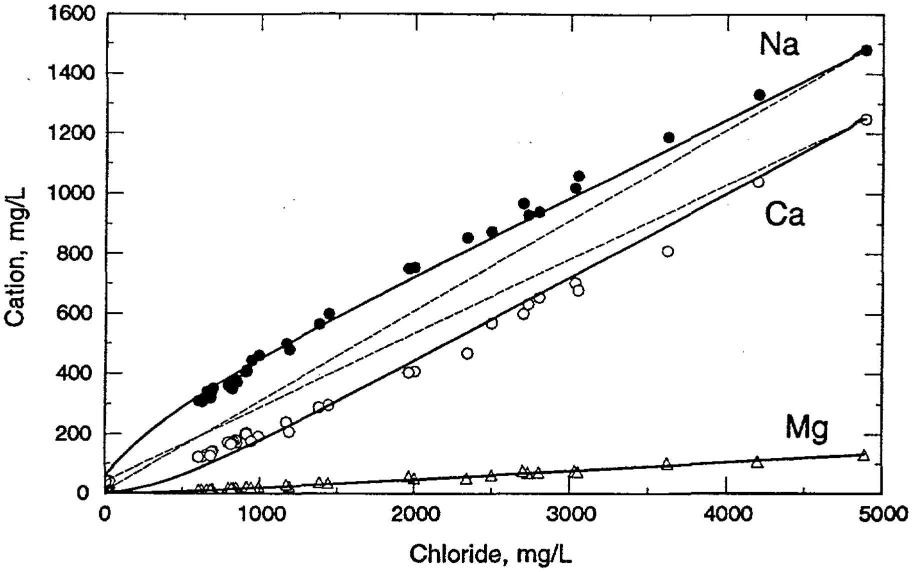

Figure 3-4. Measured concentrations of Na (solid circles), Ca (open circles), and Mg (open triangles) in redox experiment water samples are compared to predictions made with a conservative mixing model (dashed lines) and generated from EQ3/6 calculations (solid lines) for 0.1 equiv exchanger/kg of H_2O.

3.2.2 Secondary phases

During simulation of fluid mixing, EQ6 calculations predicted the precipitation of small quantities of hematite, pyrolusite, quartz, and calcite. The precipitation of hematite and pyrolusite reflects the input of oxygenated shallow water, conversion of Fe(II) to Fe(III) and Mn(II) to Mn(IV), and consequent precipitation of relatively insoluble oxides. A small quantity of quartz is predicted to precipitate throughout the mixing process, and a small quantity of calcite is predicted to precipitate early in the mixing process (<<1% shallow water input).

The effect of precipitation of these phases on the cation exchange equilibria is negligible because the major cation and anion concentrations are not significantly affected by the precipitation of these phases. It is problematic whether any of these phases would precipitate in the time frame of the redox experiment owing to the low temperatures and relatively benign chemical conditions involved. In particular, kinetic constraints would inhibit quartz from precipitating.

3.2.3 Effect of imposition of calcite equilibrium on simulation results

In order to assess the effect that dissolution of fracture-lining calcite might have on predicted fluid compositions, an EQ6 calculation was made in which a reservoir of calcite was allowed to dissolve during the simulated mixing. For 100% shallow water input, approximately 140 mg of $CaCO_3$ was predicted to dissolve per liter of mixed groundwater; owing to mixing of calcite-undersaturated shallow water with the nearly-saturated deeper water.

The net effect of allowing calcite to dissolve is to increase the predicted concentrations of *both* Ca and Na in solution by about 30 and 40 mg/L, respectively (Figure 3-5). This is in marked contrast to the effect of adding or removing ion exchanger which causes predicted Na and Ca concentrations to move in opposite directions. For this particular data set the imposition of calcite equilibrium results in better agreement between prediction and observation for Na, but the match is made worse for Ca (Figure 3-5). For other subsets of the data (not shown) the opposite occurs owing to the scatter of data illustrated in Figure 3-4.

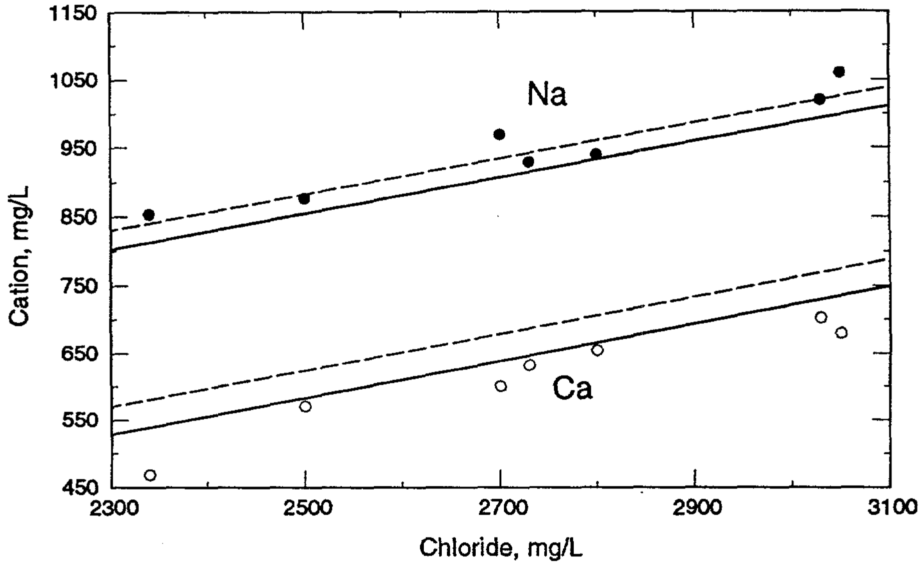

Figure 3-5. Measured concentrations of Na (solid circles) and Ca (open circles) in selected redox experiment water samples are compared to predictions made with EQ3/6 calculations for 0.1 equiv exchanger/kg of H_2O with (dashed lines) and without (solid lines) calcite equilibrium imposed.

The imposition of calcite equilibrium will also impact HCO_3 concentrations in solution. The conservative mixing model underpredicts HCO_3 concentrations by a large amount /Banwart et al., 1992/. Values for HCO_3 predicted using EQ3/6 assuming that the shallow groundwater HCO_3 concentration is equal to that estimated based on charge balance (Table 2-2) fall along a straight line that passes through the mixed groundwater data set (Figure 3-5).

The EQ3/6 predictions seem to support a conservative mixing model for HCO_3 in which the shallow endmember has a HCO_3 concentration of about 240 mg/L. The reported HCO_3 data for the shallow wells seem to be low (Figure 3-5); apparently due to loss of CO_2 prior to analysis of dissolved inorganic carbon /Banwart et al., 1992/. Hence, a conservative mixing model based on the measured values is bound to

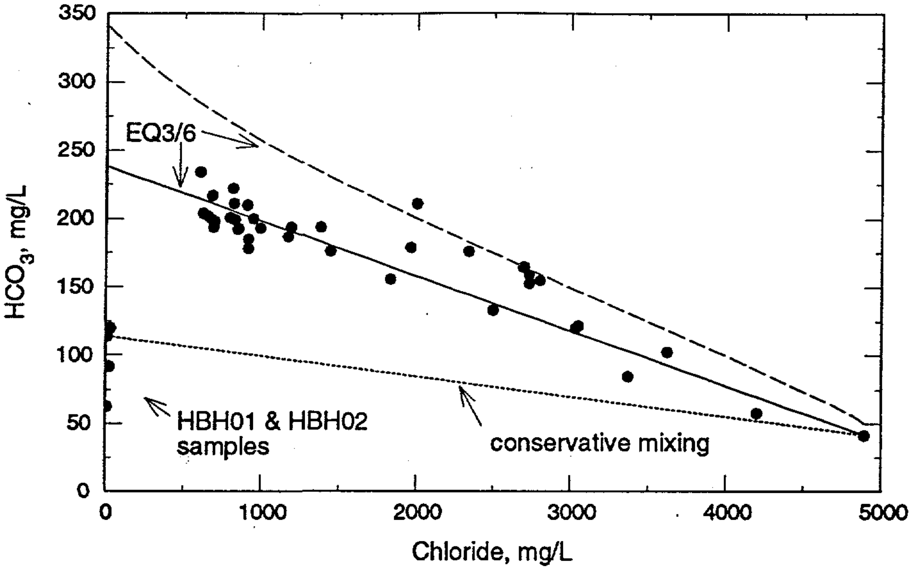

Figure 3-6. Measured concentrations of HCO_3 (solid circles) in redox experiment water samples are compared to predictions made with EQ3/6 calculations for 0.1 equiv exchanger/kg of H_2O with (dashed line) and without (solid line) calcite equilibrium imposed. Conservative mixing model prediction based on reported HCO_3 for HBH02-910912 and KA0483A-910312 is also shown (dotted line).

yield discrepancies that do not appear when HCO_3 values based on charge balance are utilized.

The imposition of calcite equilibrium results in predicted HCO_3 concentrations significantly higher than observed, especially at high ratios of shallow water input. This results from the predicted dissolution of calcite by relatively low-pH shallow water during mixing. It does not appear necessary to invoke precipitation of calcite as a means to explain the discrepancy between the conservative mixing model and the measured HCO_3 concentrations.

In summary, imposition of calcite equilibrium weakens the agreement between measurement and simulation results for Na, Ca, and HCO_3. Fluid flow may be too rapid to maintain equilibrium between fracture filling calcite and the shallow water diluent given the sluggish kinetics of mineral dissolution under low temperature, near-neutral pH conditions. It is also possible that the primary fluid pathway consists of fractures that do not contain significant quantities of calcite.

4 DISCUSSION

In order to assess whether the quantity of exchanger used to simulate fluid mixing is physically reasonable, the thickness of a layer of cation exchanger on a fracture necessary to contribute the required exchange capacity to one liter of groundwater was calculated as a function of fracture aperture (Figure 4-1). The fracture was assumed

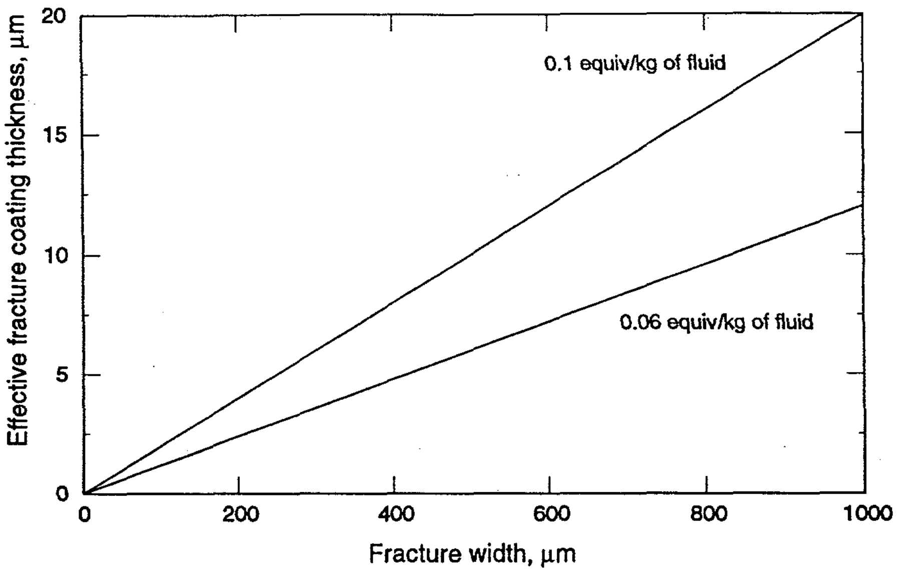

Figure 4-1. Effective thickness of fracture coating (exchanger) vs. fracture width required to allow 0.1 and 0.06 equiv exchanger to contact one liter of water contained within the fracture. (Assumptions: exchanger density = 2.5 kg/L; capacity = 1.0 equiv/kg)

to be completely filled with fluid. The estimated coating thickness (5 -20 μm) appears to be reasonable, given the types and quantities of fracture-filling minerals identified at Äspö /Tullborg et al., 1991/.

The minerals that have been identified in fractures at Äspö include small, but significant, quantities of clay minerals /Tullborg et al., 1991; Banwart et al., 1992/. Illite and smectite/illite have been identified and would be expected to be the major contributors to the exchange capacity of the fracture system. Sericitized feldspars and weathered biotites have also been identified and may contribute to the available exchange capacity of the fracture network.

The coating thickness necessary to yield a given exchange capacity varies inversely with the capacity of the exchanger; e.g., illite (0.25 equiv/kg) fracture coatings would need to be 3-5 times thicker than smectite (1.0 equiv/kg) coatings to yield the same overall exchange capacity in the fracture. For Na, Ca, and Mg, the identity of the exchanger phase is not critical because the exchange energies for these elements do not vary greatly for the exchangers identified at Äspö. However, the exchange behaviors of smectite, illite, weathered biotite, and sericite with respect to K, Cs, and Rb will be significantly different. Modeling the partitioning of these elements will require inclusion of the exchange energies and the exchanger masses and compositions appropriate to the identified fracture mineral phases.

Although the quantity of exchanger necessary to match the observed fluid compositions appears small, the amount of exchanger can serve as a significant reservoir of readily available cations; i.e., cations whose participation in chemical reactions is not limited by dissolution kinetics. Table 4-1 lists the ratios of the mass of cations associ-

Table 4-1. Ratio of predicted mass of cation on exchanger[(1)] to mass of cation in fluid for three groundwaters at Äspö

Cation	Shallow (HBH02)	Native (KA0483A)	Deep (KAS02-860 m)
Na	1.3	0.30	0.21
Ca	41.7	1.07	0.37
Mg	41.7	1.21	0.45

(1) Calculations assume 0.1 equiv/kg of H_2O.

ated with the exchanger to the mass in the fluid. For the shallow groundwater, most of the Ca and Mg, and a majority of the Na are associated with the exchanger, while in the native and deep groundwaters, a significant fraction of the cations are associated with the exchanger phases.

The effect of cation exchange on fluid mixing is likely to be most significant for relatively dilute waters. This finding coupled with the strong effect of ionic strength on heterovalent exchange may explain why ion exchange seems to play an important role in the mixing of waters at Äspö, but may not play a significant role in the mixing or evolution of concentrated groundwaters at Hästholmen, Finland /Nordstrom, 1989/ .

An alternative hypothesis to explain the deviations between predictions from the conservative mixing model and the observed fluid chemistry invokes dissolution of Na-feldspar by CO_2-bearing shallow groundwater, an attendant increase in alkalinity, and precipitation of calcite /Banwart et al., 1992/. Dissolution of Na-feldspar occurs slowly at low temperature /Knauss and Wolery, 1986/, and it seems unlikely, given the rapid mobilization of groundwater in the redox zone, that sufficient dissolution of feldspar could occur at 10 °C to raise the Na concentration high enough to account for the differences between the conservative mixing model and the experimental results.

Modeling results suggest that the deviations in HCO_3 from the conservative mixing model may be due to an unrealistically low HCO_3 value used for the shallow end-member. Finally, calculations suggest that in the absence of kinetic constraints, dissolution rather than precipitation of calcite would be most likely to occur. Simulations in which Na-feldspar is allowed to react during fluid mixing (with and without cation exchange) would have to be undertaken to directly address this hypothesis.

5 CONCLUSIONS

Conclusions pertinent to the redox zone experiment and cation exchange in general drawn from this geochemical modeling study are as follows:

- A cation exchange process is sufficient by itself to explain the observed non-conservative behavior of Na, Ca, and Mg during the mixing of shallow and native groundwater at the HRL, assuming that only two waters are involved in the mixing. The results of this work support the hypothesis of cation exchange put forward by Banwart et al. /1992/.

- The quantity of exchanger (less than 0.1 equiv/L of groundwater) necessary for the simulation to match the observed fluid data is physically reasonable, and is consistent with the observed fracture mineralogy.
- Dissolution of calcite does not appear to play a significant role in controlling either dissolved Ca or dissolved HCO_3 levels. Precipitation of calcite during mixing appears unlikely.
- The ratio of cations in the fluid phase may not vary in the same manner as cation ratios on exchanger phases in equilibrium with the fluid. Hence, they cannot be used to predict exchanger compositions.
- The influence of cation exchange on fluid mixing will be most significant when one fluid has a low ionic strength.
- Cation exchangers can be a significant reservoir of readily available cations even when present in relatively small quantities.

This preliminary study establishes cation exchange as a viable mechanism for controlling the evolution of groundwaters in the redox zone experiment. Field sampling and testing to measure the exchange capacity and exchanger compositions in HRL rocks will be necessary to test our predictions. To advance our understanding of the chemistry of groundwater at the HRL, further modeling will be required to include additional exchanger phases with appropriate exchange energies, and to more realistically simulate redox processes and dissolved organic carbon speciation and oxidation.

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