Supporting Information For

Ionic strength and pH dependent multi-site sorption of $^{137}$Cs onto a micaceous aquifer sediment

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Figure S1 Competitive sorption of $10^{-9}$ mol L$^{-1}$ Cs from a background solution of 1 mol L$^{-1}$ KCl (diamonds), 0.1 mol L$^{-1}$ KCl (circles), 0.01 mol L$^{-1}$ KCl (triangles) and 1 mol L$^{-1}$ NaCl (squares). Data points represent the average of a triplicate sample. Error bars are shown on those points where the error (standard deviation) was greater than or equal to the size of the symbol.
Figure S2 Cs sorption isotherms in a background of (a) deionised water, (b) 1 mol L\(^{-1}\) Na (as NaCl) and (c) 1 mol L\(^{-1}\) K (as KCl). Data points indicate measured experimental results (averages of three replicates) and solid line is the model output. Error bars are not shown as they were smaller than the symbol.
Section S1 Additional modelling methodology

Aqueous activity

In the generic Bradbury and Baeyens (2000) model, and in our refined version, all aqueous phases are assumed to be in thermodynamic equilibrium. The behaviour of aqueous species \( i \) is governed by its activity, \( a_i \), activity coefficient, \( \gamma_i \), molality, \( m_i \), and number of moles in solution, \( n_i \), where \( a_i = \gamma_i m_i \) and \( n_i = m_i W_{aq} \) where \( W_{aq} \) is the mass of aqueous water in solution.

The equilibrium relationship between all the aqueous species in a chemical reaction is related via a mass-action equation 1

\[
K_i = a_i \prod_{m} \gamma_m^{-c_{m,i}}
\]  

(S1)

where \( K_i \) is the temperature-dependent equilibrium constant, \( c_{m,i} \) is the stoichiometric coefficient of master species \( m \) in species \( i \), and \( M_{aq} \) is the total number of aqueous master species. The \( K_i \) values for reactions occurring in our experimental aqueous solutions were taken from the WATEQ4F.dat thermodynamic database (Ball and Nordstrom, 1991) for all modelling done at total ionic strength of <0.5 mol L\(^{-1}\). Above this the Piter.dat database (Pitzer, 1973) was used.

Activity coefficients, \( \gamma_i \), of the aqueous species are defined with the extended Debye-Hückel equation

\[
\log \gamma_i = - \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i^o \sqrt{\mu}} + b_i \mu
\]  

(S2)
or the Davies equation

\[ \log \gamma_i = A z_i^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3 \mu \right) \]  

(S3)

where \( z_i \) is the ionic charge of aqueous species \( i \), \( \mu \) is the ionic strength of the solution and \( A \) and \( B \) are temperature dependant constants.

Aqueous activity coefficients calculated using the extended Debye-Hückel equation are only valid for solutions of ionic strength \( \leq 0.1 \text{ mol L}^{-1} \) for monovalent ions (Langmuir, 1997). At concentrations above this the Davies (valid up to 0.7 mol L\(^{-1}\)) or Pitzer (valid at ionic strength up to 6 mol L\(^{-1}\)) equations must be used (Langmuir, 1997). As some of the experimental work done here is performed at ionic strength of 1 mol L\(^{-1}\) (and above) the Pitzer equation was used to calculate the \( \gamma \) for these scenarios. The Pitzer equations are explained in detail by Plummer et al. (1988).
Section S2 PHREEQCv2 Modelling code example

Notes for users
The following input file can be copy and pasted to PHREEQC. The model, when run with the wateq4f.dat thermodynamic database will then output the results presented in the Na contour plot (see main text figure 5). Other modelling outputs presented in this paper can be modelled by changing the composition of the solution terms (eg changing to K instead of Na will give the K contour plot in figure 5).

PHREEQC code

Title Initial solution

Solution 1
pH 7
Units g/l
K  0.035
Cl  0.0692
Mg  0.0404
S  0.0260
O(0)  0.1000
Na  0.0349
Si  0.0191
N  0.0045

save solution 1

end

TITLE Caesium Sorption experiment
use solution 1

EXCHANGE_MASTER_SPECIES
    X    X-
    Y    Y-
    Z    Z-

EXCHANGE_SPECIES
    Y-  =  Y-
    log_k  0.0
    Z-  =  Z-


log_k  0.0

X- = X-
log_k  0.0

H+ + X- = HX
log_k  2.5

K+ + X- = KX
log_k  0.5

Na+ + X- = NaX
log_k  0.0

Na+ + Y- = NaY
log_k  0.0

K+ + Y- = KY
log_k  0.6

H+ + Y- = HY  # Set as equal to Cs
log_k  3.6

Ca+2 + 2Y- = CaY2
log_k  0.8

Mg+2 + 2Y- = MgY2
log_k  0.6

Na+ + Z- = NaZ
log_k  0.0

K+ + Z- = KZ
log_k  1.5

H+ + Z- = HZ
log_k  1.75  # Poinsot, et al 1999

Ca+2 + 2Z- = CaZ2
log_k  0.8

Mg+2 + 2Z- = MgZ2
log_k  0.6
EXCHANGE 1
X  6.5e-3
Y  1.6e-4
Z  4.0e-6
-equilibrate solution 1

save exchange 1

end
TITLE Sorption of caesium

EXCHANGE_SPECIES
Cs+ + X^- = CsX  #planar
  log_k 1.2

Cs+ + Y^- = CsY  #TypeII
  log_k 3.6

Cs+ + Z^- = CsZ  #FES
  log_k 7.0

PHASES
Fix_H+
  H+ = H+
  log_k 0.0

SELECTED_OUTPUT
  -file [file name]
  -m Cs+ CsX CsY CsZ
  -t Cs
USE EXCHANGE 1
use solution 1

solution 2
  ph 7
  units moles/l
  Na 1.0e-1
  Cs 1.0e-9

solution 3
  ph 7
  units moles/l
  Na 1.0e-1
  Cs 5.0e-9
solution 4
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-8

solution 5
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-8

solution 6
pH 7
units moles/l
Na 1.0e-1
Cs 1.0e-7

solution 7
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-7

solution 8
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-6

solution 9
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-6

solution 10
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-5

solution 11
<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Units</th>
<th>Moles/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This table represents the pH, units, and moles/l concentrations for solutions 12 to 18.
Na 1.0e-1
Cs 1.0e-1

end

USE EXCHANGE 1
use solution 2
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 3
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 4
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 5
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 6
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 7
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 8
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 9
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
USE EXCHANGE 1
use solution 10
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 11
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 12
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 13
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 14
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 15
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 16
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 17
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

USE EXCHANGE 1
use solution 18
EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
end

References
thermodynamic database and test cases for calculating speciation of major, trace
and redox elements in natural waters.
incorporating Pitzer’s equation for calculation of geochemical reactions in brines,
Water-Resources Investigations Report, 88-4153. USGS, Virginia.