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Assessing the Role of Cation Exchange in Controlling Groundwater Chemistry During Fluid Mixing in Fractured Granite at Äspö, Sweden

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**ASSESSING THE ROLE OF CATION EXCHANGE IN
CONTROLLING GROUNDWATER CHEMISTRY DURING
FLUID MIXING IN FRACTURED GRANITE AT ÄSPÖ,
SWEDEN**

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ABSTRACT

Geochemical modeling was used to simulate the mixing of dilute shallow groundwater with deeper more saline groundwater in the fractured granite of the Redox Zone at the Äspö underground Hard Rock Laboratory (HRL). Fluid mixing simulations were designed to assess the role that cation exchange plays in controlling the composition of fluids entering the HRL via fracture flow. Mixing simulations included provision for the effects of mineral precipitation and cation exchange on fluid composition. Because the predominant clay mineral observed in fractures in the Redox Zone has been identified as illite or mixed layer illite smectite, an exchanger with the properties of illite was used to simulate cation exchange. Cation exchange on illite was modeled using three exchange sites, a planar or basal plane site with properties similar to smectite, and two edge sites that have very high affinities for K, Rb, and Cs. Each site was assumed to obey an ideal Vanselow exchange model, and exchange energies for each site were taken from the literature.

The predicted behaviors of Na, Ca, and Mg during mixing were similar to those reported in a previous study in which smectite was used as the model for the exchanger /Viani and Bruton, 1994/. The trace elements Cs and Rb were predicted to be strongly associated with the illite exchanger, and the predicted concentrations of Cs in fracture fill were in reasonable agreement with reported chemical analyses of exchangeable Cs in fracture fill. The results of the geochemical modeling suggest that Na, Ca, and Sr concentrations in the fluid phase may be controlled by cation exchange reactions that occur during mixing, but that Mg appears to behave conservatively. There is currently not enough data to make conclusions regarding the behavior of Cs and Rb.

INTRODUCTION

Previous modeling has suggested that cation exchange may explain the observed variations in Na, Ca, and Mg in groundwaters sampled during the Äspö Redox Zone Experiment at the Hard Rock Laboratory (HRL) /Viani and Bruton, 1994/. In the previous study it was shown using geochemical modeling that cation exchange reactions occurring during the mixing of shallow groundwater (< 15m) and native groundwater (at HRL tunnel depth, ~ 70m) are a plausible source for Na and sink for Ca and Mg. The cation exchanger used in the simulations was assumed to have the exchange properties of smectite. Approximately 0.1 equivalent of exchange capacity per liter of groundwater was required for the simulated mixing results to match the observed fluid compositions. This quantity of exchanger was thought to be consistent with the observed fracture mineralogy and mineral abundances.

The major goal of the present study is to extend our previous work by:

- Using the exchange properties of illite to model cation exchange when simulating groundwater mixing in the Redox Zone. Illite is more consistent with the observed fracture mineralogy than is smectite.
- Comparing simulation results with the complete Redox Zone water chemistry data base, rather than the more limited data set reported in Banwart et al. /1992/ that was used for the previous comparison (data was limited to the initial 7.5 months of the 42 month sampling period).
- Testing the effect that cation exchange equilibrium has on the partitioning of minor and trace elements (Cs, Rb, and Sr) between groundwater and fracture minerals.

1.1

APPROACH

For the cations Na, Ca, Mg, and Sr, the approach taken to test the effect of cation exchange on elemental concentrations during mixing is the same as that used previously /Viani and Bruton, 1994/, namely:

- Assume that groundwater sampled at the HRL tunnel is derived from two sources: the native and shallow groundwater.
- Simulate the mixing of the two groundwaters in the presence of a cation exchanger that is initially in equilibrium with the native groundwater.
- Compare simulation results with observed compositions of groundwater sampled from the tunnel boreholes and with compositions calculated assuming that Cl is conserved during mixing.

Because of the limited quantity of trace element data for Redox Zone groundwaters and fracture minerals, the effect of groundwater mixing on trace element concentrations could not be adequately tested. However, geochemical

modeling was used to predict the exchangeable trace element composition of illite in equilibrium with various groundwaters in the Redox Zone.

METHODS AND DATA

2.1

EQ3/6 MODELING

The geochemical modeling was performed using the version of EQ3/6 /Wolery et al., 1990; version 3245R116/ and thermodynamic data base used by Viani and Bruton /1994/. Simulations were carried out assuming 0.1 equivalents of exchanger per liter of groundwater and a temperature of 10 °C. The conceptual model of fluid mixing imposed by EQ3/6 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, and that mixing occurs only in the presence of a cation exchanger that is initially in equilibrium with the native groundwater.

2.1.1

Cation exchanger used in EQ3/6 simulations

In Viani and Bruton's /1994/ study, the exchanger phase was assumed to be a smectite that contained a single type of exchange site. Analysis of fracture-filling minerals in the Redox Zone has identified the layer silicates chlorite, illite-rich interstratified smectite/illite, and sericite /Tullborg, 1995/. A survey of cation exchange energies /Bruggenwert and Kamphorst, 1982/ reveals that for the cations Ca, Mg, Sr, and Na, there is not a large difference in the exchange properties for different layer silicates. In contrast, for K, Rb, Cs, and NH_4 , the energies for cation exchange are strongly dependent on mineral type, especially when trace quantities of these cations are involved. Based on the observed mineralogy, illite was chosen as the most appropriate exchanger to use to simulate the exchange components of the fracture fill.

Illite differs from smectite by having a smaller cation exchange capacity (CEC) and having multiple (as many as three) exchange sites that differ markedly in their exchange energies /Brouwer et al., 1983/. The major portion of the exchange capacity of illite is associated with the outer or basal planes of the illite crystal (planar site; Figure 2-1). This site has exchange energies similar to smectite (Table 2-1); exchange of Na and divalent cations are almost

Figure 2-1. Schematic of illite crystallite or illitic region of interstratified smectite/illite showing postulated relationship between site type and crystallite structure.

identical to that in smectite. The other sites on illite (sites I & II) are present in relatively small amounts and are associated with the edges of the illite crystallites ("frayed edge sites") /Brouwer et al., 1983/. These two sites show a high affinity for monovalent cations, especially those with small hydration energies (e.g., K, Rb, Cs; Table 2-1). Binary exchange energies and relative quantities for the three sites on illite were taken from Brouwer et al. /1983/ or calculated from data therein. As in the previous study, a cation exchange model employ-

ing the Vanselow convention /Sposito, 1981/ was used for the simulations.

Table 2-1. Cation exchange energies for illite and smectite at 25 °C⁽¹⁾.

Exchange Reaction	Exchange Energy, kcal/equiv			
	Illite			Smectite
	Site I	Site II	Planar Site	
Na --> 0.5 (Ca, Mg, Sr, Ba) ⁽²⁾	1.4	0.2	0 ⁽³⁾	-0.12
Na --> K	-2.2	-2.3	-1.22	-0.35
Na --> Rb	-6.5	-4.2	-1.62	-0.63
Na --> Cs	-7.8	-4.2	-2.10	-1.08
Relative fraction of sites	0.005	0.03	0.965	1.00

(1) Data for illite from Brouwer et al. /1983/ Tables I and II/. Data for smectite from Fletcher and Sposito /1989/ except for Na --> (Rb, Cs) which are from Gast /1972/. Note: these data are strictly accurate at 25 °C only. It was assumed that for the purposes of these simulations the variation of exchange energy between 25 and 10 °C is a second order effect.

(2) Na --> 0.5 (Ca, Mg, Sr, Ba) signifies the conversion of 1 equivalent of exchanger from the Na form to the Ca, Mg, Sr, or Ba form.

(3) The exchange energy for Na --> 0.5 (Ca, Mg, Sr, Ba) deduced from Brouwer et al.'s /1983/ data for the planar site was adjusted to be consistent with their data for Cs --> Na, Rb --> Na, and Rb --> (Ca, Mg, Sr, Ba) exchange.

2.2 GROUNDWATER DATA

The shallow and native groundwaters used as the two endmembers for the mixing simulation 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), for samples collected from the inflow from the tunnel roof (YA0513T), and for shallow boreholes (HBH01, HBH02). The groundwater composition data were obtained from the computer file WKSHOP94.xls supplied by SKB for use in Äspö geochemical modeling exercises /Wikberg, 1994/. These data are also included as a part of the groundwater data set compiled by Nilsson /1995/. Only samples for which analyses of Cl, Na, K, Ca, Mg, and Sr were reported were used to compare with the simulation results.

In addition to the above analyses, trace element analyses for HBH02 and the KR001xB wells (KBS samples) /Nilsson, 1995; Appendix 2., Table A2-6/

were combined with the major element analyses for the same sampling dates / Nilsson, 1995; Appendix 1, Table A1-1/ to predict the composition of the exchanger in equilibrium with these waters. Because there was no trace element analysis of the native groundwater, the concentrations of Cs and Rb in this sample were estimated in a similar manner to Landström and Tullborg / 1995/. The estimates were made by plotting the measured Cs and Rb vs. Na and interpolating to obtain the concentrations for the native groundwater (Figures 2-2 and 2-3).

Figure 2-2. Relationship between Cs and Na that was used to estimate the dissolved concentration of Cs in the native groundwater. The data points (circles) are taken from Landström and Tullborg /1995/ (KBH well) and Nilsson /1995/ (HBH02, KR001xB wells). The

2.3

SIMULATION RUNS

Simulations that were made using EQ3/6 are summarized in Table 2-2. Assumptions regarding the charge balance, Eh, and thermodynamic data for mixing calculations were identical to those used by Viani and Bruton /1994; Table 2-2/.

Figure 2-3. Relationship between Rb and Na that was used to estimate the dissolved concentration of Rb in the native groundwater. The data points (solid circles) are taken from Landström and Tullborg / 1995/ (KBH well) and Nilsson /1995/ (HBH02, KR001xB wells).

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

Simulation	Calculation type	Groundwater analyses used for simulations	Exchanger amount, equiv/kg of H ₂ O	Precipitation considered ⁽¹⁾
Predict composition of illite exchanger in equilibrium with specific groundwater samples	EQ3	HBH02-910912	trace	no
		KA0483A-910312		
		HBH02/KBS2111-930612		
		HBH02/KBS2131-930706		
		HBH02/KBS2145-930817		
		HBH02/KBS2168-930921		
		KR0012B/KBS2084-930324		
		KR0012B/KBS2107-930611		
		KR0012B/KBS2127-930705		
		KR0012B/KBS2141-930816		
		KR0012B/KBS2193-931108		
		KR0013B/KBS2085-930324		
		KR0013B/KBS2108-930611		
		KR0013B/KBS2128-930705		
		KR0013B/KBS2142-930816		
		KR0013B/KBS2194-931108		
		KR0015B/KBS2086-930325		
		KR0015B/KBS2109-930611		
		KR0015B/KBS2129-930705		
		KR0015B/KBS2143-930816		
		KR0015B/KBS2195-931108		
Predict the effect of illite exchanger on mixing shallow and native groundwaters	EQ3 -> EQ6	HBH02-910912 KA0483A-910312	0.10	yes

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

3.1

PREDICTED EXCHANGER COMPOSITIONS

Because of the similarity of the exchange properties of smectite and those of the planar site in illite, the major cation occupancies (Na, Ca, and Mg) predicted for the illite exchanger are very similar to those predicted by Viani and Bruton /1994/ for smectite (Figure 3-1). In contrast, because of the high selec-

Figure 3-1. Comparison of the predicted compositions of smectite and illite cation exchangers in equilibrium with shallow (HBH02-910912) and native (KA0483A-910312) groundwaters ($R = \Sigma\{K, Rb, Cs, Sr\}$).

tivity of the edge sites on illite for monovalent cations with low hydration energies, these sites are predicted to be enriched in Cs, Rb, K, and Na relative to the planar site (Figures 3-2 and 3-3). Although the edge sites occupy only 3.5% of the total exchange capacity of illite, greater than 98% of the exchangeable Cs and Rb and 25 to 35% of the exchangeable K are predicted

Figure 3-2. Predicted occupancies within exchange sites of illite in equilibrium with shallow (HBH02) groundwater.

Figure 3-3. Predicted occupancies within exchange sites of illite in equilibrium with native (KA0483A-910312) groundwater.

to be associated with these sites (Table 3-1).

Table 3-1. Predicted distribution of Cs, Rb, and K among illite exchange sites

Groundwater	Cs, %			Rb, %			K, %		
	Site I	Site II	Planar	Site I	Site II	Planar	Site I	Site II	Planar
Shallow HBH02- 910912	99.74	0.17	0.09	97.96	1.66	0.38	16.11	19.44	64.45
Native KA0483A- 910312	98.95	0.67	0.38	92.19	6.28	1.53	4.39	21.31	74.30

The predicted compositions of illite in equilibrium with waters from HBH02, KA0483A and KR001xB boreholes are shown in Table 3-2. The relative occu-

Table 3-2. Composition of illite exchanger predicted to be in equilibrium with various groundwaters from the Redox Zone at Äspö.

Groundwater	Predicted illite exchanger composition, equiv-%						
Borehole	Na	Ca	Mg	Sr	K	Rb	Cs
Shallow HBH02-910912 ⁽¹⁾	0.74	87.08	10.92	0.155	0.90	0.1578	0.0264
KR0012B ⁽²⁾	17.68	62.56	17.74	0.487	1.33	0.1265	0.0653
KR0013B	20.93	61.04	16.56	0.472	0.82	0.0890	0.0818
KR0015B	18.14	64.06	16.23	0.485	0.89	0.1146	0.0823
Native KA0483A-910312	24.02	61.99	12.21	0.580	0.97	<u>0.1380</u> ⁽³⁾	<u>0.0880</u>

(1) The solution concentrations of Cs and Rb used to predict the exchanger composition for HBH02 were averaged from the values presented in Nilsson /1995/, 0.05 and 1.9 µg/L, respectively, and combined with the major element analysis for the 910912 sample.

(2) The predicted compositions for the KR samples are averages for the five samples listed in Nilsson /1995/. The coefficient of variation in the predicted compositions of the exchangers for the different samples was less than 10%.

(3) Underlined values are predictions based on estimated solution concentrations of Cs and Rb (see section 2.2).

pancies of Na, Cs, and Sr are larger and Ca is smaller on illite in equilibrium with the native groundwater compared to illite in equilibrium with the shallow water. The predicted levels of Mg, K, and Rb are approximately the same for

the shallow and native groundwaters. Except for Mg, K, and Rb, the predicted illite compositions for the KR001xB wells are intermediate between those of the shallow and native groundwaters.

3.2

FLUID MIXING SIMULATIONS

3.2.1

Cation exchange and solution composition

Measured groundwater compositions were compared to compositions based on a conservative mixing model and on mixing in the presence of 0.1 equiv of illite exchanger (Figures 3-4 to 3-9). The comparison was made by assuming

Figure 3-4. Measured concentrations of Na (solid circles) and Ca (open circles) 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 illite exchanger/kg of H_2O .

that Cl is conserved during mixing; that is, the Cl concentration in the groundwater is the sole determinant of the relative proportions of the two endmember fluids. The variation of the observed Na, Ca, and Sr with respect to Cl is consistent with the variation expected if mixing occurs in the presence of a cation exchanger that is initially in equilibrium with the native groundwater. In contrast, the observed variation of Mg with Cl appears consistent with conservative mixing. For K, Cs, and Rb neither conservative mixing or cation exchange can be inferred from the data because of either the scatter in, or scarcity of, the data.

Figure 3-5. Measured concentrations of Sr (circles) in Redox Experiment water samples are compared to predictions made with a conservative mixing model (dashed line) and generated from EQ3/6 calculations (solid line) for 0.1 equiv illite exchanger/kg of H_2O .

Figure 3-6. Measured concentrations of Mg (circles) in Redox Experiment water samples are compared to predictions made with a conservative mixing model (dashed line) and generated from EQ3/6 calculations (solid line) for 0.1 equiv illite exchanger/kg of H_2O .

As noted by Viani and Bruton /1994/, precipitation of small quantities of

Figure 3-7. Measured concentrations of K (solid circles) in Redox Experiment water samples are compared to predictions made with a conservative mixing model (dashed line) and generated from EQ3/6 calculations (solid line) for 0.1 equiv illite exchanger/kg of H_2O .

Figure 3-8. Measured concentrations of Cs (solid circles) in Redox Experiment water samples are compared to predictions made with a conservative mixing model (dashed line) and generated from EQ3/6 calculations (solid line) for 0.1 equiv illite exchanger/kg of H_2O .

hematite, pyrolusite, quartz, and calcite are predicted by EQ6 during the mixing simulation. However, the effect of precipitation of these phases on the cation exchange equilibria is negligible because the major cation and anion

Figure 3-9. Measured concentrations of Rb (circles) in Redox Experiment water samples are compared to predictions made with a conservative mixing model (dashed line) and generated from EQ3/6 calculations (solid line) for 0.1 equiv illite exchanger/kg of H_2O .

concentrations are not significantly affected by the precipitation of these phases.

4.1

CATION EXCHANGE VS. CONSERVATIVE MIXING

The predicted effect of cation exchange by illite on fluid composition during mixing is similar to that presented previously for smectite /Viani and Bruton, 1994; Figure 3-4/. However, comparison of model results with the additional groundwater data from the Redox Zone that was not available to Viani and Bruton /1994/ yields a somewhat different picture of ion exchange vs. conservative mixing. For Ca, Na, and especially Sr, it appears that the *form* of the observed relationship between these cations and Cl is not the same as that predicted by the cation exchange model. A number of causes might contribute to this discrepancy:

- The actual mixing of fluids in the fracture system is not adequately simulated by the simple mixing algorithm embodied in EQ3/6.
 - i) The method of simulating mixing does not allow the shallow water to progressively react with the ion exchanger.
 - ii) Because of discrete fracture pathways, mixing in the presence of an exchanger may occur only in restricted parts of the flow path.
 - iii) A fraction of the shallow water or native water might short circuit the cation exchange process by preferential movement along fractures that lack or contain very small quantities of exchanger.

Because of the potentially large ratio of cations on the exchanger to those in the fluid /Viani and Bruton, 1994/, differences between the simulated mixing process and the actual mixing process would probably have the greatest effect on the most dilute mixed fluids.

- More than two "endmember" fluids may be involved in the mixing and cation exchange process.
- The cation exchange model (e.g., Vanselow, Gapon, Gaines-Thomas, etc.), energies, or assumption of exchange equilibrium may not be correct. Of these potential shortcomings, only the last would probably result in significant differences in predicted concentrations.
- Cation exchange does not play a significant role in controlling solution composition, or there are additional sources and/or sinks for Na, Ca, and Sr.

For Mg, inclusion of the full set of observed fluid data requires us to reverse our earlier finding and conclude that a simple conservative mixing model is better at describing the data than the cation exchange model. However, it is difficult to envision why cation exchange should control Ca and Sr during mixing, but not Mg, because the exchange energies of Mg, Ca, and Sr are

essentially identical.

4.2

PREDICTED EXCHANGEABLE ("MOBILE") CS, RB, AND SR IN FRACTURE FILLING MATERIAL

The predicted equiv-% occupancies of Cs, Rb, and Sr on the illite exchanger can be used to calculate their mass concentration in the fracture fill (Table 4-1). The sum of the exchangeable and dissolved fractions of a metal is often

Table 4-1. Predicted concentration of exchangeable Cs, Rb, and Sr in fracture fill in exchange equilibrium with Redox Zone groundwaters (ppm).⁽¹⁾

Sample	Cs	Rb	Sr
Shallow HBH02-910912	0.35	1.35	0.68
KR0012B	0.87	1.08	2.13
KR0013B	1.09	0.76	2.07
KR0015B	1.09	0.98	2.13
Native KA0483A-910312	1.17	1.18	2.54

⁽¹⁾ The concentrations were calculated assuming that illite in the fracture fill is the sole source of the exchangeable cation; that the fracture fill contains 5 wt-% of illite; and that the CEC of the illite is 0.2 equiv/kg. Concentrations, C_{ppm} , were calculated according to:

$$C_{ppm} = \frac{E \cdot Mw \cdot CEC \cdot A_I}{10 \cdot v}$$

where E is the equivalent percent of the cation on illite predicted by EQ3/6, Mw is the molecular weight of the cation, CEC is the exchange capacity of illite (equiv/kg), A_I is the weight-percent abundance of illite in the fracture fill material, and v is the valence of the cation.

termed the "mobile" fraction /Landström and Tullborg, 1995/. For Cs and Rb this fraction is dominated by the exchangeable fraction (see section 4.4 below). The values tabulated in Table 4-1 are based on the assumption that all of the exchangeable element derives from the illite only. Because it is also assumed that the fracture fill material is in exchange equilibrium with the groundwater, the concentrations in Table 4-1 are independent of the ratio of exchanger to fluid. The calculated exchange cation concentrations are directly proportional to the CEC and weight fraction of the illite in the fracture filling material.

The assumption that the exchangeable cations derive solely from illite is reasonable for Cs and Rb because of the high selectivity of illite for these elements. However, this assumption is probably not valid for Sr because other

exchangers such as smectite, chlorite, or sericite would also contribute to the exchangeable Sr pool. Hence, the values for Sr in Table 4-1 are underestimates.

Landström and Tullborg /1995/, using a sequential extraction technique, found that 0.64 ppm Cs was exchangeable and/or dissolved (mobile) in a sample of fracture gouge collected from the Redox Zone. Their measurement agrees surprisingly well with the predicted Cs concentrations in Table 4-1. Although the total concentrations of Rb and Sr in the fracture gouge were also analyzed by Landström and Tullborg /1995/, the fraction that was exchangeable was not reported.

4.3

ESTIMATES OF THE QUANTITY OF CATION EXCHANGER IN THE REDOX ZONE FRACTURE SYSTEM

No measurement of the exchange capacity of fracture filling material has been made to date. However, several indirect estimates of the quantity of cation exchanger associated with the Redox Zone fracture system have been made. Viani and Bruton /1994/ estimated the exchange capacity to be on the order of 0.06 to 0.1 equiv of exchanger per *liter of groundwater* based on matching predicted to observed Na and Ca groundwater concentrations. Calculations in EQ3/6 are actually made in terms of equiv per kg of H₂O which, for the relatively dilute groundwaters considered in this study, is essentially equal to equiv per liter of groundwater.

Banwart et al. /1995b/ presented two estimates: 0.083 and 0.004-0.03 equiv/L. The former estimate was based on fitting mass balance and cation exchange mass action equations to the observed concentration of Na in Äspö groundwaters. The latter estimate was based on the observed fracture mineralogy, fracture fill particle size distribution, fracture fill porosity, and CEC values for various clay minerals /Table 2, Banwart et al., 1995b/. This estimate is much lower than those based on cation exchange models. However, the exchange capacity estimate listed in Table 2 of Banwart et al. /1995b/ appears to be actually expressed on a per unit volume of *fracture fill* basis rather than per unit volume of *groundwater*. Using the exchange capacities (0.2-1.4 equiv/kg of clay) and the clay to groundwater ratio (0.140 kg of clay/L of groundwater) listed in Banwart et al.'s /1995b/ Table 2, we estimate the exchange capacity of the fracture filling per L of *groundwater* to be 0.03-0.20 equiv/L. Our estimate is about an order of magnitude greater than that in Banwart et al.'s Table 2 and is also consistent with the two estimates deduced from cation exchange modeling.

4.4

RESERVOIR OF EXCHANGE CATIONS

Table 4-2 lists the ratios of the mass of cations associated with the exchanger

Table 4-2. Ratio of predicted mass of trace cation on exchanger⁽¹⁾ to mass of cation in fluid for three groundwaters at Äspö

Cation	Shallow (HBH02-910912)	Native (KA0483A-910312)	KR0013B
Sr	42	1.2	3.9
Rb	7100	420	900
Cs	70000	3900	8400

⁽¹⁾ Calculations assume 0.1 equiv of illite/kg of H₂O.

to their mass in the fluid. The distribution of Sr is essentially equal to that previously computed for Ca and Mg considering a smectite exchanger /Viani and Bruton, 1994/. Cs and Rb are almost completely associated with the exchanger and this reservoir would be expected to control the dynamics of the mobile pool of these elements in the fracture system.

The simulated behavior of Sr closely parallels that of Ca, that is, it is not conserved during mixing, and appears to be controlled by ion exchange. This similarity in behavior is consistent with the nearly linear relationship between Sr and Ca noted by Wallin and Peterman /1994a/. Although Sr concentrations increase by two orders of magnitude between the shallow and native endmembers, $\delta^{87}\text{Sr}$ -values in Redox Zone groundwaters are nearly constant, on the order of +10 o/oo /Wallin and Peterman, 1994b/. These values are significantly heavier than those in fracture calcites and indicate that Sr in the groundwater is not in isotopic equilibrium with the bulk of the Sr in the fracture calcites. However, isotopic equilibrium would be expected between dissolved and exchangeable Sr because exchange equilibrium is rapid. Compared to total Sr concentrations in fracture fill and altered wall rock (~500 - 700 ppm) /Tullborg, 1995/, the exchangeable Sr concentrations are predicted to be small (Table 4-1). Nevertheless, exchangeable Sr accounts for more than half of the "mobile" pool of Sr (Table 4-2) and may have helped to buffer the Sr isotopic signature in the Redox Zone fracture network.

CONCLUSIONS

Geochemical modeling simulations of the role of cation exchange in fluid mixing and in trace metal partitioning suggest that this phenomenon plays an important role in the short term chemical dynamics that are occurring in the Redox Zone.

- Because of the similarity of the exchange properties of smectite and those of the planar site in illite, the major cation occupancies (Na, Ca, and Mg) predicted for the illite exchanger are very similar to those predicted for a smectite exchanger.
- Cation exchange is a plausible mechanism to explain apparent sources and/or sinks for Ca, Sr, and Na during mixing of dilute shallow groundwater and native groundwater in the Redox Zone. This mechanism alone cannot explain the behavior of Mg. In particular, the mixing of more than two sources of groundwater, as has been postulated by Laaksoharju et al. /1995/, must be considered. A more realistic model of the mixing process must also be incorporated into the geochemical modeling.
- Cation exchange simulation of the partitioning of Cs and Rb onto illite predicts that almost all of the "mobile" pool of these elements is associated with the exchanger. The predicted level of exchangeable Cs and that measured by sequential extraction of fracture gouge are in reasonable agreement.
- The quantity of exchanger (~ 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. This estimate agrees with estimates by Banwart et al. /1995b/ that are based on modeling and on fracture fill material properties.

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REFERENCES

- Banwart, S., Laaksoharju, M., Nilsson, A-C., Tullborg, E-L., and Wallin, B. 1992. *The Large Scale Redox Experiment: Initial Characterization of the Fracture Zone*. SKB Äspö Hard Rock Laboratory Progress Report 25-92-04, Stockholm.
- Banwart, S., Laaksoharju, M., Gustafsson, E., Pitkänen, P., Snellman, M., Landström, O., Aggeryd, I., Mathiasson, L., and Sundblad, B. 1995a. The hydrochemistry of conservative natural tracers. pp. 47-80 *In* Banwart, S. (ed.) *The Redox Experiment in Block Scale: Final Reporting of Results from the Three Year Project*. SKB Äspö Hard Rock Laboratory Progress Report 25-95-06, Stockholm.
- Banwart, S., Laaksoharju, M., Pitkänen, P., Snellman, M., and Wallin, B. 1995b. Development of a site model for reactive element dynamics. pp. 188-218. *In* Banwart, S. (ed.) *The Redox Experiment in Block Scale: Final Reporting of Results from the Three Year Project*. SKB Äspö Hard Rock Laboratory Progress Report 25-95-06, Stockholm.
- Bruggenwert, M.G.M., and Kamphorst, A. 1982. Survey of experimental information on cation exchange in soil systems. pp. 141-203. *In* Bolt, G.H. (ed.) *Soil Chemistry B. Physico-Chemical Models*. Elsevier, Amsterdam.
- Brouwer, E., Baeyens, B., Maes, A., and Cremers, A. 1983. Cesium and rubidium ion equilibria in illite clay. *J. Phys. Chem.* 87: 1213
- Fletcher, P. and Sposito, G. 1989. The chemical modeling of clay-electrolyte interactions for montmorillonite. *Clay Minerals*, v. 24, p. 375-391.
- Gast, R.G. 1972. Alkali metal cation exchange on Chambers montmorillonite. *Soil Sci. Soc. Amer. Proc.* 36:14.
- Laaksoharju, M., Banwart, S., Skarman, C., Gustafsson, E., Pitkänen, P., and Snellman, M. 1995. Hydrochemistry overview. pp. 17-46. *In* Banwart, S. (ed.) *The Redox Experiment in Block Scale: Final Reporting of Results from the Three Year Project*. SKB Äspö Hard Rock Laboratory Progress Report 25-95-06, Stockholm.
- Landström, O., and Tullborg, E-L. 1995. *Interactions of U, Th, REE, Ra, Cs, and Sr with Clay Minerals, Fe-Oxyhydroxide and Calcite: Examples on Geochemical Processes in Natural Systems from the Äspö HRL*. Draft manuscript to be published as an SKB Report.
- Nilsson, A-C. 1995. *Compilation of Groundwater Chemistry Data From Äspö 1990 - 1994*. SKB Äspö Hard Rock Laboratory Progress Report 25-95-02, Stockholm.
- Sposito, G. 1981. *Thermodynamics of Soil Solutions*. Oxford University Press, New York, NY.
- Tullborg, E-L. 1995. Mineralogical/geochemical investigations in the frac-

ture zone. pp. 81-101. In Banwart S. (ed) *The Redox Experiment in Block Scale: Final Reporting of Results from the Three Year Project*. SKB Äspö Hard Rock Laboratory Progress Report 25-95-06, Stockholm.

Tullborg, E.-L., Wallin, B. and Landström, O. 1991. *Hydrogeochemical Studies of Fracture Minerals from Water Conducting Fractures and Deep Groundwaters at Äspö*. SKB Swedish Hard Rock Laboratory Progress Report 25-90-01, Stockholm.

Viani, B.E. and Bruton, C.J. 1994. Modeling fluid-rock interactions at Äspö using EQ3/6. pp. 78-96. In Banwart, S. (ed.) *Proceedings of the Äspö International Geochemistry Workshop*, June 2-3, 1994, SKB Äspö International Report, Stockholm.

Wallin, B. and Peterman, Z.E. 1994a. *SKB/DOE Hard Rock Laboratory Studies: Task 3. Geochemical Investigations Using Stable and Radiogenic Isotopic Methods*, SKB International Cooperation Report 94-06, Stockholm.

Wallin, B. and Peterman, Z.E. 1994b. Isotopic systematics in groundwater and hydrogenic deposits at the Äspö Hard Rock Laboratory, S.E. Sweden. pp. 97-117. In Banwart, S. (ed.) *Proceedings of the Äspö International Geochemistry Workshop*, June 2-3, 1994, SKB Äspö International Report, Stockholm.

Wikberg, P. 1994. Hydrogeochemical modelling of the Äspö and Redox Zone system: Background information and recommended groundwater datasets. (with accompanying computer data files). SKB - Memo of June 22, 1994, from Peter Wikberg to HRL project participants.

Wolery, T.J., Jackson, K.J., Bourcier, W.L., Bruton, C.J., Viani, B.E., Knauss, K.G. and Delany, J.M. 1990. Current status of the EQ3/6 software package for geochemical modeling. pp. 104-116. In Melchior, D.C. and Bassett, R.L. (eds.) *Chemical Modeling of Aqueous Systems II*. American Chemical Society, Washington, D.C.

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