Behavior of Sorbed ^{90}Sr in Contaminated Subsurface Sediments

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Motivation

Overall Concern:

^{90}Sr is a high yield fission product. Mega curies released to the ground. Two major groundwater plumes. Will ^{90}Sr get to the Columbia in 10 half-lives (280 y)?

Scientific Issues:

Multi-component ion exchange, isotopic exchange, exchanger composition and identity, cold Sr isotope dynamics, Ca-Mg-Sr carbonate equilibria

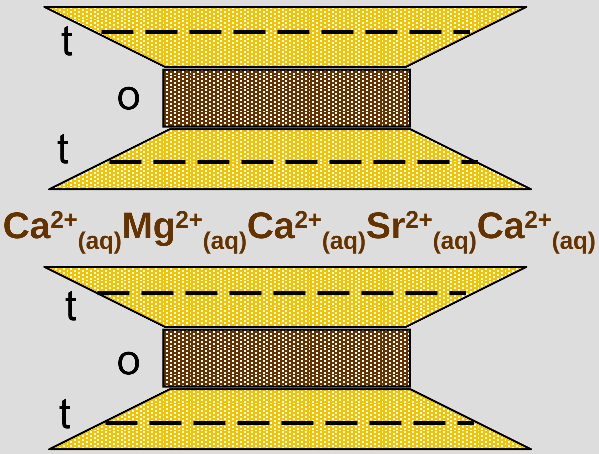
Objective I:

Develop a generalized ion exchange model for Hanford sediments of variable lithology

Objective II:

Evaluate selected in-ground ^{90}Sr plumes as to retardation mechanism and future mobility

Ion Exchange and Isotope Exchange



$\rightleftarrows$ $Ca^{2+}_{(aq)}$, $Na^{+}_{(aq)}$, $Sr^{2+}_{(aq)}$ $\quad Mg^{2+}_{(aq)}$ $\rightleftarrows$ $CaCO_{3(s)}$, $Na[AlSi_3O_8]\text{-}Ca[Al_2Si_2O_8]_{(s)}$

$$vAX_{u(s)} + uB^{u+}_{(aq)} = uBX_{v(s)} + vA^{u+}$$

K_{ex}

$$K_{ex} = (BX_v)^u(A^{u+})^v/(AX_u)^v(B^{v+})^u$$

- Cold $^{86,87}Sr$ liberated by rock weathering is the dominant Sr source
- Solid-liquid distribution α to $[Ca^{2+}]$, $[Mg^{2+}]$
- Adsorption of trace ^{90}Sr follows the distribution of cold isotopes ($^{86,87}Sr$)
  - Driven by isotopic exchange
  - K_d-$^{90}Sr = K_d$-Sr
  - $K_d \; \alpha \; K_{ex}, [Ca^{2+}]/[Mg^{2+}]$

Developing an Ion Exchange Model

1. Na-acetate extraction to remove $CaCO_3$

2. Characterization of clay mineralogy

3. Ca^{2+} - saturation
   (Na saturated phase unstable)

4. Ca-Sr, Ca-Mg, Ca-Na exchange isotherms
   T_N = 0.001, 0.01, 0.1; F_{Me} = .05-1.0
   Complete delineation of the equilibrium state
   - Aqueous phase
   - Exchanger phase (NH_4Cl)

5. Ion exchange modeling
   - G-T
   - Vanselow

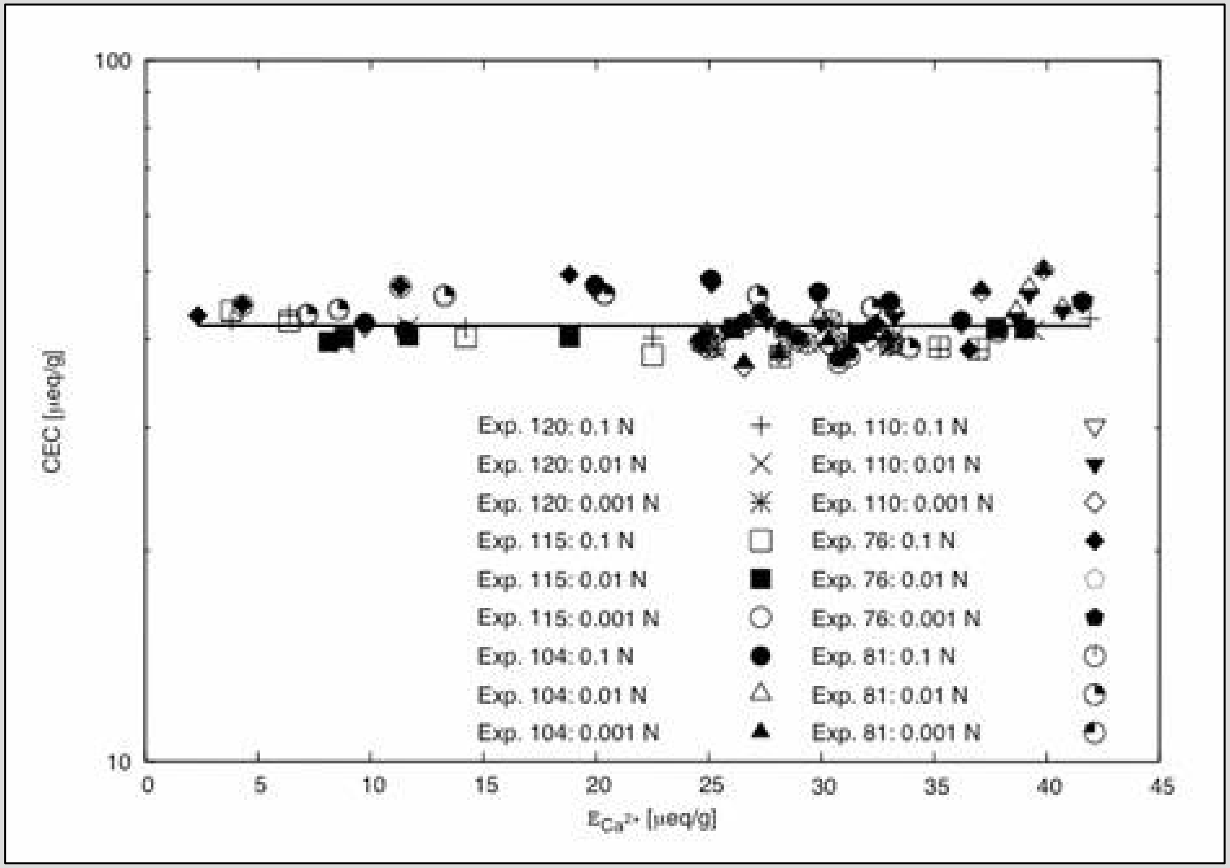
   PEST

Analytical Results from Ca-Mg Exchange Experiment

		Initial Solution			Equilibrium Solution					Ammonium Extractable					
Soln	Target Total Norm. (Mg+Ca)	Initial [Ca] (mol/L)	Initial [Mg] (mol/L)	Initial [Sr][2] (mol/L)	$[Ca]_{aq}$[1] (mol/L) (ICP)	$[K]_{aq}$[1] (mol/L) (ICP)	$[Mg]_{aq}$[1] (mol/L) (ICP)	$[Sr]_{aq}$[1] (mol/L) (ICP)	$[Na]_{aq}$[1,3] (mol/L) (ICP)	$[Ca]_{ads}$[1] (ueq/g) (ICP)	$[K]_{ads}$[1] (ueq/g) (ICP)	$[Mg]_{ads}$[1] (ueq/g) (ICP)	$[Sr]_{ads}$[1] (ueq/g) (ICP)	$[Na]_{ads}$[1] (ueq/g) (ICP)	Sum (ueq/g)
A1	0.1	0 [3]	4.322E-02	0	3.048E-04	4.522E-05	4.602E-02	3.081E-07	7.825E-05	4.98	0.69	40.86	0.01	0.61	47.2
A2	0.1	1.257E-03	4.427E-02	5.151E-08	1.477E-03	6.689E-05	4.373E-02	3.196E-07	5.429E-05	6.14	0.46	41.00	0.01	0.35	48.0
A3	0.1	2.519E-03	4.183E-02	1.033E-07	2.666E-03	7.277E-05	4.290E-02	3.995E-07	6.007E-05	7.56	0.50	40.32	0.01	0.27	48.7
A4	0.1	4.966E-03	4.119E-02	2.036E-07	5.076E-03	6.836E-05	4.148E-02	4.965E-07	5.179E-05	9.38	0.53	37.43	0.01	0.25	47.6
A5	0.1	1.508E-02	3.215E-02	6.180E-07	1.429E-02	4.102E-05	3.150E-02	1.016E-06	4.512E-05	18.80	0.38	27.57	0.01	0.27	47.0
A6	0.1	2.497E-02	2.287E-02	1.024E-06	2.344E-02	3.936E-05	2.300E-02	1.546E-06	4.024E-05	26.44	0.43	17.47	0.01	0.27	44.6
A7	0.1	3.501E-02	1.427E-02	1.435E-06	3.271E-02	6.662E-05	1.404E-02	2.111E-06	5.190E-05	34.45	0.60	10.94	0.01	0.25	46.3
A8	0.1	4.493E-02	4.835E-03	1.842E-06	4.133E-02	7.223E-05	4.655E-03	2.608E-06	4.499E-05	42.45	0.62	4.57	0.01	0.20	47.9
A9	0.1	4.750E-02	2.385E-03	1.948E-06	4.370E-02	7.248E-05	2.378E-03	2.728E-06	4.128E-05	45.04	0.37	2.71	0.01	0.09	48.2
A10	0.1	4.870E-02	1.219E-03	1.996E-06	4.605E-02	4.120E-05	1.270E-03	2.802E-06	3.152E-05	44.08	0.41	1.81	0.01	0.16	46.5
A11	0.1	4.999E-02	1.561E-05 [2]	2.049E-06	5.053E-02	1.294E-05	7.890E-05	2.785E-06	1.286E-05	33.81	0.58	0.88	0.01	0.15	35.4
B1	0.01	0 [3]	4.924E-03	0	6.058E-04	3.102E-05	4.063E-03	4.793E-07	8.409E-05	11.41	0.70	34.59	0.02	0.50	47.2
B2	0.01	1.263E-04	4.606E-03	5.178E-09	7.604E-04	4.601E-05	4.016E-03	6.106E-07	6.205E-05	11.92	0.51	32.67	0.02	0.27	45.4
B3	0.01	2.535E-04	4.550E-03	1.039E-08	7.859E-04	3.299E-05	3.917E-03	4.052E-07	4.087E-05	13.10	0.50	31.94	0.02	0.33	45.9
B4	0.01	4.976E-04	4.322E-03	2.040E-08	9.960E-04	3.159E-05	3.743E-03	4.337E-07	3.978E-05	15.50	0.52	30.31	0.02	0.29	46.6
B5	0.01	1.515E-03	3.362E-03	6.209E-08	1.788E-03	3.404E-05	3.027E-03	4.908E-07	3.740E-05	22.05	0.42	22.58	0.02	0.33	45.4
B6	0.01	2.508E-03	2.419E-03	1.028E-07	2.605E-03	2.102E-05	2.256E-03	5.649E-07	2.816E-05	28.96	0.52	16.20	0.02	0.27	46.0
B7	0.01	3.524E-03	1.440E-03	1.445E-07	3.444E-03	3.082E-05	1.437E-03	6.163E-07	2.103E-05	34.57	0.45	10.26	0.02	0.30	45.6
B8	0.01	4.519E-03	4.842E-04	1.853E-07	4.345E-03	3.496E-05	5.763E-04	6.905E-07	4.037E-05	40.97	0.43	4.78	0.02	0.24	46.4
B9	0.01	4.775E-03	2.387E-04	1.958E-07	4.545E-03	3.650E-05	3.557E-04	8.674E-07	3.507E-05	40.97	0.47	3.32	0.02	0.24	45.0
B10	0.01	4.908E-03	1.262E-04	2.012E-07	4.657E-03	3.460E-05	2.604E-04	7.818E-07	2.552E-05	41.80	0.41	2.68	0.02	0.30	45.2
B11	0.01	5.015E-03	2.287E-06 [2]	2.057E-07	4.594E-03	BDL	1.464E-04	5.935E-07	1.020E-05	42.79	0.08	2.08	0.02	0.20	45.2
C1	0.001	0 [3]	5.119E-04	0	2.918E-04	2.079E-05	2.420E-04	2.168E-07	3.684E-05	31.48	0.77	16.15	0.03	0.47	48.9
C2	0.001	1.261E-05 [3]	4.746E-04	5.168E-10	2.809E-04	1.696E-05	2.280E-04	9.701E-08	2.199E-05	29.36	0.77	15.33	0.03	0.36	45.9
C3	0.001	2.522E-05 [3]	4.718E-04	1.034E-09	2.772E-04	1.898E-05	2.281E-04	1.312E-07	1.242E-05	29.62	0.42	15.07	0.03	0.32	45.5
C4	0.001	4.966E-05	4.388E-04	2.036E-09	2.905E-04	1.432E-05	2.212E-04	1.255E-07	1.633E-05	30.43	0.49	14.57	0.03	0.33	45.9
C5	0.001	1.508E-04	3.474E-04	6.183E-09	3.428E-04	1.870E-05	2.033E-04	1.255E-07	1.796E-05	32.33	0.38	12.91	0.03	0.40	46.1
C6	0.001	2.500E-04	2.407E-04	1.025E-08	3.480E-04	1.967E-05	1.651E-04	1.027E-07	1.275E-05	33.10	0.52	11.04	0.03	0.31	45.0
C7	0.001	3.511E-04	1.463E-04	1.440E-08	3.941E-04	1.836E-05	1.391E-04	1.255E-07	2.620E-05	35.39	0.53	9.43	0.03	0.40	45.8
C8	0.001	4.513E-04	5.131E-05	1.850E-08	4.050E-04	1.650E-05	1.073E-04	1.027E-07	1.083E-05	37.58	0.70	7.61	0.03	0.36	46.3
C9	0.001	4.754E-04	2.437E-05	1.949E-08	4.089E-04	1.767E-05	9.883E-05	1.084E-07	4.272E-06	37.81	0.66	7.14	0.03	0.35	46.0
C10	0.001	4.889E-04	1.270E-05	2.004E-08	4.142E-04	1.578E-05	9.434E-05	1.027E-07	1.445E-05	38.83	0.68	7.03	0.03	0.34	46.9
C11	0.001	5.005E-04	4.104E-07 [2]	2.053E-08	4.259E-04	5.857E-06	9.214E-05	5.706E-08	1.072E-05	39.63	0.72	7.00	0.04	0.21	47.6
														Average =	46.1

[1] = Average of two samples except X1 and X11 which are single analyses.
[2] = Strontium and magnesium as contaminants with calcium nitrate.
[3] = Pending re-analysis of ICP sample.
BDL =Below detection limit.

The Sum of NH_4Cl Extractable Cations Defines the CEC



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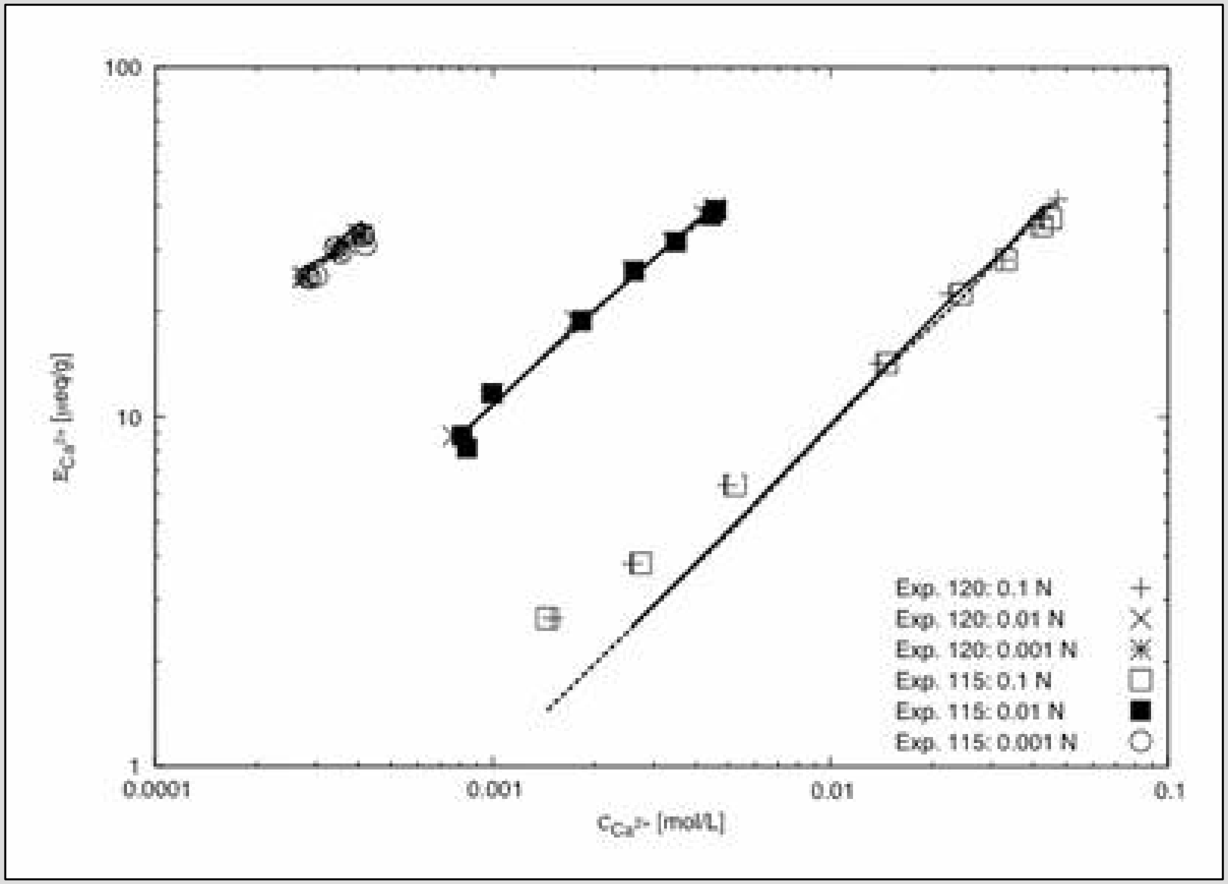
Ca^{2+} Exchange Isotherm from Ca-Mg Electrolytes



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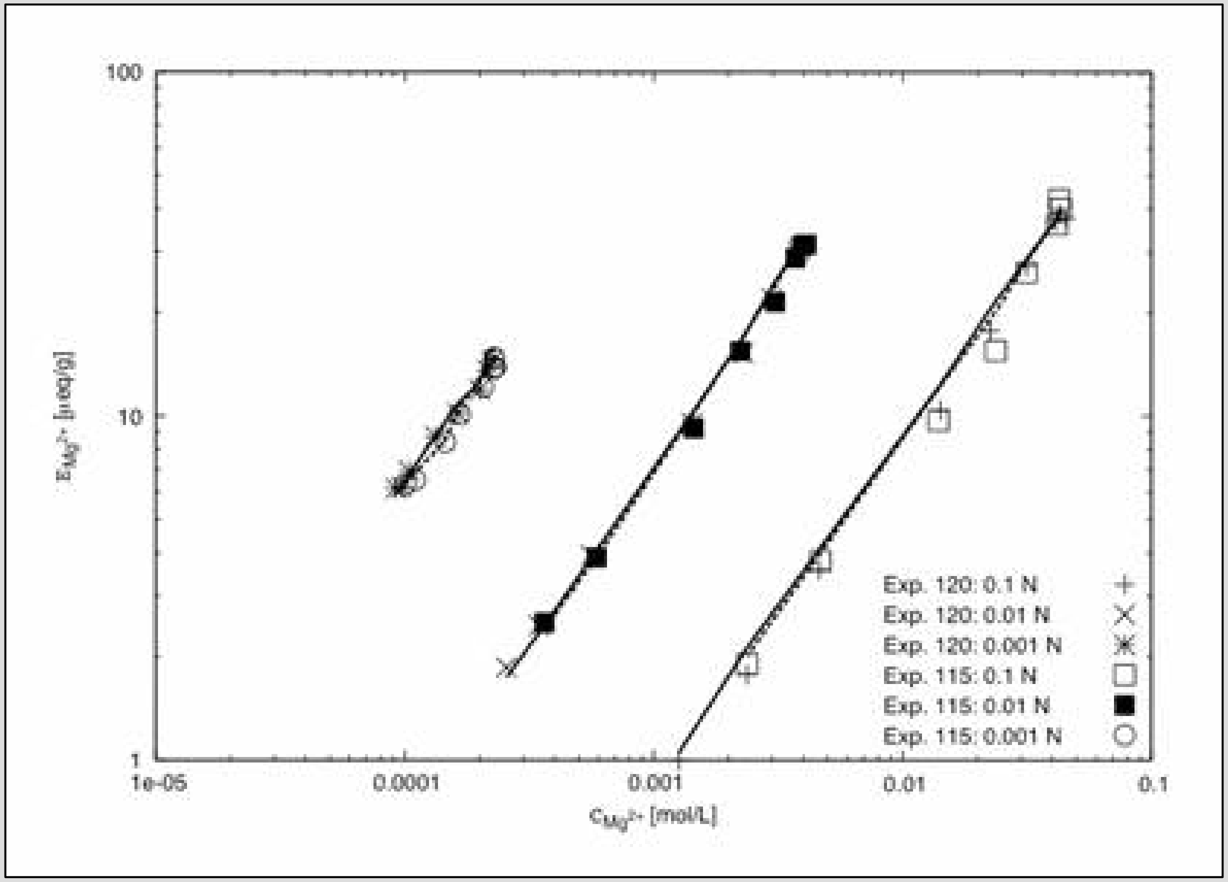
Mg^{2+} Exchange Isotherm from Ca-Mg Electrolyte



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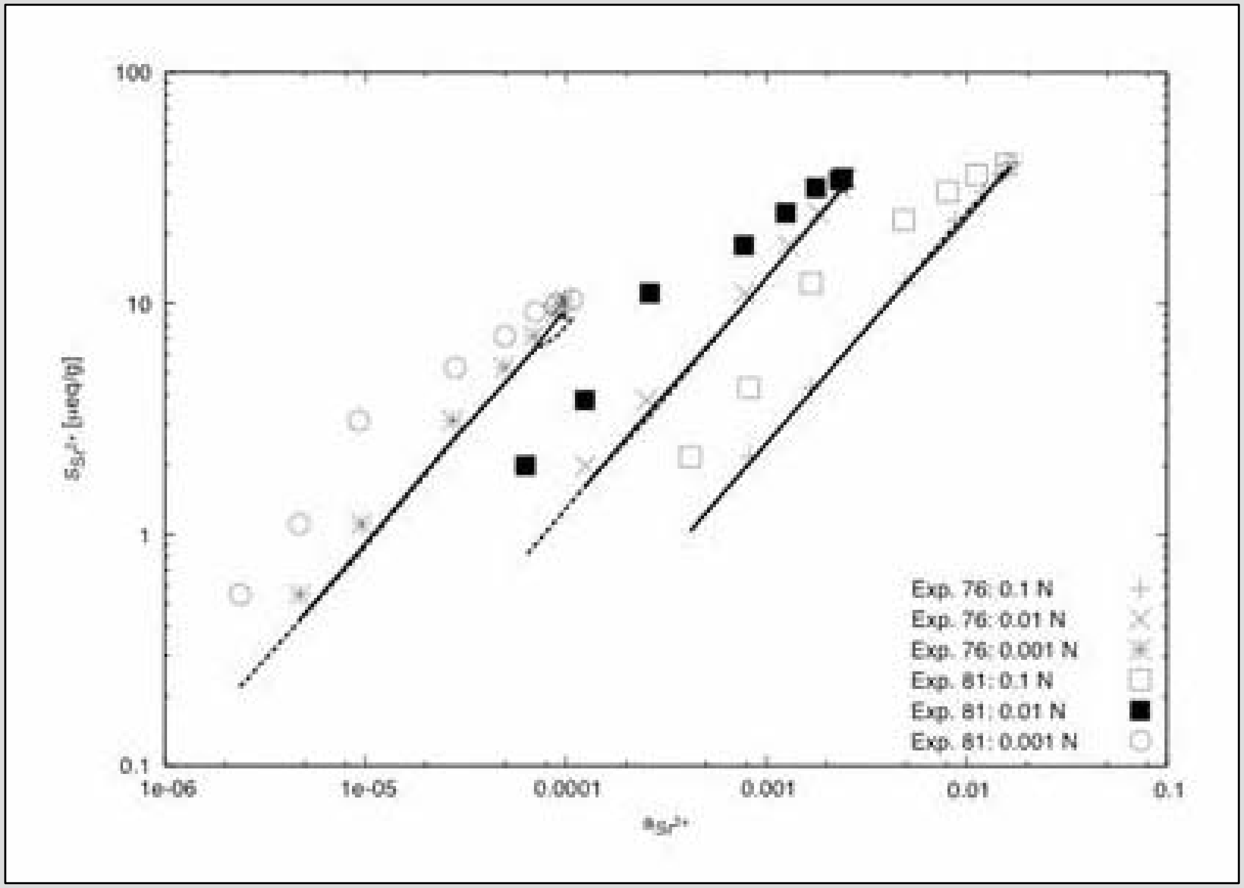
Sr^{2+} Exchange Isotherm from Ca-Sr Electrolyte



Half-Reaction Selectivity Coefficients Fit from Isotherm Data

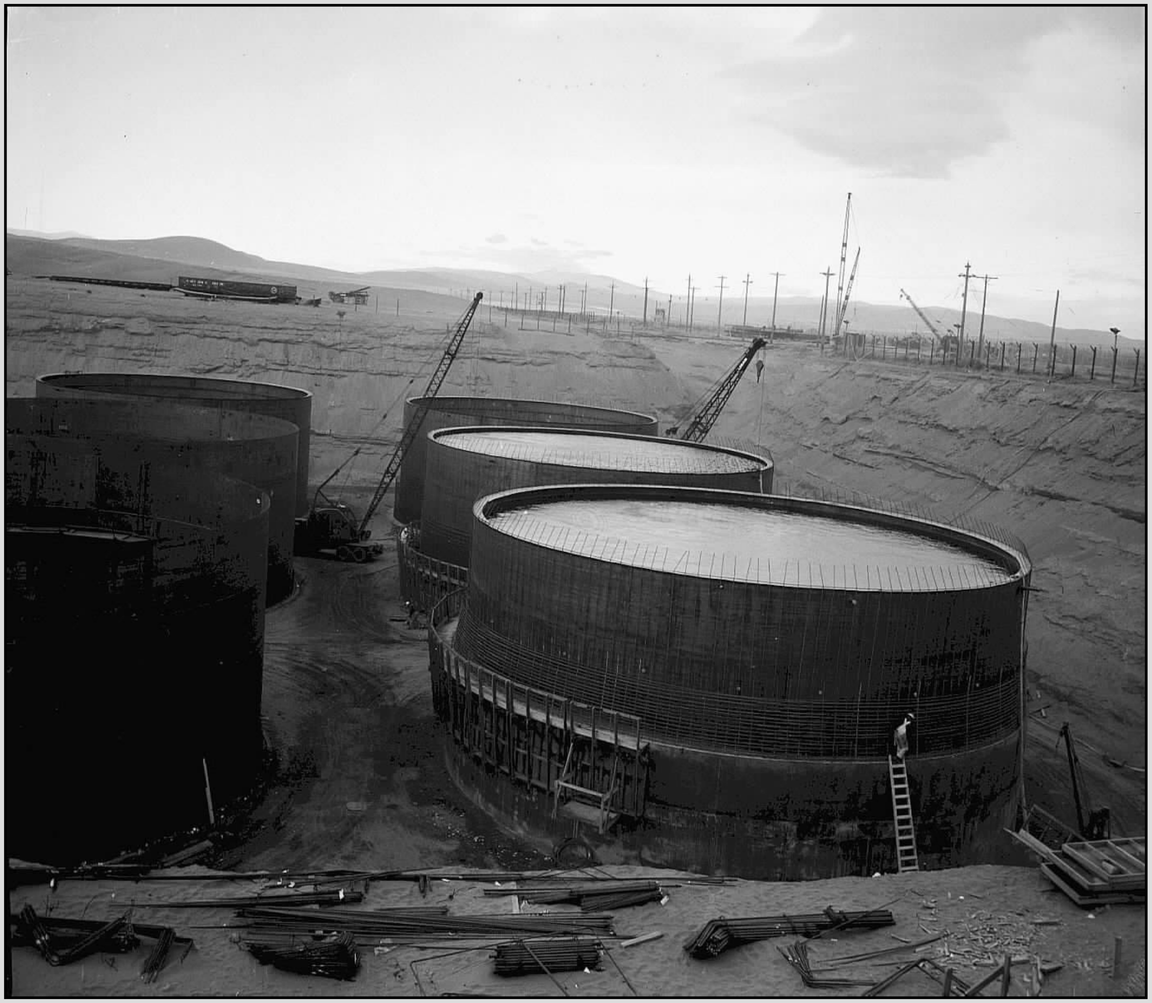
$K_{Ca} = 1.0$

$K_{Mg} = 0.690$

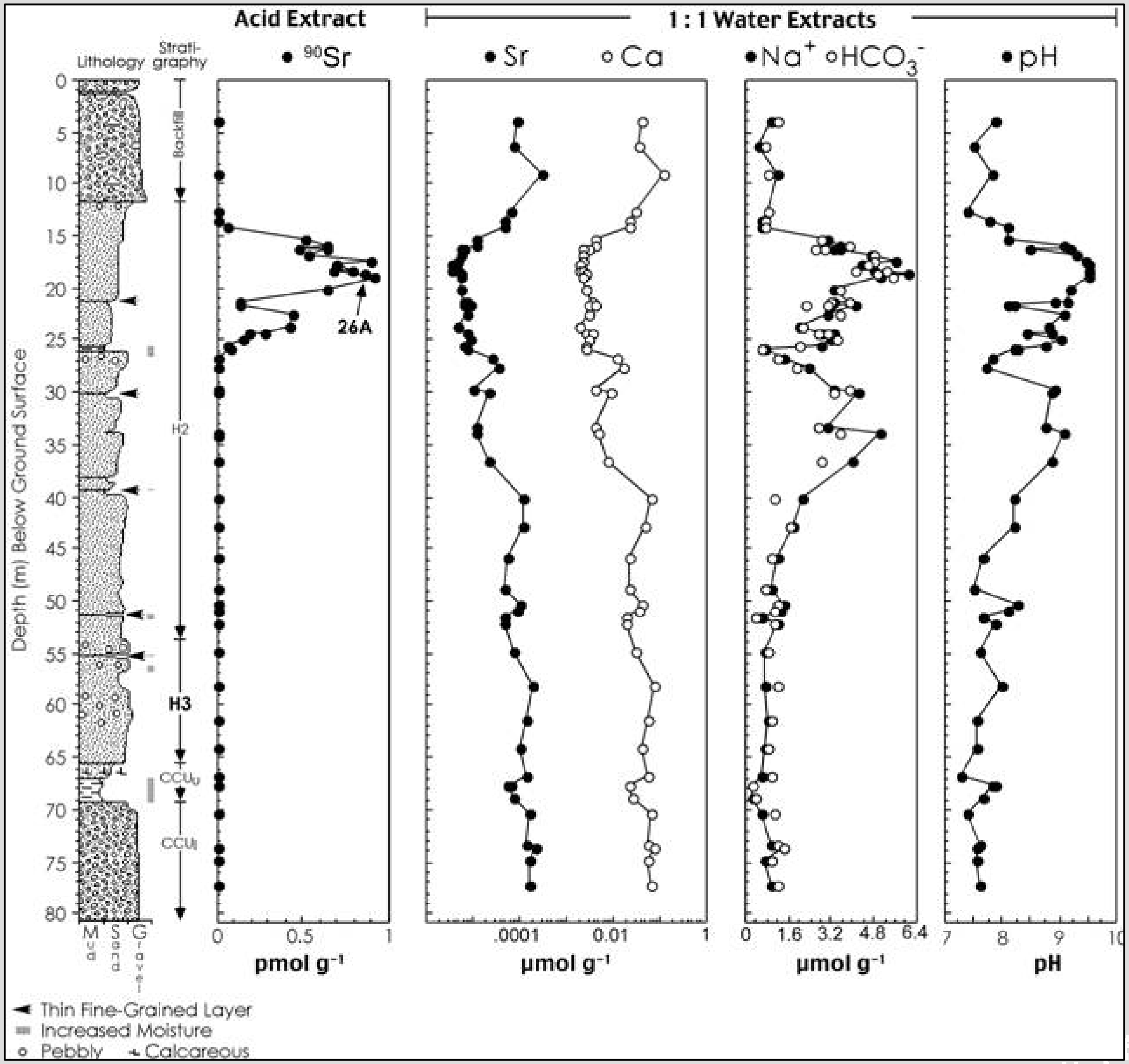
$K_{Sr} = 1.0$

$K_{Na} = 0.298$

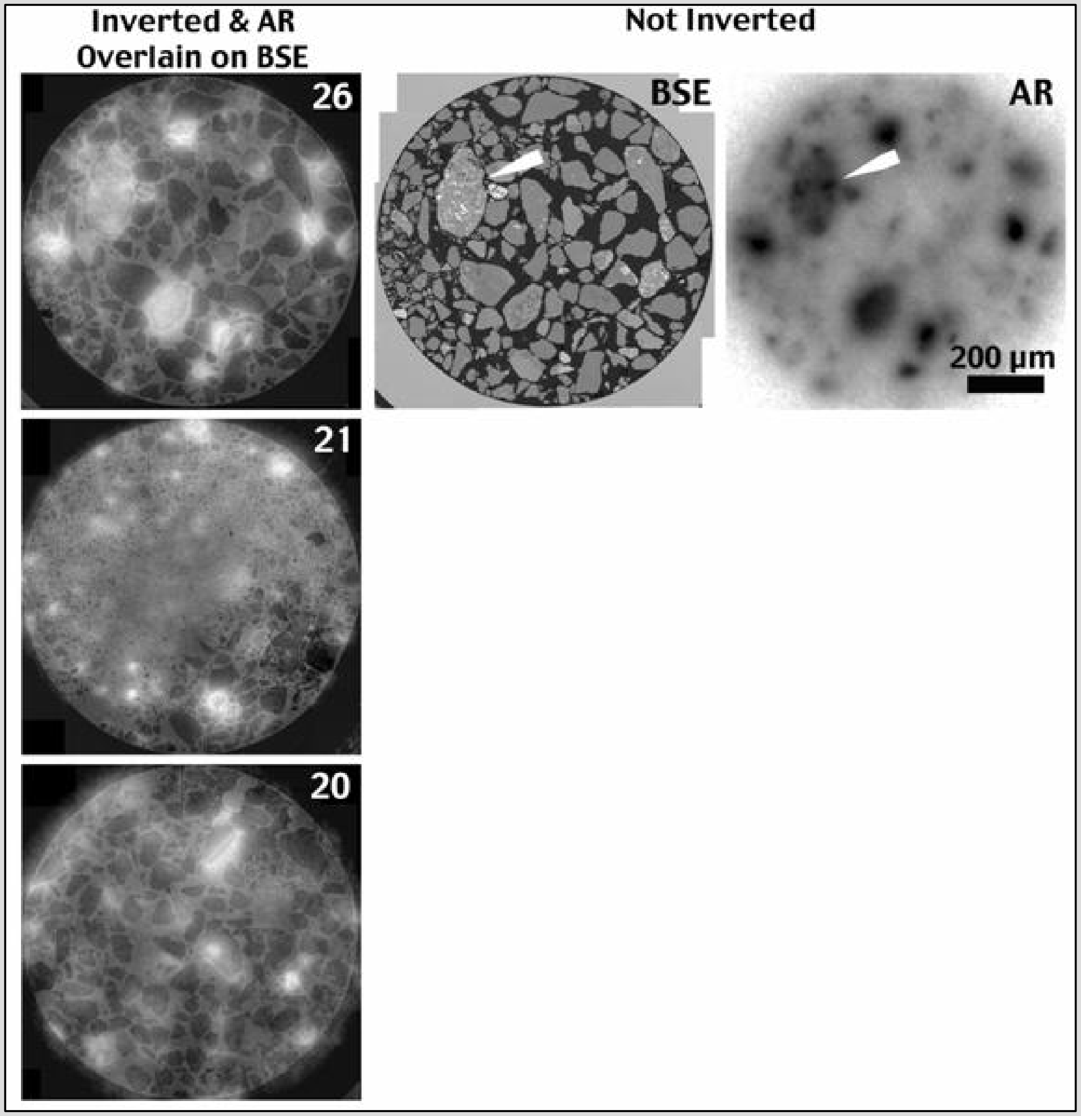
B-BX-BY Tank Farm



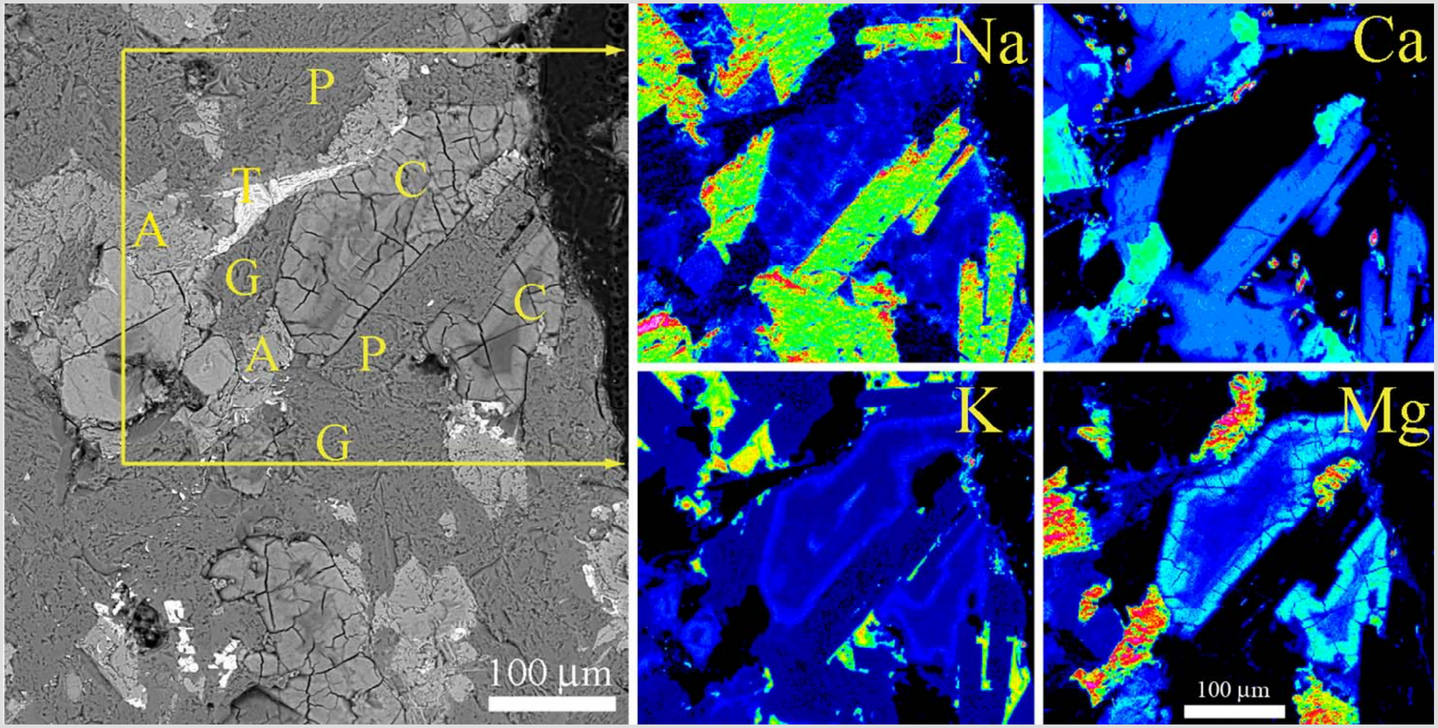
Extractable Ion Trends Beneath Leaked Tank B-110



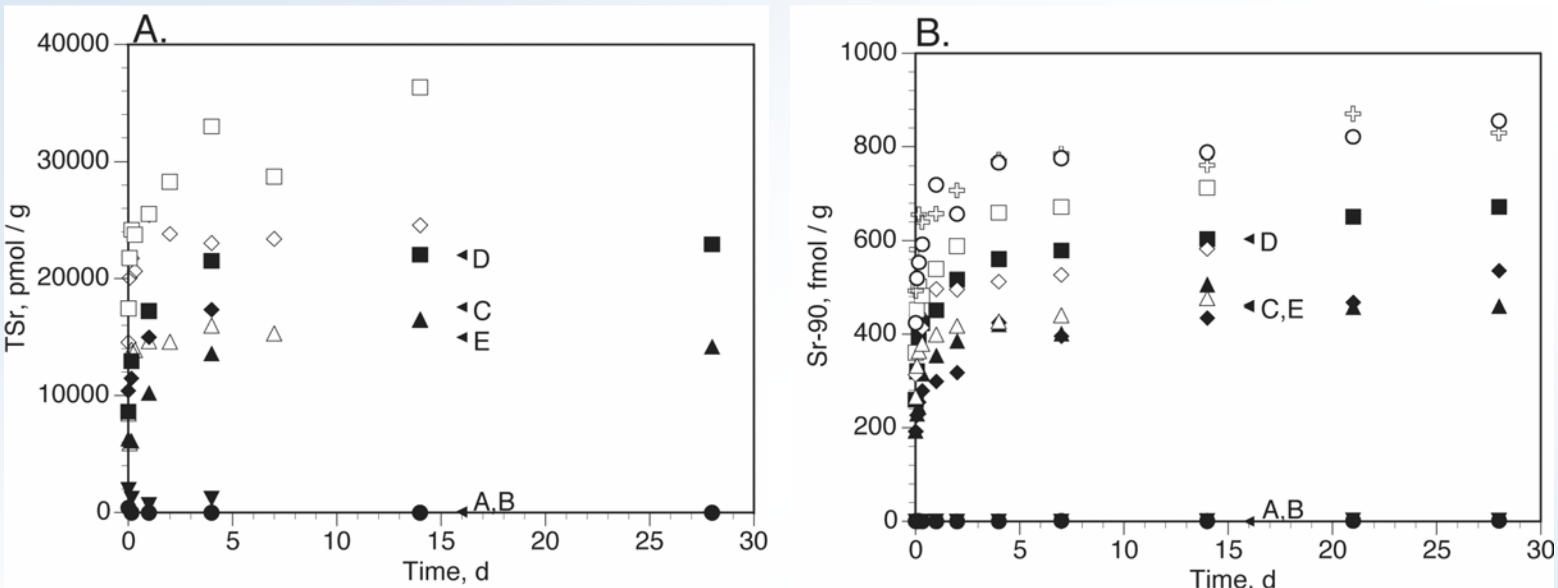
Backscattered Electron Images (BSE) and Autoradiographs of B-110 Sediments



Backscattered Electron Image and Elemental Abundance for ^{90}Sr-Containing Intragrain Region

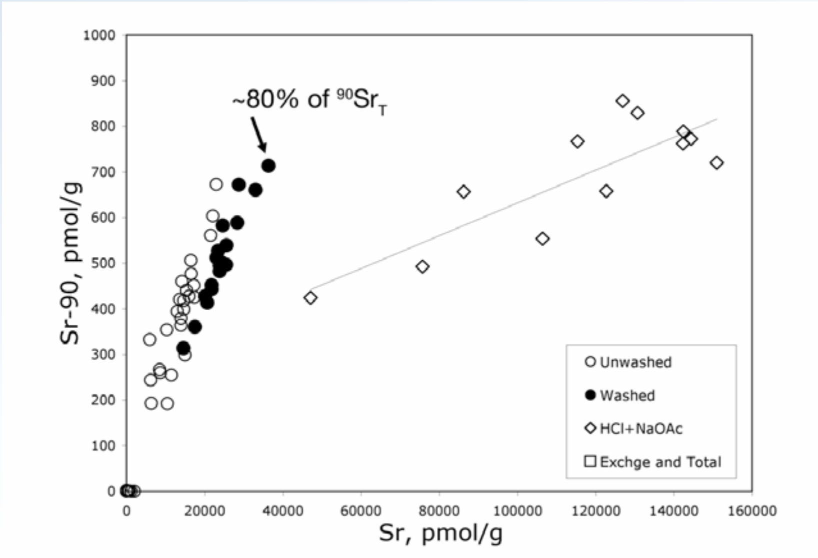


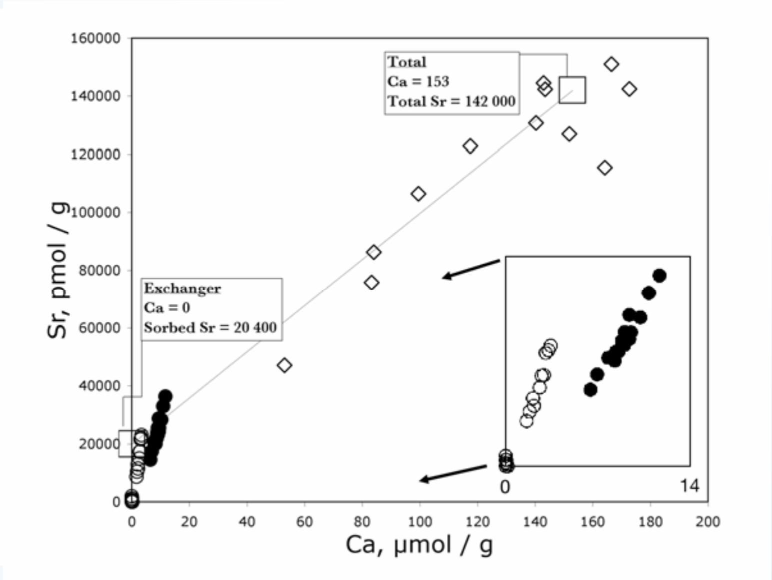
Desorption of Sr from Contaminated Sediment 26A



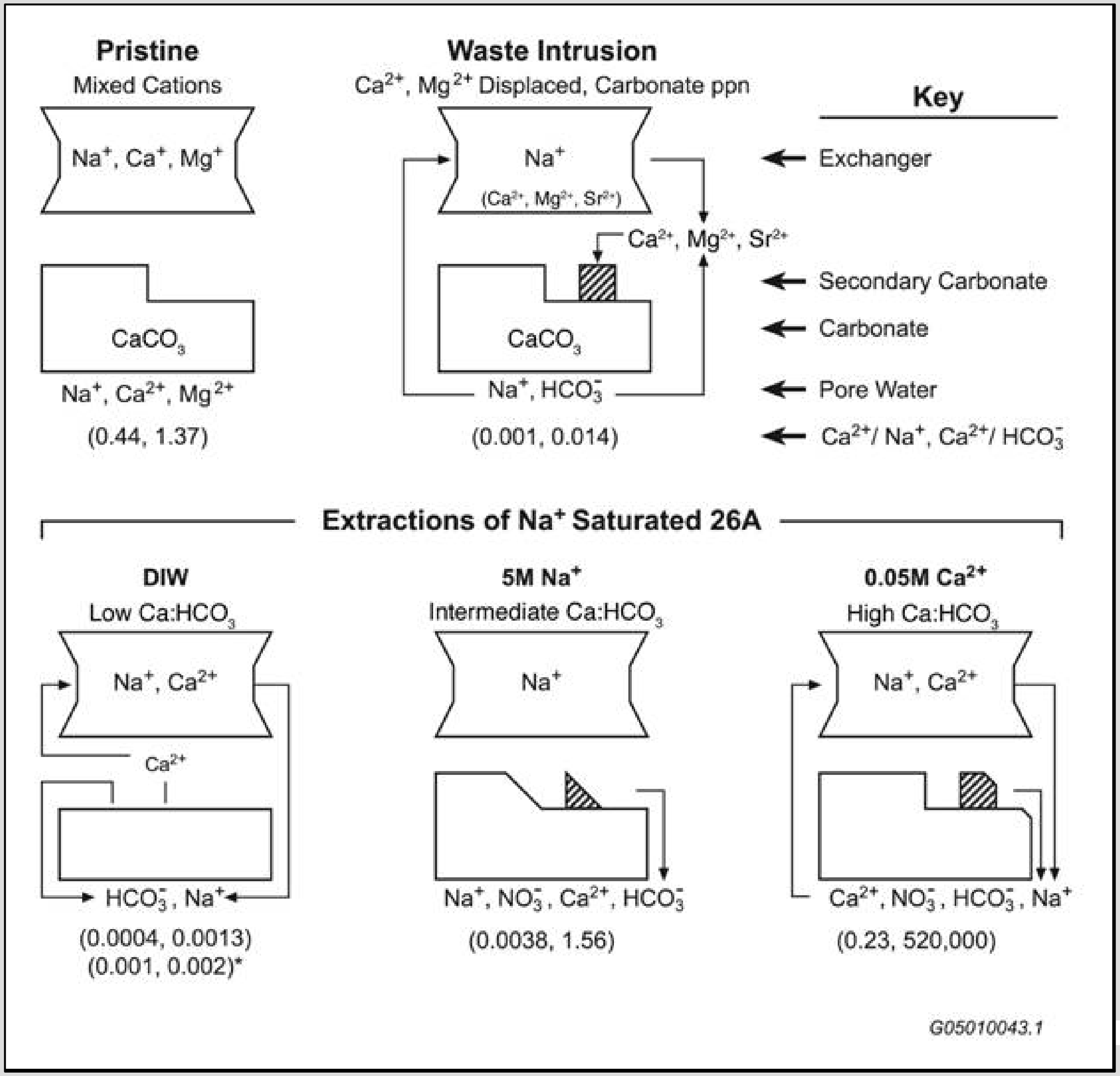
	Conc. Mol L^{-1}	Cation	(Modeled) W=washed
◆	DIW		(A)
●	0.01	Na^+	(B)
◆	1.0	Na^+	(C)
■	5.0	Na^+	(D)
•	0.05	Ca^{2+}	(E)
o	1.0	Na^+	W
g	5.0	Na^+	W
1	0.05	Ca^{2+}	W
♱	0.5	HCl	
!	1.0	NaOAc	
k	Model Results		

Relationships Between ^{90}Sr and $^{c}Sr^{2+}$ and Ca^{2+} in Desorption Experiments





Conceptual Model for Ion Exchange in Calcite Containing Sediments



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Reactions Used for Experiment Modeling

Exchange reactions:

	K_g	$\log K_r$
$2NaX + Sr^{2+} = SrX_2 + 2Na^+$	90.402	3.218
$2NaX + Ca^{2+} = CaX_2 + 2Na^+$	76.720	3.147
$2NaX + Mg^{2+} = MgX_2 + 2Na^+$	36.869	2.829
$NaX + K^+ = KX + Na^+$	21.010	1.322

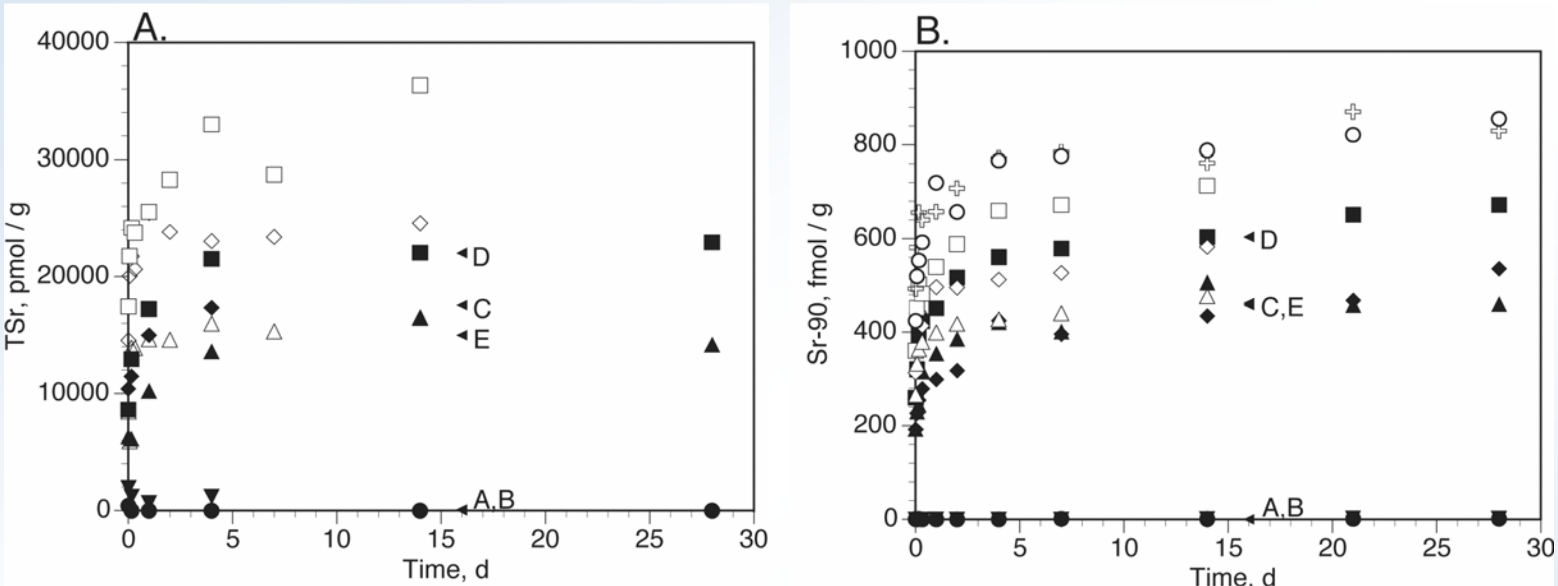
Aqueous species and their stability constants:

Species	**Reaction**	**log K**	**Source**
$SrOH^+$	$Sr^{2+} + H_2O - H^+ = SrOH^+$	-13.177	NIST
$SrCO_3(aq)$	$Sr^{2+} + CO_3^{2-} = SrCO_3(aq)$	2.81	NIST
$SrHCO_3^+$	$Sr^{2+} + CO_3^{2-} + H^+ = SrHCO_3^+$	11.539	NIST
$SrNO_3^+$	$Sr^{2+} + NO_3^+ = SrNO_3^+$	0.6	NIST
$NaNO_3$	$Na^+ + NO_3^- = NaNO_3$	-1.044	GMIN
$NaCO_3^-$	$Na^+ + CO_3^{2-} = NaCO_3^-$	1.27	NIST
$NaHCO_3$	$Na^+ + CO_3^{2-} + H^+ = NaHCO_3(aq)$	10.079	NIST
$CaOH^+$	$Ca^{2+} + H_2O - H^+ = CaOH^+$	-12.697	NIST
$CaCO_3(aq)$	$Ca^{2+} + CO_3^{2-} = CaCO_3(aq)$	3.20	NIST
$CaHCO_3^+$	$Ca^{2+} + CO_3^{2-} + H^+ = CaHCO_3^+$	11.599	NIST
$MgOH^+$	$Mg^{2+} + H_2O - H^+ = MgOH^+$	-11.397	NIST
$MgCO_3(aq)$	$Mg^{2+} + CO_3^{2-} = MgCO_3(aq)$	2.92	NIST
$MgHCO_3^+$	$Mg^{2+} + CO_3^{2-} + H^+ = MgHCO_3^+$	11.339	NIST
Calcite	$Ca^{2+} + CO_3^{2-} = CaCO_3$	8.48	NIST

Initial and Modeled Equilibrium Concentrations for Desorption from Sediment 26A

	µmol g^{-1}					pmol g^{-1}	fmol g^{-1}	pH
	IC[a]	Na[b]	Ca	K	Mg	^{T}Sr	^{90}Sr	
Exchanger:		43	1.17[c]	4.66[d]	0.53[e]	20400[c]	578[j]	
Leachant								
	Total Initial Concentration							
DIW	7.81	43	8.98[f]	20.26[g]	0.84[h]	26523[i]	775[k]	9.84
0.01 Na	4.93	63	6.10[f]	14.50[g]	0.73[h]	24265[i]	775[k]	9.53
0.05 Ca	0.19	43	101.36[f]	5.02[g]	0.54[h]	20548[i]	580[l]	7.65
1.0 Na	2.37	2043	3.54[f]	9.38[g]	0.62[h]	22258[i]	608[l]	8.40
5.0 Na	2.09	10043	3.26[f]	8.82[g]	0.61[h]	22038[i]	604[l]	8.16
	Modeled Equilibrium Aqueous Concentration							
DIW	7.81	29	0.05	1.75	0.01	99	0	9.84
0.01 Na	4.93	38	0.02	0.97	0.00	48	0	9.53
0.05 Ca	0.19	43		3.50	0.46	15000	462	7.65
1.0 Na	2.37	1998	2.81	6.15	0.49	17583	458	8.40
5.0 Na	2.09	9994	3.25	7.66	0.56	22038	604	8.16

Desorption of Sr from Contaminated Sediment 26A



	Conc. Mol L^{-1}	Cation	(Modeled) W=washed
◆	DIW		(A)
●	0.01	Na^+	(B)
◆	1.0	Na^+	(C)
■	5.0	Na^+	(D)
•	0.05	Ca^{2+}	(E)
o	1.0	Na^+	W
g	5.0	Na^+	W
1	0.05	Ca^{2+}	W
✞	0.5	HCl	
!	1.0	NaOAc	
k	Model Results		

Conclusions

- Characterizing the ion exchange process complicated by rapid primary mineral dissolution
  - Mineral dissolution and $CaCO_3$ solubility jointly control native exchanger phase composition

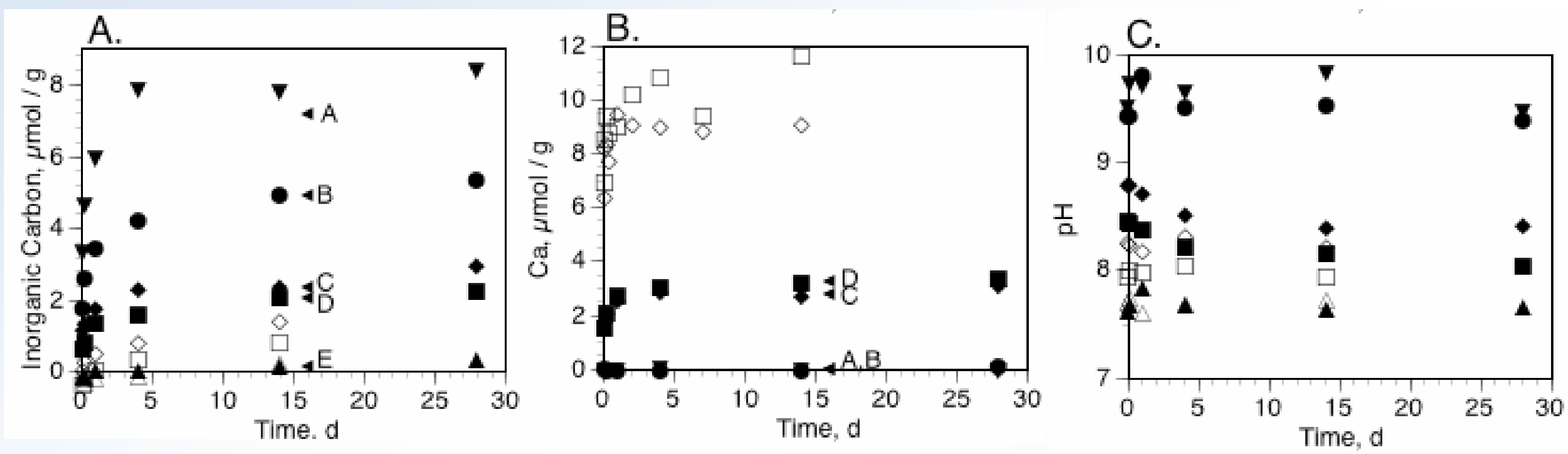
- An unusual exchanger phase identified in coarse-textured sediments: intragrain smectite derived from basaltic glass
  - Imparts diffusion – controlled kinetics to ion exchange

- A linked ion exchange – $CaCO_3$ solubility process controls ^{90}Sr mobility in the vadose zone
  - K_{ex}-Ca ≈ K_{ex}-Sr ≈ 1 > K_{ex}-Mg >> K_{ex}-Na

- ^{90}Sr immobile under current conditions
  - No counts in low I water

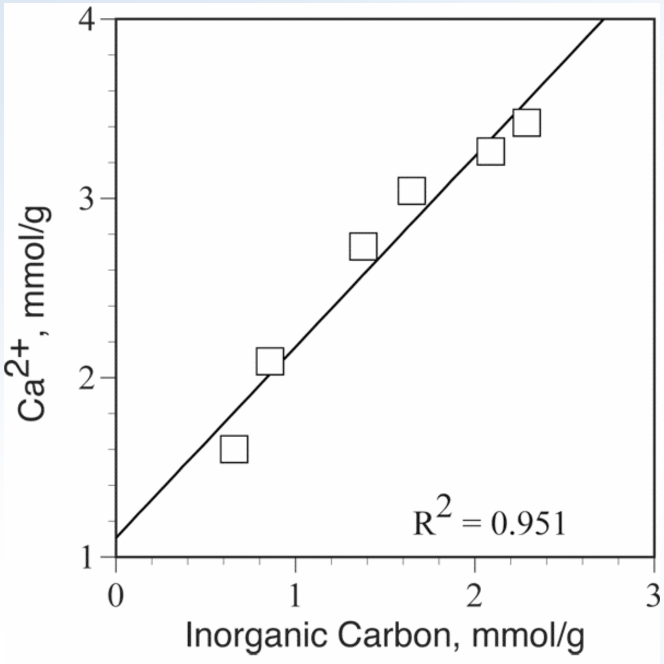
- Differences observed in other plumes
  - Temperature effects
  - Absence of $CaCO_3$
  - Matrix composition and size

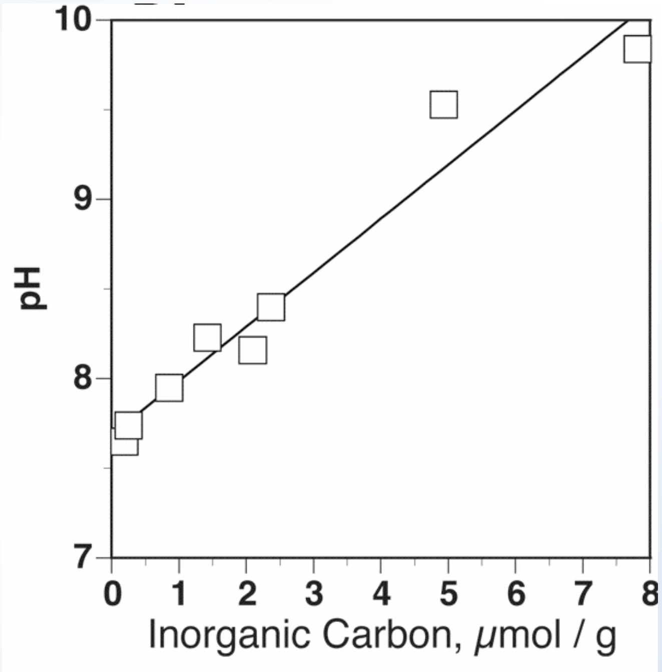
Ion Concentrations and pH Associated with Sr Desorption from Sediment 26A



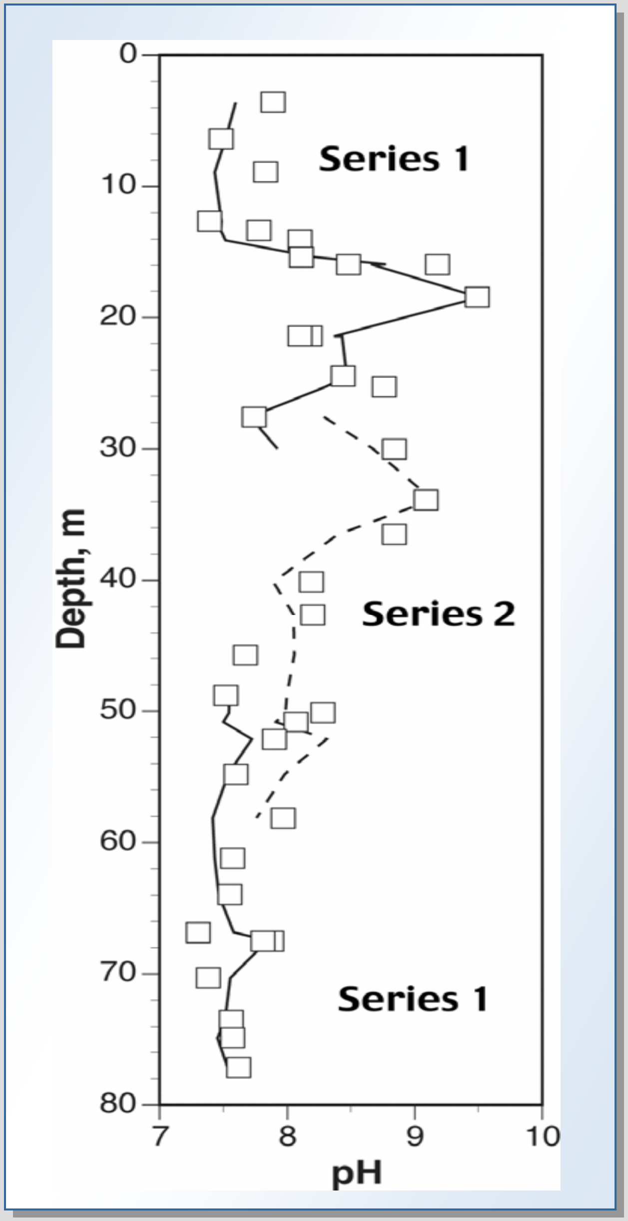
	Conc. Mol L^{-1}	Cation	(Modeled) W=washed
◆	DIW		(A)
●	0.01	Na^{+}	(B)
◆	1.0	Na^{+}	(C)
■	5.0	Na^{+}	(D)
⬩	0.05	Ca^{2+}	(E)
0	1.0	Na^{+}	W
g	5.0	Na^{+}	W
1	0.05	Ca^{2+}	W
✞	0.5	HCl	
!	1.0	NaOAc	
k	Model Results		

Relationships Between Ca^{2+}, DIC (HCO_3^- + CO_3^{2-}) and pH in Desorption Experiments





pH of B-110 Sediments Calculated from Inorganic Carbon Concentrations



Pore Water Compositions After Centrifugation

Sample No.	Depth m	Chge Bal. %	Cations, mmol/L					
			Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	Sr^{2+}	$H_4SiO_4^{0}$
20b	15.3	28.6	0.168	0.700	0.070	8.174	0.000457	0.553
21a	16.2	9.1	0.184	0.415	0.074	12.348	0.000457	0.490
36a	24.4	12.2	0.182	0.541	0.086	10.609	0.000457	0.490
38a	25.3	11.2	0.139	0.274	0.057	13.696	0.000342	0.550
84	51.4	12.6	2.168	0.541	1.189	7.435	0.005822	0.518
105c	63.7	-35.3	1.145	0.305	0.531	3.861	0.002854	0.728
110b	67.6	16.5	2.825	0.374	1.313	5.174	0.007420	0.547
113	68.9	20.2	1.330	0.333	0.605	2.965	0.003539	0.447
Sample No.	**pH**	**Aragonite SI**	**Anions, mmol/L**					
			NO_3^{-}	F^{-}	Cl^{-}	SO_4^{2-}	PO_4^{2-}	HCO_3^{-}
20b	8.23		0.129	0.632	0.204	0.324	0.019	3.541
21a	8.69	0.472	0.277	0.758	0.366	0.969	0.023	7.672
36a	8.39	0.149	0.081	1.300	0.203	0.629	0.000	6.311
38a	8.45	0.085	0.215	1.484	0.501	1.188	0.000	6.902
84	8.02	0.046	7.774	0.026	0.600	0.993	0.000	1.033
105c	7.00	-0.509	3.242	0.095	1.837	2.938	0.000	4.705
110b	7.16	-0.483	4.355	0.000	0.927	1.813	0.000	1.000
113	7.41	-0.744	1.694	0.000	0.451	0.828	0.000	0.967

Cation Exchange Capacity for Sediment 26A Estimated from Different Extraction Conditions

	Extractant			
	Unwashed[b] 1 mol L^{-1} NH_4Cl	Unwashed[a] 5 mol L^{-1} $NaNO_3$ and 0.05 mol L^{-1} $Ca(NO_3)_2$	Unwashed[a] 1 mol L^{-1} $NaNO_3$ and 0.05 mol L^{-1} $Ca(NO_3)_2$	Washed[a] 5 mol L^{-1} $NaNO_3$ and 0.05 mol L^{-1} $Ca(NO_3)_2$
Total[c] µeq g^{-1}	52.8	53.7	48.7	52.2
E(Na)[d]	0.343	0.676	0.745	0.256
E(K)	0.088	0.183	0.116	0.260
E(Ca)	0.569	0.121	0.115	0.447
E(Mg)	ND	0.020	0.023	0.034
E(^{T}Sr)	0.00082[e]	0.00082[e]	0.00035	0.0014

[a] Fourteen day extraction.

[b] Two hour extraction with water followed by two hour extraction with NH4Cl.

[c] Sum of extractable Na, K, Ca, Mg, and Sr.

[d] Fractional equivalents

[e] i.e., 0.022 mmol kg-1

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