Supporting Information For

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

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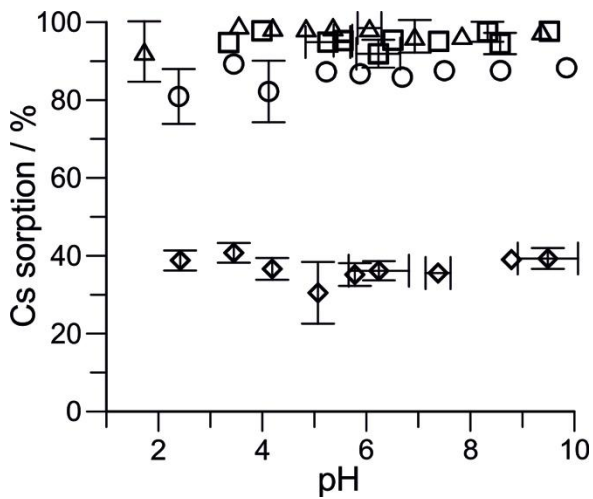[c]National Nuclear Laboratories, Chadwick House, Warrington Road, Birchwood Park, Warrington, WA3 6AE, UK

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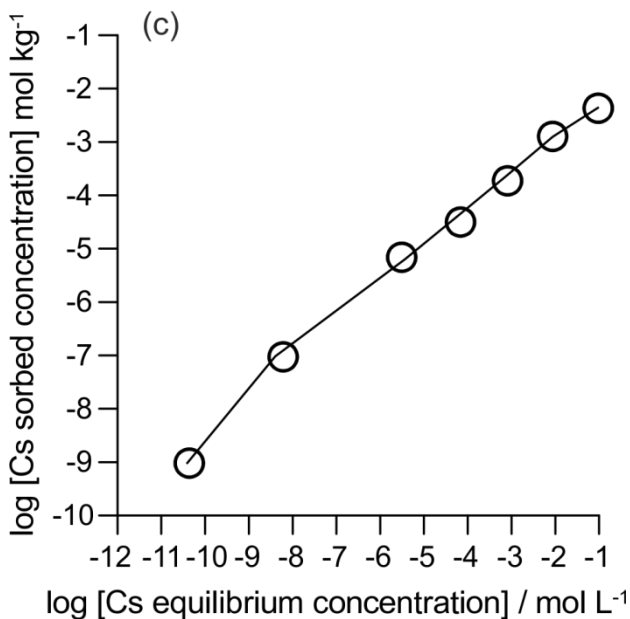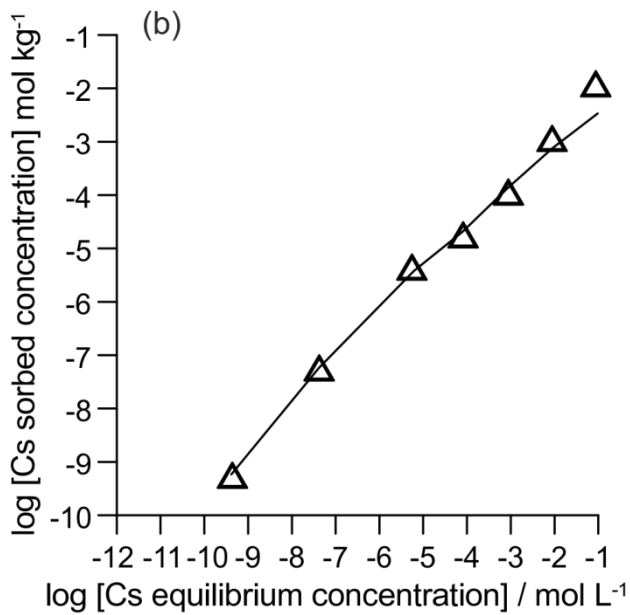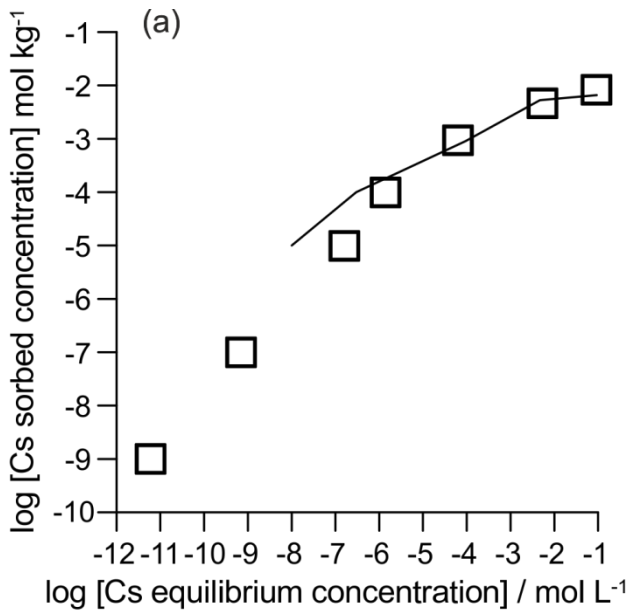
Figure S2 Cs sorption isotherms in a background of (a) deionised water, (b) 1 mol L^{-1} Na (as NaCl) and (c) 1 mol L^{-1} K (as KCl). Data points indicate measured experimental results (averages of three replicates) and solid line is the model output. Error bars are not shown as they were smaller than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

$$K_i = a_i \prod_m^{M_{aq}} a_m^{-c_{m,i}}$$

(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, γ, of the aqueous species are defined with the extended Debye-Hückel

equation

$$log\gamma_i = -\frac{Az_i^2\sqrt{\mu}}{1 + Ba_i^o\sqrt{\mu}} + b_i\mu$$

(S2)

or the Davies equation

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

(S3)

where z_i is the ionic charge of aqueous species i, 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 ≤ 0.1 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-
```

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```
        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

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

solution 12
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-4

solution 13
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-4

solution 14
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-3

solution 15
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-3

solution 16
ph 7
units moles/l
Na 1.0e-1
Cs 1.0e-2

solution 17
ph 7
units moles/l
Na 1.0e-1
Cs 5.0e-2

solution 18
ph 7
units moles/l

```
    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
```

end

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

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.