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2 **Supporting Information For**
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6 **Ionic strength and pH dependent multi-site sorption of**
7 **¹³⁷Cs onto a micaceous aquifer sediment**
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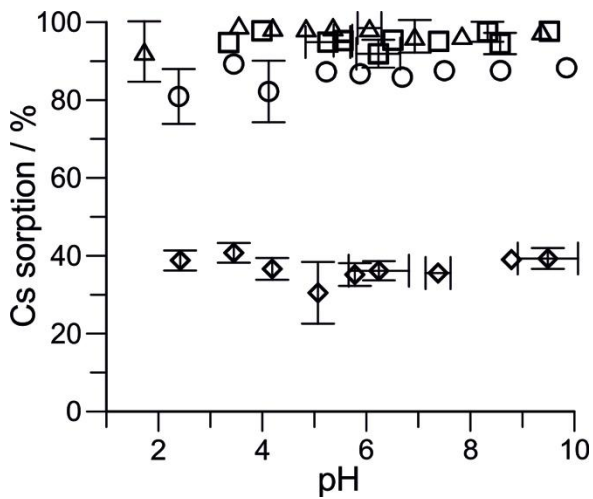


Figure S1 Competitive sorption of 10^{-9} mol L⁻¹ Cs from a background solution of 1 mol L⁻¹ KCl (diamonds), 0.1 mol L⁻¹ KCl (circles), 0.01 mol L⁻¹ KCl (triangles) and 1 mol L⁻¹ NaCl (squares). Data points represent the average of a triplicate sample. Error bars are shown on those points where the error (standard deviation) was greater than or equal to the size of the symbol.

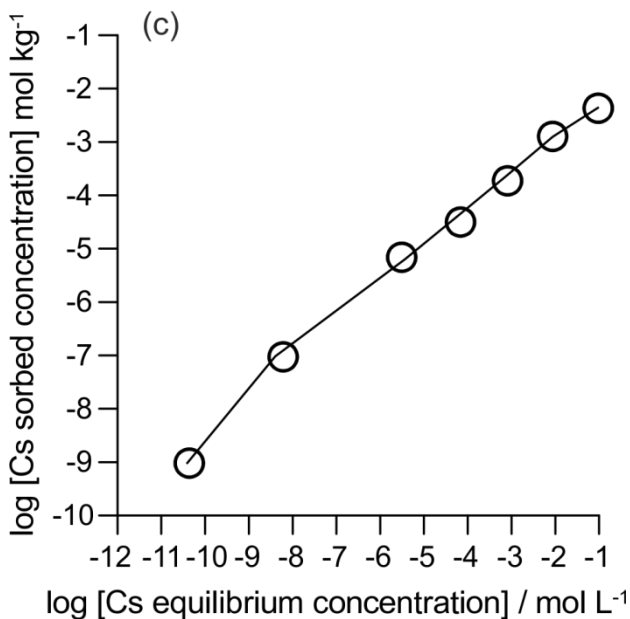
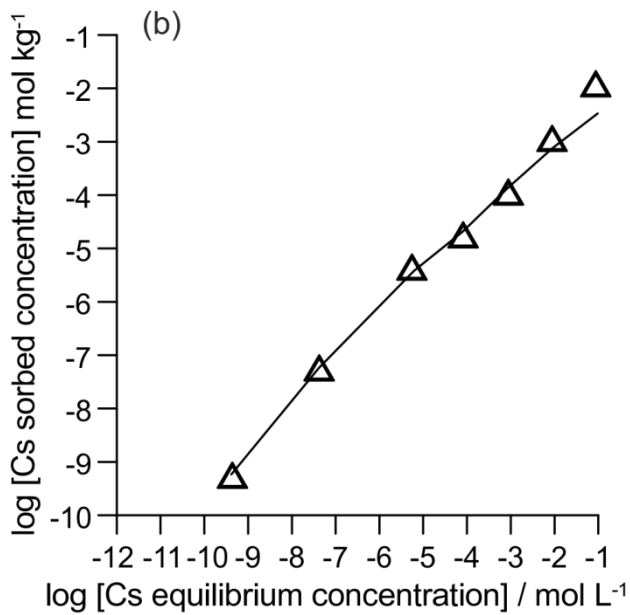
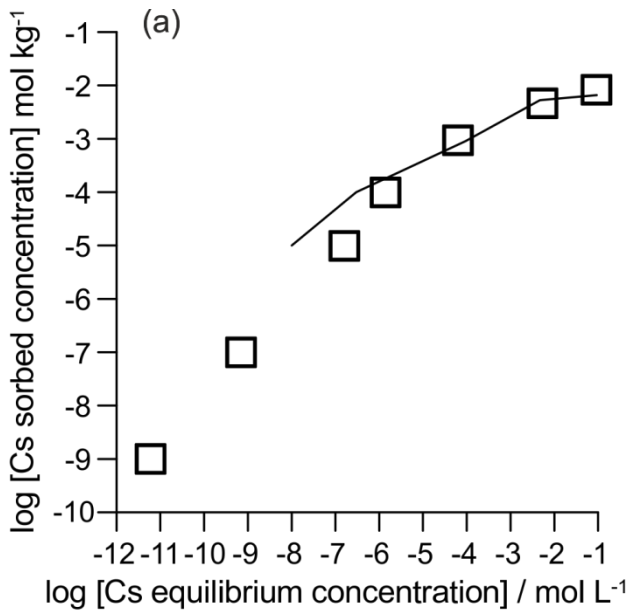


Figure S2 Cs sorption isotherms in a background of (a) deionised water, (b) 1 mol L⁻¹ Na (as NaCl) and (c) 1 mol L⁻¹ K (as KCl). Data points indicate measured experimental results (averages of three replicates) and solid line is the model output. Error bars are not shown as they were smaller than the 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, γ_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

$$K_i = a_i \prod_m^{M_{aq}} a_m^{-c_{m,i}} \quad (\text{S1})$$

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 $<0.5 \text{ mol L}^{-1}$. Above this the Pitzer.dat database (Pitzer, 1973) was used.

Activity coefficients, γ , of the aqueous species are defined with the extended Debye-Hückel equation

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{\mu}}{1 + Ba_i^o \sqrt{\mu}} + b_i \mu \quad (\text{S2})$$

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or the Davies equation

$$\log \gamma_i = Az_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad (\text{S3})$$

where z_i is the ionic charge of aqueous species i , μ 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 γ 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-

```

1      log_k 0.0
2
3      X- = X-
4      log_k 0.0
5
6
7      H+ + X- = HX
8      log_k 2.5
9
10
11     K+ + X- = KX
12     log_k 0.5
13
14
15     Na+ + X- = NaX
16     log_k 0.0
17
18
19     Na+ + Y- = NaY
20     log_k 0.0
21
22
23     K+ + Y- = KY
24     log_k 0.6
25
26
27
28     H+ + Y- = HY      # Set as equal to Cs
29     log_k 3.6
30
31
32     Ca+2 + 2Y- = CaY2
33     log_k 0.8
34
35
36     Mg+2 + 2Y- = MgY2
37     log_k 0.6
38
39
40     Na+ + Z- = NaZ
41     log_k 0.0
42
43
44     K+ + Z- = KZ
45     log_k 1.5
46
47
48     H+ + Z- = HZ
49     log_k 1.75 # Poinso, et al 1999
50
51
52
53     Ca+2 + 2Z- = CaZ2
54     log_k 0.8
55
56
57     Mg+2 + 2Z- = MgZ2
58     log_k 0.6
59
60
61
62
63
64
65

```

```

1  EXCHANGE 1
2  X    6.5e-3
3  Y    1.6e-4
4  Z    4.0e-6
5  -equilibrate solution 1
6
7
8  save exchange 1
9
10
11 end
12 TITLE Sorption of caesium
13
14
15 EXCHANGE_SPECIES
16     Cs+ + X- = CsX    #planar
17     log_k 1.2
18
19
20
21     Cs+ + Y- = CsY    #Typell
22     log_k 3.6
23
24
25     Cs+ + Z- = CsZ    #FES
26     log_k 7.0
27
28
29 PHASES
30 Fix_H+
31     H+ = H+
32     log_k 0.0
33
34
35
36 SELECTED_OUTPUT
37     -file [file name]
38     -m Cs+ CsX CsY CsZ
39     -t Cs
40
41 USE EXCHANGE 1
42 use solution 1
43
44
45
46 solution 2
47 ph 7
48 units moles/l
49 Na 1.0e-1
50 Cs 1.0e-9
51
52
53
54 solution 3
55 ph 7
56 units moles/l
57 Na 1.0e-1
58 Cs 5.0e-9
59
60
61
62
63
64
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```


1 solution 4
2
3 ph 7
4 units moles/l
5 Na 1.0e-1
6 Cs 1.0e-8
7
8
9
10 solution 5
11 ph 7
12 units moles/l
13 Na 1.0e-1
14 Cs 5.0e-8
15
16
17
18 solution 6
19 pH 7
20 units moles/l
21 Na 1.0e-1
22 Cs 1.0e-7
23
24
25
26 solution 7
27 ph 7
28 units moles/l
29 Na 1.0e-1
30 Cs 5.0e-7
31
32
33
34 solution 8
35 ph 7
36 units moles/l
37 Na 1.0e-1
38 Cs 1.0e-6
39
40
41
42 solution 9
43 ph 7
44 units moles/l
45 Na 1.0e-1
46 Cs 5.0e-6
47
48
49
50
51 solution 10
52 ph 7
53 units moles/l
54 Na 1.0e-1
55 Cs 1.0e-5
56
57
58
59
60 solution 11
61
62
63
64
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1 ph 7
2 units moles/l
3 Na 1.0e-1
4 Cs 5.0e-5
5
6
7 solution 12
8 ph 7
9 units moles/l
10 Na 1.0e-1
11 Cs 1.0e-4
12
13
14
15 solution 13
16 ph 7
17 units moles/l
18 Na 1.0e-1
19 Cs 5.0e-4
20
21
22
23 solution 14
24 ph 7
25 units moles/l
26 Na 1.0e-1
27 Cs 1.0e-3
28
29
30
31 solution 15
32 ph 7
33 units moles/l
34 Na 1.0e-1
35 Cs 5.0e-3
36
37
38
39 solution 16
40 ph 7
41 units moles/l
42 Na 1.0e-1
43 Cs 1.0e-2
44
45
46
47 solution 17
48 ph 7
49 units moles/l
50 Na 1.0e-1
51 Cs 5.0e-2
52
53
54
55 solution 18
56 ph 7
57 units moles/l
58
59
60
61
62
63
64
65

```
1 Na 1.0e-1
2 Cs 1.0e-1
3
4 end
5
6
7
8 USE EXCHANGE 1
9 use solution 2
10 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
11 end
12
13
14
15 USE EXCHANGE 1
16 use solution 3
17 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
18 end
19
20
21
22 USE EXCHANGE 1
23 use solution 4
24 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
25 end
26
27
28
29 USE EXCHANGE 1
30 use solution 5
31 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
32 end
33
34
35
36 USE EXCHANGE 1
37 use solution 6
38 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
39 end
40
41
42
43 USE EXCHANGE 1
44 use solution 7
45 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
46 end
47
48
49
50 USE EXCHANGE 1
51 use solution 8
52 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
53 end
54
55
56
57 USE EXCHANGE 1
58 use solution 9
59 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
60 end
61
62
63
64
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```

```
1 end
2
3 USE EXCHANGE 1
4 use solution 10
5 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
6 end
7
8
9 USE EXCHANGE 1
10 use solution 11
11 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
12 end
13
14
15 USE EXCHANGE 1
16 use solution 12
17 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
18 end
19
20
21 USE EXCHANGE 1
22 use solution 13
23 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
24 end
25
26
27 USE EXCHANGE 1
28 use solution 14
29 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
30 end
31
32
33 USE EXCHANGE 1
34 use solution 15
35 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
36 end
37
38
39 USE EXCHANGE 1
40 use solution 16
41 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
42 end
43
44
45 USE EXCHANGE 1
46 use solution 17
47 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
48 end
49
50
51 USE EXCHANGE 1
52 use solution 18
53 EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0
54 end
55
56
57
58
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60
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62
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```

EQUILIBRIUM_PHASES 1; Fix_H+ -7.0 NaOH 10.0

end

References

Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATEQ4F with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, New Jersey.

Pitzer, K.S., 1973. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 77, 268-277.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., Dunkle, S.A., 1988. A computer program incorporating Pitzer's equation for calculation of geochemical reactions in brines, Water-Resources Investigations Report, 88-4153. USGS, Virginia.