



Working Report 2017-41

Sorption of Alkaline Earth Metals on Biotite of Olkiluoto Bedrock

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Working Reports contain information on work in progress
or pending completion.

SORPTION OF ALKALINE EARTH METALS ON BIOTITE OF OLKILUOTO BEDROCK

ABSTRACT

The sorption of alkaline earth cations Ca, Sr, Ba and Ra was investigated in batch experiments on Na-converted biotite, the main sorbing mineral in granitic bedrock at the nuclear waste disposal site in Olkiluoto, Finland. The experiments were conducted in anoxic conditions of a glovebox by varying the concentration of the alkaline earth cation (Ca, Sr and Ba 10^{-8} M – 10^{-5} M; Ra 10^{-10} M – 10^{-7} M) in 0.01 M to 0.1 M and 1 M NaClO₄ solutions buffered to pH 8. Additional experiments were conducted with Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA.

The retention of Ca, Sr, Ba and Ra followed a Freundlich representation of an adsorption isotherm. The linear fit to the experimental data was good with R² values ranging from 0.968 to 0.999. The values of *N* ranged from 0.599 to 1.33.

The retention of Ca, Sr, Ba and Ra showed dependence on the ionic strength of the NaClO₄ solution. As a general trend, the retention of alkaline earth cations decreased upon (i) increasing initial concentration in the liquid phase and (ii) increasing NaClO₄ solution concentration. The *K_d* values decrease in the order of Ra > Ba > Sr > Ca.

The highest retention of Ca, Sr, Ba and Ra among the Olkiluoto reference groundwaters was observed in OLGA, followed by ALLMR, where the *K_d* values increased in the order of Ca < Sr < Ba < Ra for both solutions. No retention of Ca, Sr or Ra took place in relatively high ionic strength OLSR and OLBA, whereas Ba was slightly retained in OLBA.

The sorption of Ca, Sr, Ba and Ra was modelled in 0.01 M, 0.1 M and 1 M NaClO₄ solutions and Olkiluoto reference groundwaters using mechanistic three-site cation exchange model developed by Kyllönen et al. (2008, 2014) for Cs sorption on biotite. The model gave generally a good fit to experimental results in 0.01 M and 0.1 M NaClO₄ solutions and ALLMR and OLGA, whereas in 1 M NaClO₄ solutions and OLSR and OLBA it gave slightly overestimated values since no sorption was observed in the experimental sorption tests.

Keywords: alkaline earth cations, sorption, speciation, sorption modelling, cation exchange, biotite

MAA-ALKALIMETALLIEN SORPTIO OLKILUODON PERUSKALLION BIOTIITTIIN

TIIVISTELMÄ

Maa-alkalimetallien Ca, Sr, Ba ja Ra sorptiota tutkittiin eräkokein Na-muotoiseen biotiittiin, joka on Suomen ydinjätteen loppusijoituspaikan Olkiluodon graniittisen peruskallion pääasiallinen sorboiva mineraali. Kokeet suoritettiin typpikaapin hapettomissa olosuhteissa vaihdellen maa-alkalimetallin pitoisuuksia (Ca, Sr ja Ba 10^{-8} M – 10^{-5} M; Ra 10^{-10} M – 10^{-7} M) 0.01 M, 0.1 M ja 1 M NaClO₄ liuoksissa, jotka oli puskuroitu pH-arvoon 8. Lisäksi sorptiokokeita tehtiin Olkiluodon referenssipohjavesillä ALLMR, OLSR, OLGA ja OLBA.

Ca:n, Sr:n, Ba:n ja Ra:n retentio noudatti Freundlichin adsorptioisotermiä. Suoran sovitus kokeelliseen dataan oli hyvä R² arvojen vaihdellessa välillä 0.968 – 0.999. N:n arvot vaihtelivat luvusta 0.599 lukuun 1.33.

Ca:n, Sr:n, Ba:n ja Ra:n sorptio osoitti riippuvuutta NaClO₄ taustaliuoksen ionivahvuudesta. Yleisenä trendinä maa-alkalimetallien sorptio pieneni kun (i) maa-alkalimetallin alkukonsentraatio liuoksessa kasvoi ja (ii) taustaliuoksen ionivahvuus kasvoi. Maa-alkalimetallien K_d arvot pienenivät järjestyksessä Ra > Ba > Sr > Ca.

Korkein retentio Olkiluodon referenssipohjavesissä havaittiin OLGA:ssa ja seuraavaksi korkein ALLMR:ssä Ca:lle, Sr:lle, Ba:lle ja Ra:lle. Näissä vesissä Ca:n, Sr:n, Ba:n ja Ra:n K_d arvot kasvoivat järjestyksessä Ca < Sr < Ba < Ra. Ca:n, Sr:n tai Ra:n sorptiota ei havaittu suhteellisen korkean ionivahvuuden OLSR- ja OLBA-vesissä, kun taas Ba pidättyi hieman OLBA:ssa.

Ca:n, Sr:n, Ba:n ja Ra:n sorptiota mallinnettiin 0.01 M, 0.1 M ja 1 M NaClO₄ liuoksissa sekä Olkiluodon referenssipohjavesissä käyttäen mekanistista kolmipaikkaista kationinvaihtomallia, joka on kehitetty Cs:n sorptiolle biotiittiin (Kyllönen et al. 2008, 2014). Malli sopi hyvin kokeellisiin tuloksiin 0.01 M ja 0.1 M NaClO₄ liuoksissa sekä ALLMR:ssa ja OLGA:ssa referenssipohjavesissä, kun taas 1 M NaClO₄ liuoksessa sekä OLSR:ssa and OLBA:ssa se hieman yliarvio K_d arvoja johtuen olemattomasta kokeellisesta sorptiosta.

Avainsanat: maa-alkalimetallit, sorptio, spesiaatio, sorptiomallinnus, kationinvaihto, biotiitti

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ABBREVIATIONS

ALLMR (modified Allard)	Fresh mildly reducing granitic reference groundwater
ICP-MS	Inductively coupled plasma mass spectrometer
LOG	Logarithm of a specified value
K_d	Mass distribution coefficient
OLBA	Carbonate containing reducing brackish reference groundwater
OLGA	Glacial anoxic meltwater (synthetic composition)
OLSR	Saline reducing reference groundwater
PhreeqC	Geological modelling program
Thermoddem	Thermodynamic database developed to be used for environmental modelling

1 INTRODUCTION

Calcium (Ca; $Z=20$), strontium (Sr; $Z=38$), barium (Ba; $Z=56$) and radium (Ra; $Z=88$) are alkaline earth metals belonging to the second group in the Periodic Table of Elements. They all have full outer s-electron shell accommodating two electrons, and electron shell number is 4 for Ca, 5 for Sr, 6 for Ba and 7 for Ra. The electronegativity of Ca and Sr is 1.0 on Pauling's scale, whilst the respective value for Ba and Ra is 0.9. Because of their low electronegativity, alkaline earth metals readily lose their outer electrons to form M^{2+} cation in the solution. In their compounds alkaline earth metals are present at oxidation state +II.

The most important radioisotopes of Ca in the context of nuclear waste, mainly in the concrete of reactor shielding buildings, are ^{41}Ca ($t_{1/2} = 1 \times 10^5$ y) and ^{45}Ca ($t_{1/2} = 163$ d). From these ^{41}Ca decays by electron capture and ^{45}Ca by beta decay ($E_{\beta, \text{max}} = 257$ keV). ^{41}Ca and ^{45}Ca are both activation products, as ^{41}Ca is formed in the neutron activation of stable Ca isotope ^{40}Ca and ^{45}Ca in the respective activation of ^{44}Ca .

The radioisotopes ^{89}Sr ($t_{1/2} = 50$ d) and ^{90}Sr ($t_{1/2} = 29$ y) are both fission products present in the nuclear fuel, but are rather unimportant in the long time scales due to their rather short half-lives. Their yields in the fission of ^{235}U are 4.7% and 5.8%, respectively. ^{89}Sr and ^{90}Sr are both pure beta emitters with $E_{\beta, \text{max}} = 1480$ keV for ^{89}Sr and $E_{\beta, \text{max}} = 540$ keV for ^{90}Sr .

Ba does not have any radioisotope present in the nuclear waste at significant levels at the long time scales. ^{140}Ba is the most important radioisotope, but it has a half-life of only 13 days. However, its cumulative fission yield in the thermal fission of ^{235}U is 6.3%. ^{140}Ba decays by beta decay and emits several β^- particles with different intensities.

Ra is a radioactive element and naturally created in the decay chains of uranium and thorium. Ra is present in the spent nuclear fuel, and the most important isotope is the alpha emitter ($E_{\alpha} = 4784$ keV) ^{226}Ra ($t_{1/2} = 1600$ y).

The evaluation of radioactive waste nuclides in Posiva's spent nuclear fuel safety assessment and the corresponding one of SKB consider that ^{226}Ra is of considerable significance for the evaluation of far-field dose rates (Crawford, 2010; Hakanen et al., 2014). ^{90}Sr is in the list of significant radionuclides, but owing to its relatively short half-life it has only a minor significance for far-field transport assessment. Radioisotopes of Ca and Ba are not present in the spent fuel, but as the constituents of Olkiluoto groundwaters and as possible analogues for Sr and Ra, respectively, they are relevant to understanding the behavior of Ra and Sr. Especially the competitive ion exchange reactions between the alkaline earth metals can be estimated more thoroughly when they are all considered and studied. For assessing their mobility the K_d values have been estimated based on a scarce set of experimental data on crushed rock and often assuming analogical behaviour.

This research focused on the sorption of alkaline earth metals Ca, Sr, Ba and Ra on the most important sorbing mineral, biotite, at the nuclear waste disposal site in Olkiluoto, Finland. The sorption of alkaline earth metals was studied by batch experiments at anoxic conditions using crushed biotite separated from Olkiluoto mica gneiss. The experiments were conducted in pH 8 buffered 0.01 M, 0.1 M and 1 M NaClO_4 solution and in Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. The sorption of Ca, Sr, Ba

and Ra on biotite was modelled using mechanistic three-site cation exchange model presented by Kyllönen et al. (2008).

2 MATERIALS

2.1 Biotite

The biotite used in this work was originally separated from other minerals present in <0.5 mm grain size fraction of crushed mica gneiss rock drill core sample (code KR2) taken from the depth of 200–500 m of Olkiluoto bedrock by heavy liquid and magnetic methods (Kyllönen et al., 2008; Kyllönen et al., 2014). The mineral purity of the separated biotite was 94% with an additional 6% content of chlorite, that could not be separated from the biotite (Kyllönen et al., 2008). Fe/Mg ratio of KR2 biotite was determined to be 1.82 (Kyllönen et al., 2008), CEC 16.7 $\mu\text{eq/g}$ (Kyllönen et al., 2014) and N_2 -BET surface area 0.64 m^2/g (Kyllönen et al., 2008). Its chemical composition was found to be typical for mica gneiss biotites present in Olkiluoto bedrock (Kyllönen et al., 2008).

2.2 Solutions

All the solutions used in the experiments were prepared in 18 M Ω deionised MilliQ water using analytical grade reagents. Depending on the nature of the solution, the preparation was done either in the glovebox (groundwaters) or in the normal laboratory atmosphere (electrolyte solutions). All the solutions prepared outside the glovebox, and pure MilliQ water to be used inside the glovebox, were vacuum degassed to remove dissolved gases (CO_2 and O_2) and bubbled with N_2 gas for 30 min prior to transferring them to the glovebox.

2.2.1 Groundwater simulants

The classification of groundwaters is typically executed based on the content of total dissolved solids (TDS) in the solution. Four categories are separated according to increasing TDS, namely fresh water (TDS <1000 mg/L), brackish water (1000 mg/L < TDS < 10 000 mg/L), saline water (10 000 mg/L < TDS < 100 000 mg/L) and brine (TDS > 100 000 mg/L). At Olkiluoto and former geological final repository investigation sites at Hästholmen, Kivetty and Romuvaara, fresh, brackish and saline groundwaters have been encountered (Vuorinen et al., 1998). All these water types together with brine are considered as possible far-field reference waters in the performance assessment of final repository.

Reference groundwater simulants used in the sorption experiments of alkaline earth cations were fresh mildly reducing ALLMR, which is a modification of simulated granitic groundwater Allard; saline reducing OLSR; glacial anoxic meltwater OLGA; and carbonate containing brackish OLBA (Hellä et al., 2014; Vuorinen et al., 1998). Table 1 combines the chemical composition and pH of each reference groundwater simulant (ALLMR, OLSR, OLGA and OLBA).

Reference groundwaters were prepared in the nitrogen box using MilliQ water, that was let to equilibrate with the nitrogen atmosphere for a week or two before being used. Each component listed in Table 1 were added from higher concentration stock solutions to produce 1 L of reference groundwater simulant with the desired chemical composition. When necessary, solution pH was adjusted with addition of 0.1 M HCl or 0.1 M NaOH

until the desired pH value was attained. The chemicals used in the preparation of the groundwater simulants ALLMR, OLSR, OLGA and OLBA are summarised in Table 2.

Table 1. The chemical composition (mg/L, pH) and ionic strength (*I*, mmol/L) of the reference groundwater simulants ALLMR, OLSR, OLGA and OLBA (Hellä et al., 2014; Vuorinen et al., 1998)

Ion	Concentration of the ion (mg/l)			
	ALLMR fresh mildly reducing granitic groundwater	OLSR saline reducing groundwater	OLGA glacial anoxic meltwater	OLBA carbonate containing brackish anoxic groundwater
Na ⁺	52.5	4800	0.66	1750
K ⁺	3.9	21	0.6	18.9
NH ₄ ⁺	–	–	–	0.33
Mg ²⁺	0.7	54.6	0.3	26.5
Ca ²⁺	5.1	4000	0.52	84.5
Sr ²⁺	–	35	–	0.1
B ³⁺	–	0.92	–	0.62
Cl ⁻	48.8	14500	3	2530
HCO ₃ ⁻	165	–	–	111
SiO ₂	17	–	0.1	6.1
SO ₄ ²⁻	9.6	4.2	0.2	458
F ⁻	–	1.2	–	0.3
I ⁻	–	0.9	–	–
Br ⁻	–	104.7	–	13.1
pH	8.8	8.3	5.8	7.6
<i>I</i> (mmol/L)	4.31	515	0.123	91.4

Table 2. The chemicals, their reagent grade and amount used in the preparation of the reference groundwater simulants ALLMR, OLSR, OLGA and OLBA.

Chemical	Reagent grade	ALLMR (mg/L)	OLSR (mg/L)	OLGA (mg/L)	OLBA (mg/L)
CaCl ₂ ×2H ₂ O	fur analyse	18.85	14672.2	1.91	310.02
NaCl	puriss p.a.	56.34	12115.7	1.33	3776.45
MgCl ₂ ×6H ₂ O	pro analysi	5.97	456.5	2.51	221.33
KCl	suprapur	7.46	39.55	0.83	22.62
SrCl ₂ ×6H ₂ O	extra pure	–	106.5	–	0.3
NH ₄ Cl	fur analyse	–	–	–	0.98
KF	purum p.a.	–	–	–	0.91
KBr	purum p.a.	–	–	–	19.56
NaF	purum p.a.	–	2.63	–	–
NaBr	99+%	–	134.8	–	–
KI	AnalaR Normapur	–	1.11	–	–
H ₃ BO ₃	purum p.a.	–	5.26	–	3.55
Na ₂ SO ₄ ×10H ₂ O	pro analysi	28.24	12.35	–	1535.68
K ₂ SO ₄	pro analysi	–	–	0.73	–
Na ₂ SiO ₃ ×9H ₂ O	Baker analysed	7.96	–	0.47	–
NaHCO ₃	analytical reagent	89.56	–	–	–

2.2.2 Electrolyte solutions

In the sorption experiments of alkaline earth cations Ca, Sr, Ba and Ra, NaClO₄ (Fluka) electrolyte solutions of 0.01 M, 0.1 M and 1 M concentrations were used as solutions. 0.08 M TRIS (TRIS(hydroxymethyl)–aminomethan, Merck) buffer solution was prepared and used in the experiments at 1×10^{-4} M concentration level. Stock solutions of Ca, Sr and Ba carriers with an initial concentration of 0.05 M were prepared from solid Ca(ClO₄)₂ × 4H₂O (Aldrich), Sr(ClO₄)₂ × 6H₂O (AlfaAesar), and Ba(ClO₄)₂ (AlfaAesar) and diluted into suitable concentration levels to be used in the sorption experiments. All the solutions were stored under nitrogen atmosphere of the nitrogen filled glovebox at O₂ level of <0.1 ppm.

2.2.3 Radioactive tracer solutions

Radioactive tracers ⁴⁵Ca, ⁸⁵Sr, ¹³³Ba and ²²⁶Ra were purchased from PerkinElmer (⁴⁵Ca and ⁸⁵Sr), Czech Metrology Institute (¹³³Ba) and Eckert & Ziegler (²²⁶Ra). The initial chemical form was ⁴⁵CaCl₂ in water, ⁸⁵SrCl in 0.5 M HCl, ¹³³BaCl₂ in 0.08 M HCl and ²²⁶Ra(NO₃)₂ in 1 M HNO₃. Before the tracer was introduced to the sorption samples, the daughter radionuclides of ²²⁶Ra, the most important one being ²²²Rn, needed to be removed from the solution by evaporating the liquid to dryness. The evaporation residue was dissolved in 2×10^{-4} M HCl, transferred into 20 mL polyethylene (PE) liquid scintillation bottle, weighed and the activity of the tracer solution was verified with 1220 Quantulus liquid scintillation counter (LKB Wallac). Radioactive tracers ⁴⁵Ca, ⁸⁵Sr and ¹³³Ba were used without any treatment.

3 METHODS

The methods described in this section were applied during the conditioning of biotite, execution of the sorption experiments as well as in the modelling of the speciation of alkaline earth cations and their sorption on biotite.

3.1 Biotite conversion into Na-form

For the execution of the sorption experiments, KR2 biotite was sieved into grain size fraction of 0.071–0.15 mm and converted into monoionic Na-form according the method described by Kyllönen et al. (2014). In this method, 4 g of crushed biotite was packed in a column and perfused continuously with 0.1 M NaCl solution with approximately 1 month equilibration time and systematic ICP–MS (inductively coupled mass spectrometer) analysis of the effluents for exchangeable cations. In our column conditioning system peristaltic pumps passed continuously 0.01 M NaCl electrolyte solution through the column at a flow rate of 2.0 mL/h. Kyllönen et al. (2014) considered biotite to be converted into the monoionic Na-form when the content of exchangeable cations (mainly K, but also Mg, Ca, Al and Fe) was below 1% of their content in the first collected fractions, and the same reasoning was applied in our conditioning method. The cation concentration of the effluents was measured with Agilent 7800 ICP–MS. The approximated concentration of sodium passed through the column at the end of the conversion corresponded to 176–times the CEC of the biotite packed inside the column. After finishing the conditioning, the biotite was washed with MilliQ water on 71 µm sieve and placed for approximately two weeks in a heat cupboard at 50–55 °C for drying.

3.2 Sorption experiments

The isotherm batch sorption experiments of alkaline earth metals Ca, Sr, Ba and Ra were conducted in nitrogen filled glovebox using 40 mL polypropylene (PP) centrifuge tubes (Sorvall®). Approximately 25 mg of Na-converted KR2 biotite was weighed into acid washed tubes and the tubes were transferred in the glovebox. Then 40 mL of matrix solution (0.01 M, 0.1 M and 1 M NaClO₄ or reference groundwater) and buffer solution TRIS at 10⁻⁴ M concentration level were added one day prior the ⁴⁵Ca, ⁸⁵Sr, ¹³³Ba or ²²⁶Ra tracer and stable Ca, Sr or Ba carrier addition. In the experiments of Ca, Sr and Ba the applied concentration range was 0.01 M – 10⁻⁸ M, whereas the respective one for Ra was 10⁻⁷ M – 10⁻¹¹ M. Ba carrier was used in the sorption experiments of ¹³³Ba and ²²⁶Ra in the absence of stable Ra carrier. In preliminary tests it was seen that Ba carrier concentration up 10⁻⁷ M did not affect the sorption of radium compared to a solution with no barium present. Three parallel samples were done for each experiment. After tracer and carrier introduction the sample tubes were packed in resealable plastic bags and placed in nitrogen filled and light shielded reciprocal shaker for three days. After incubation time the samples were transferred back to glovebox and approximately 20 mL aliquot of the solution was filtered through a 0.20 µm syringe filter (PALL Life Sciences, Supor® membrane). Solution pH was measured from the non-filtered solution, whereas activity measurement was conducted for the filtrate.

3.2.1 Sorption experiments in reference groundwaters

To elucidate how the retention of alkaline earth cations (Ca, Sr, Ba and Ra) changes under differing water composition, batch sorption experiments were conducted in Olkiluoto reference groundwater simulants (Vuorinen et al., 1998) ALLMR, OLSR, OLGA and OLBA (Table 1). ALLMR is fresh, mildly reducing granitic reference groundwater, OLSR saline reducing reference groundwater, OLGA glacial anoxic meltwater and OLBA carbonate containing reducing brackish reference groundwater. Only ^{45}Ca tracer was added in the sorption experiments with Olkiluoto reference groundwaters because the concentration of stable Ca in all the waters was rather high and ranged from the minimum of 1.29×10^{-5} M in OLGA to the maximum of 9.98×10^{-2} M in OLSR. The concentration of stable Sr in OLSR and OLBA were 4.00×10^{-4} M and 1.14×10^{-6} M, respectively, and thus no stable Sr carrier was added in the experiments conducted with these waters. For ALLMR and OLGA, the experiments were conducted by adding ^{85}Sr tracer at 3.36×10^{-14} M concentration level or by adding the tracer together with the stable Sr carrier at 10^{-8} M concentration level. For Ba and Ra, on the one hand, the sorption experiments with all the Olkiluoto reference groundwaters were done by adding the tracer (^{133}Ba at 1.99×10^{-12} M and ^{226}Ra at 1.02×10^{-11} M level) or by adding the tracer and Ba carrier at 10^{-8} M concentration level. Three days incubation time was used. Otherwise the experimental setup was identical with the isotherm experiments.

3.3 Radioactivity counting and calculation of distribution coefficient

The final activity of the ^{45}Ca , ^{85}Sr , ^{133}Ba or ^{226}Ra tracers were measured from every sorption sample. In case of ^{45}Ca , 5 mL of filtered solution was pipetted into 20 mL polyethylene scintillation vial (Perkin Elmer) and 15 mL Ultima Gold AB liquid scintillation cocktail (PerkinElmer) was added. The vials were shaken to guarantee the thorough mixing of the ^{45}Ca tracer within the cocktail. The vials were placed inside the 1220 Quantulus liquid scintillation counter and let to stabilize for one hour before starting the activity measurement for 600 s. At every measurement series background samples containing equal volume of the same matrix solution as the sorption samples, and activity standards having the same volume and activity of ^{45}Ca as the sorption samples, were measured. From the activity measurements mass distribution coefficient, K_d , of calcium was calculated from Equation 1 by comparing the initial and final activities of ^{45}Ca in the solution:

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V \text{ (mL)}}{m \text{ (g)}} \quad [1]$$

where A_i is the initial concentration of ^{45}Ca in the solution, A_f is the final concentration of ^{45}Ca in the solution, V is the volume (mL) of the solution and m (g) is the mass of the biotite.

The final activity of ^{85}Sr and ^{133}Ba were measured with Wizard 3'' 1480 gamma counter (Perkin Elmer - Wallac) together with background samples and activity standards. The

sample volume was 10 mL and 600 s measurement time was applied. The K_d was calculated from Equation 1.

For the activity measurement of ^{226}Ra , a different approach was used. 20 mL of solution was filtered into 50 mL beaker glass and the solution was evaporated to dryness in order to remove the daughter nuclides of ^{226}Ra . This step needed to be done because the alpha decaying daughters, particularly ^{222}Rn , would otherwise interfere with the alpha measurement considerably. After the evaporation, the beaker glass was washed three times in total of 5 mL of 0.02 M HCl to transfer ^{226}Ra into 20 mL scintillation vial. 15 mL Ultima Gold AB liquid scintillation cocktail was added and the procedure was continued as described for ^{45}Ca .

3.4 Modelling

3.4.1 Alkaline earth cation speciation modelling

Geological modelling program PhreeqC is freely distributed and widely used to simulate chemical reactions and transport processes in various environments (Appelo, 1993). It has gained widespread popularity in the speciation modelling of solutes as well as their surface complexation and ion exchange reactions, and dispersion and diffusion within geological media. PhreeqC contains certain databases distributed with the program, and various databases can be included to the program to be used in the modellings. Thermoddem is a thermodynamic database developed to model geochemical reactions in environmental studies with special emphasis on the waste issues such as waste material management, pollutant behaviour and deep underground disposal (Blanc et al., 2012). Thermoddem database is based on the rules of traceability, flexibility and consistency in regard to parameter selection. PhreeqC modelling program and Thermoddem database were used to model the speciation of alkaline earth cations Ca, Sr, Ba and Ra in the experimental electrolyte solutions (NaClO_4) and Olkiluoto reference groundwaters.

3.4.2 Sorption modelling

PhreeqC and Thermoddem database were used in the modelling of the experimental sorption results of the alkaline earth cations Ca, Sr, Ba and Ra on biotite in the experimental electrolyte solutions and reference groundwaters. The modelling was based on cation exchange reactions using a mechanistic three-site model previously reported by Kyllönen et al. (2008, 2014) for Cs sorption on biotite. The site occupancies of the planar ion exchange sites (site X), so-called intermediate sites (Z) and FES sites (R) were assumed to be the same as given in Kyllönen et al. 2014. The selectivity coefficients of each site for Ca, Sr, Ba and Ra were gained through iteration for the best fit for the sorption result of the sample having the lowest alkaline earth cation concentration in the isotherm experiments. For Ca, Sr and Ba this indicated the sample having 10^{-8} M carrier concentration, whereas for Ra carrier-free sample at 10^{-11} M ^{226}Ra concentration was applied. After finding the best fit for the specified sample in 0.01 M, 0.1 M and 1 M NaClO_4 solutions, the whole sorption isotherms were modelled to verify the goodness of the model.

4 EXPERIMENTAL RESULTS

The experimental results from Ca, Sr, Ba and Ra speciation modelling (4.1), sorption isotherm experiments (4.2) and sorption modelling (4.3) are presented in this section.

4.1 Speciation of alkaline earth cations

The speciation of an element may bear a considerable effect on its sorption and transport behaviour in the solution – bedrock system. The results on alkaline earth cation speciation modelling in reference groundwaters ALLMR, OLSR, OLGA and OLBA, and NaClO₄ solutions are discussed here. Table 3 compiles the reactions and their values of equilibrium constants used in the speciation modelling.

Table 3. The reactions of Ca, Sr, Ba and Ra used in the speciation modelling and their equilibrium constants.

Reaction	LOG K
$\text{Ba}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Ba}(\text{CO}_3) + \text{H}^+$	3.4
$\text{Ba}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Ba}(\text{HCO}_3)^+$	4.1
$\text{Ba}^{2+} + \text{Cl}^- \leftrightarrow \text{BaCl}^+$	4.1
$\text{Ba}^{2+} + \text{F}^- \leftrightarrow \text{BaF}^+$	4.1
$\text{Ba}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ba}(\text{OH})^+ + \text{H}^+$	4.1
$\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Ca}(\text{HCO}_3)^+$	4.1
$\text{Ca}^{2+} + \text{Cl}^- \leftrightarrow \text{CaCl}^+$	4.1
$\text{Ca}^{2+} + 2\text{Cl}^- \leftrightarrow \text{CaCl}_2$	3.4
$\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Ca}(\text{CO}_3) + \text{H}^+$	3.4
$\text{Ca}^{2+} + \text{F}^- \leftrightarrow \text{CaF}^+$	4.1
$\text{Ca}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{OH})^+ + \text{H}^+$	4.1
$\text{Ca}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{Ca}(\text{SO}_4)$	3.4
$\text{Ca}^{2+} + \text{NH}_4^+ \leftrightarrow \text{CaNH}_3^{2+} + \text{H}^+$	-9.144
$\text{Ca}^{2+} + 2\text{NH}_4^+ \leftrightarrow \text{Ca}(\text{NH}_3)_2^{2+} + 2\text{H}^+$	-18.788
$\text{Sr}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Sr}(\text{CO}_3) + \text{H}^+$	3.4
$\text{Sr}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Sr}(\text{HCO}_3)^+$	4.1
$\text{Sr}^{2+} + \text{Cl}^- \leftrightarrow \text{SrCl}^+$	4.1
$\text{Sr}^{2+} + \text{F}^- \leftrightarrow \text{SrF}^+$	4.1
$\text{Sr}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{Sr}(\text{SO}_4)$	3.4
$\text{Sr}^{2+} + \text{NH}_4^+ \leftrightarrow \text{SrNH}_3^{2+} + \text{H}^+$	-9.344
$\text{H}^+ + \text{Ra}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{Ra}(\text{HCO}_3)^+$	10.92
$\text{Ra}^{2+} + \text{Cl}^- \leftrightarrow \text{RaCl}^+$	-0.1
$\text{Ra}^{2+} + 2\text{Cl}^- \leftrightarrow \text{RaCl}_2$	-0.1
$\text{H}^+ + \text{Ra}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ra}(\text{OH})^+$	-13.49
$\text{H}^+ + \text{Ra}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Ra}(\text{OH})_2$	-28.07
$\text{Ra}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{Ra}(\text{CO}_3)$	2.5
$\text{Ra}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{Ra}(\text{SO}_4)$	2.76
$\text{Ra}^{2+} + \text{F}^- \leftrightarrow \text{RaF}^+$	0.48

Table 3. continued

Reaction	LOG K
$\text{Ca}_2\text{MgSi}_2\text{O}_7 + 6\text{H}^+ + \text{H}_2\text{O} \leftrightarrow 2\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{H}_4\text{SiO}_4$ (Akermanite mineral)	46.083
$\text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$ (Anhydrite mineral)	-4.436
$\text{CaCl}_2 \times 6\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}$ (Antarcticite mineral)	3.947
$\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{HCO}_3^- + \text{Ca}^{2+}$ (Aragonite mineral)	2.014
$\text{BaSO}_4 \leftrightarrow \text{Ba}^{2+} + \text{SO}_4^{2-}$ (Barite mineral)	-10.051
$\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{HCO}_3^- + \text{Ca}^{2+}$ (Calcite mineral)	1.847
$\text{SrSO}_4 \leftrightarrow \text{Sr}^{2+} + \text{SO}_4^{2-}$ (Celestite mineral)	-6.620
$\text{CaMg}(\text{SiO}_3)_2 + 4\text{H}^+ + 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{H}_4\text{SiO}_4$ (Diopside mineral)	21.732
$\text{CaMg}(\text{CO}_3)_2 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$ (Dolomite mineral)	3.533
$\text{CaF}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{F}^-$ (Fluorite mineral)	-10.510
$\text{CaSO}_4 \times 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$ (Gypsum mineral)	-4.605
$\text{Ca}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \times 2\text{H}_2\text{O} + 4\text{H}^+ + 1.5\text{H}_2\text{O} \leftrightarrow 2\text{Ca}^{2+} + 3\text{H}_4\text{SiO}_4$ (Gyrolite mineral)	22.338
$\text{CaCO}_3 \times 2\text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{H}_2\text{O}$ (Monohydrocalcite mineral)	2.728
$\text{CaMgSiO}_4 + 4\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$ (Monticellite mineral)	30.086
$\text{Ca}(\text{OH})_2 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ (Portlandite mineral)	22.812
$\text{SrCO}_3 + \text{H}^+ \leftrightarrow \text{Sr}^{2+} + \text{HCO}_3^-$ (Strontianite mineral)	1.057
$\text{CaSiO}_3\text{CaSO}_4\text{CaCO}_3 \times 15\text{H}_2\text{O} + 3\text{H}^+ \leftrightarrow 3\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + \text{SO}_4^{2-} + \text{HCO}_3^-$ (Thaumasite mineral)	10.314
$(\text{Ca}_2\text{Mg}_5)\text{Si}_8\text{O}_{22}(\text{OH})_2 + 14\text{H}^+ + 8\text{H}_2\text{O} \leftrightarrow 2\text{Ca}^{2+} + 5\text{Mg}^{2+} + 8\text{H}_4\text{SiO}_4$ (Tremolite mineral)	67.283
$\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{HCO}_3^- + \text{Ca}^{2+}$ (Vaterite mineral)	2.427
$\text{CaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$ (Wollastonite mineral)	14.024

The speciation of alkaline earth cations was modelled by taking solution composition from Table 2 for Olkiluoto reference groundwaters and by setting the pH to a certain value on pH range 2–12 before running the code. Each pH value was thus modelled independently, and at each step the solution pH was incremented by a unity. The same approach was applied for Ca, Sr, Ba and Ra in 0.01 M, 0.1 M and 1 M NaClO₄ solutions. From each modelling time, the solution equilibrium pH, pE and concentration of Ca²⁺/Sr²⁺/Ba²⁺/Ra²⁺ were received in addition to possible alkaline earth cation complexes and saturation indices of possibly forming mineral phases (Table 3).

4.1.1 Reference groundwaters

The predominant form of calcium in mildly reducing granitic Olkiluoto reference groundwater ALLMR is Ca²⁺ cation at the pH scale on 2 to 9 (Figure 1). At higher pH values its contribution decreases rapidly being 0% at pH 12. At pH values higher than 9, CaCO₃ complex rises as a dominating one. The fraction of other calcium bearing complexes, such as CaSO₄ or Ca(HCO₃)⁺, remains under 4% throughout the studied pH range. The possibly precipitating minerals at pH values higher than 9 in ALLMR include Aragonite, Calcite, Dolomite, Monohydrocalcite, Tremolite and Vaterite. The formed complexes and their quantities of Sr and Ba are almost identical with those of Ca.

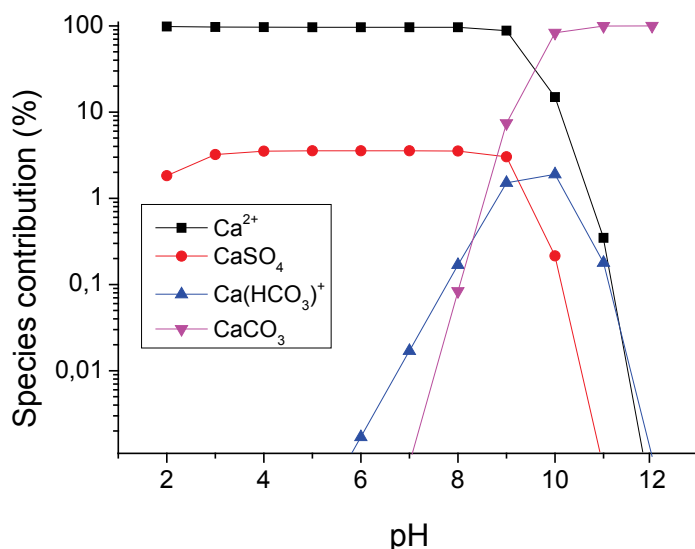


Figure 1. The speciation of calcium ($c[Ca]_{tot} = 1.27 \times 10^{-4}$ M) in ALLMR reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

On the other hand, Ra (Figure 2) differs from the other investigated alkaline earth metals in the sense that no Ra(HCO₃)⁺ complex is present at notable amounts at any of the modelled pH value. The fraction of RaSO₄ increases rapidly from <10⁻⁶% to approximately 3.5% at pH 7 and begins to decrease from there on. At pH 10, the fractions of Ra²⁺ and RaCO₃ are equal, and the contribution of the latter starts to increase at higher pH values. In case of Sr, Ba and Ra, the possibly forming minerals were the same as for

Ca. When considering the execution of the sorption experiments, the nominal pH value for ALLMR is 8.8, which would indicate the dominance of M^{2+} ($M = \text{Ca}/\text{Sr}/\text{Ba}/\text{Ra}$) cation in the solution over other forms present.

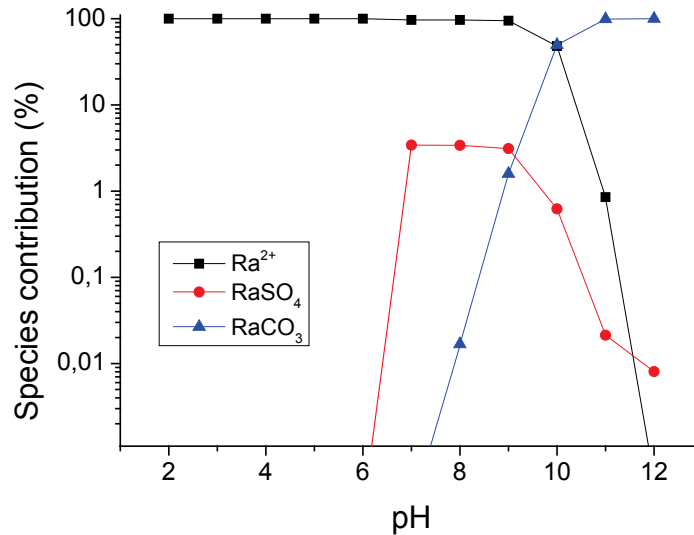


Figure 2. The speciation of radium ($c[\text{Ra}]_{\text{tot}} = 10^{-11} \text{ M}$) in ALLMR reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

The speciation of the alkaline earth cations Ca, Sr, Ba and Ra in saline Olkiluoto reference groundwater OLSR is dominated by the free M^{2+} cation throughout the pH range of 2 to 12 (see Figure 3 for Ca). The fractions of Ca^{2+} , Sr^{2+} , Ba^{2+} and Ra^{2+} are approximately 94.2%, 95.0%, 97.2% and 90.0%, respectively, at the pH range of 2–12. The second most abundant form is MCl^+ complex at a relative contribution varying from 2.7% (Ba) to 8.3% (Ra). The importance of MOH^+ complex increased with pH for all the investigated alkaline earth cations, being the highest at 5.6% for Ca at pH 12. For Sr, Ba and Ra its contribution is smaller. Other possible complexes included MCl_2 and MSO_4 , but their fraction is generally below 1%. Only for Ra the fraction of RaCl_2 remained at a steady value of 1.6% throughout the pH range of 2 to 12. The possibly forming mineral phase is Fluorite at pH values ranging from 5 to 12 (saturation index <0.06 at all pH values).

In OLGA, glacial anoxic meltwater, the dominant form of Ca, Sr, Ba and Ra at pH values of 2–12 is M^{2+} cation accounting on average from 97.6% (Ra) to 99.6% (Sr) (see Figure 4 for Ca). Only at elevated pH value of 12, the fraction of other alkaline earth cation complex, MOH^+ , is above 1% (range 1.8% for Ba to 9.0% for Ca). MSO_4 complexes are also formed throughout the studied pH range, but their maximum contribution is approximately 0.1%. Diopside and Tremolite are the two possibly forming mineral phases at pH 12.

In reducing brackish Olkiluoto reference groundwater OLBA, the main species is free M^{2+} cation irrespective of the solution pH (see Figure 5 for Ca). $CaSO_4$ and $SrSO_4$ complexes are present at the second highest concentration, and their respective fractions are on average 18.6% and 17.4%. MCl^+ complexes are also present at every studied pH value, even though they have a steady but rather low contribution ranging from 0.6% (Ba) to 1.8% (Ra). Ca, Sr, and Ba also form $M(HCO_3)^+$ complexes at pH range of 7 to 9 with an average fraction of 2.5%. At elevated pH values of 9-12, the fraction of $CaCO_3$, $SrCO_3$ and $BaCO_3$ complexes increase drastically and approach the respective fraction of free M^{2+} cation (e.g. the respective fractions being 42.8% and 44.4% for Ca at pH 12). Oppositely to other investigated alkaline earth cations, for Ra (Figure 6) the fraction of $RaSO_4$ complex is higher at elevated pH values than that of $RaCO_3$ complex. The contribution of $RaSO_4$ is $<10^{-6}\%$ at pH 6, but increases considerably with pH being 20.1% at pH 12. At the same pH value of 12, the fraction of $RaCO_3$ complex is lesser at only 3.6%.

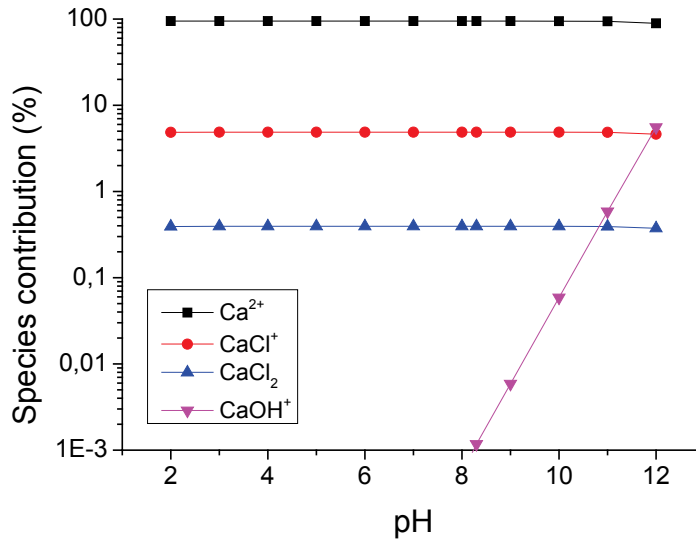


Figure 3. The speciation of calcium ($c[Ca]_{tot} = 1.01 \times 10^{-1} M$) in OLSR reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

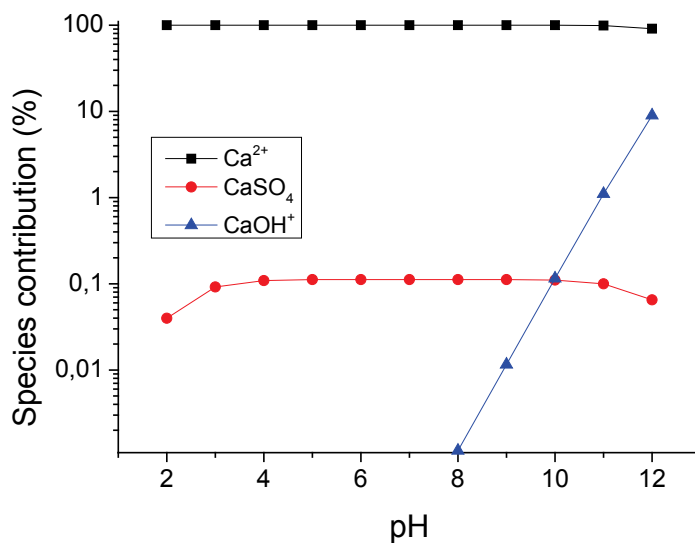


Figure 4. The speciation of calcium ($c[Ca]_{tot} = 1.3 \times 10^{-5} M$) in OLGA reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

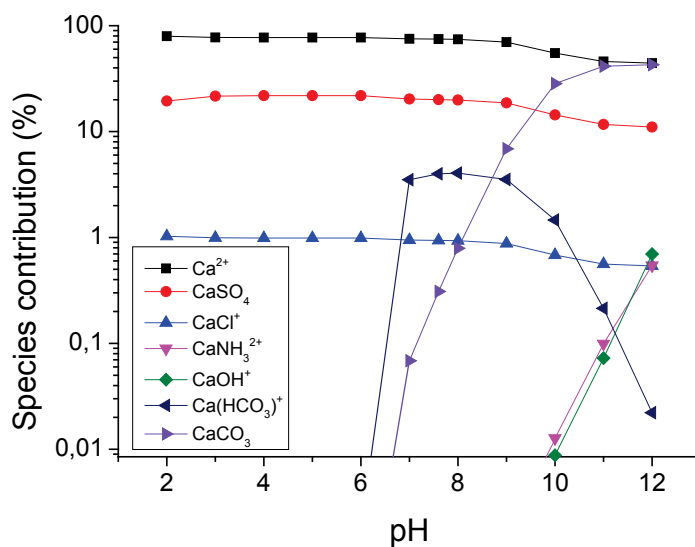


Figure 5. The speciation of calcium ($c[Ca]_{tot} = 2.13 \times 10^{-3} M$) in OLBA reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

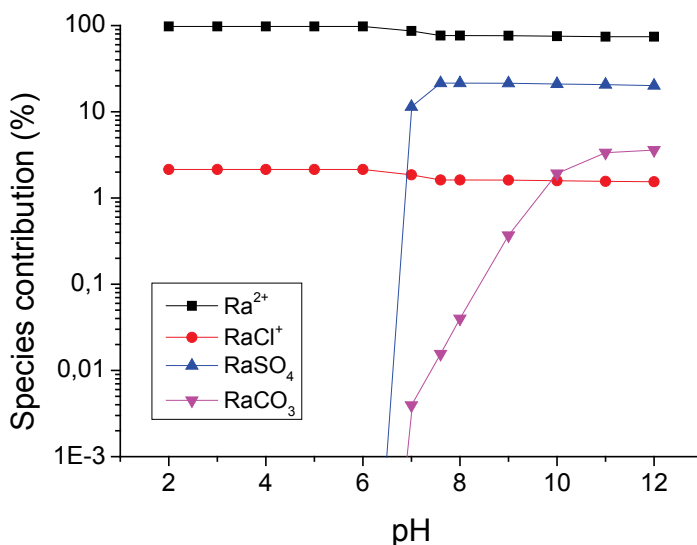


Figure 6. The speciation of radium ($c[\text{Ra}]_{\text{tot}} = 10^{-11} \text{ M}$) in OLBA reference groundwater solution as a function of pH. Speciation modelled with PhreeqC program and Thermoddem database.

4.1.2 NaClO₄ solutions

The speciation of the alkaline earth cations Ca, Sr, Ba and Ra in solutions of 0.01 M, 0.1 M and 1 M NaClO₄ are dominated by the M^{2+} cation. No other forms are present (<0.001%) in significant amounts irrespective of the alkaline earth cation or NaClO₄ concentration.

4.2 Sorption experiments

The experimental results on the isotherm experiments of the alkaline earth cations Ca, Sr, Ba and Ra are presented and discussed in the following section (4.2.1).

4.2.1 Isotherm

Adsorption isotherm is a graphical presentation of an equilibrium situation where the concentration of an analyte in the solid phase is plotted against its concentration in the solution. Since the plotting of the values rarely gives a straight line or any quantitative specific information on the sorption reaction itself, it is sensible to present the data with a mathematical description (Essington, 2004). The results from the sorption experiments of Ca, Sr, Ba and Ra are presented in the form of Freundlich adsorption isotherm (Equation 2), since the data failed to conform Langmuir representation.

$$\text{LOG } c[\text{M}^{2+}]_{\text{liquid}} = \text{LOG } K_F + N \times \text{LOG } c[\text{M}^{2+}]_{\text{solid}} \quad [2]$$

where $\text{LOG } c[\text{M}^{2+}]_{\text{solid}}$ and $\text{LOG } c[\text{M}^{2+}]_{\text{liquid}}$ are the logarithms of Ca, Sr, Ba or Ra concentration in the solid (mmol/kg) and liquid (mmol/L) phases, and K_F and N are positive numerical adjustable parameters. N is related to surface charge heterogeneity; as

$N \rightarrow 0$, the heterogeneity of the sorption sites increases and the closer N is to unity, the more homogeneous the sorption sites are.

When the sorption data conforms to the Freundlich isotherm, then $\text{LOG } c[M^{2+}]_{\text{solid}}$ as a function of $\text{LOG } c[M^{2+}]_{\text{liquid}}$ gives a straight line, as depicted in Figures 7-10. The linear fitting of experimental data in Freundlich isotherms (Figures A1–A4, Appendix 1) generally yielded a good fit with correlation coefficient values (R^2) ranging from 0.968 to 0.999. The values of N ranged from 0.599 to 1.33 in the fits, probably indicating variation in the nature of the sorption sites participating in alkaline earth cation retention on biotite.

From Figures 7-12 can be observed that $\text{LOG } c[M^{2+}]_{\text{solid}}$ values of Ca, Sr, Ba and Ra are the highest in the most dilute solution of 0.01 M NaClO_4 and consequently the lowest in the most concentrated solution of 1 M NaClO_4 . When the $\text{LOG } c[M^{2+}]_{\text{solid}}$ values increase, the experimental data points can approach each other and finally even intersect, as is the case for Ba in Figure 9.

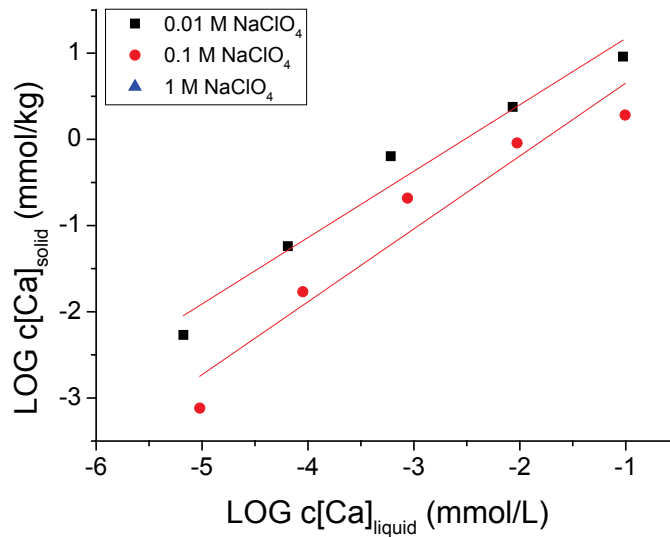


Figure 7. The Freundlich isotherm presentation of Ca retention on biotite in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH 8. The initial Ca carrier concentration in the experiments was 10^{-2} M – 10^{-8} M. Data points for 1 M NaClO_4 solution are not shown because no sorption took place in this solution.

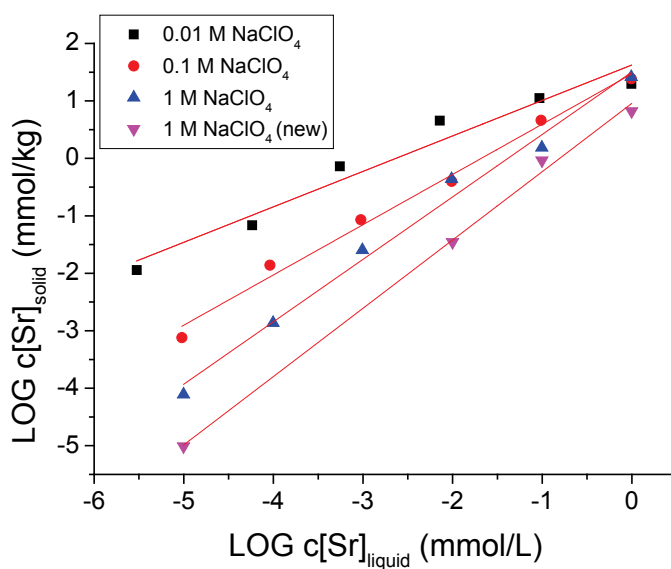


Figure 8. The Freundlich isotherm presentation of Sr retention on biotite in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH 8. The initial Sr carrier concentration in the experiments was 10⁻² M – 10⁻⁸ M.

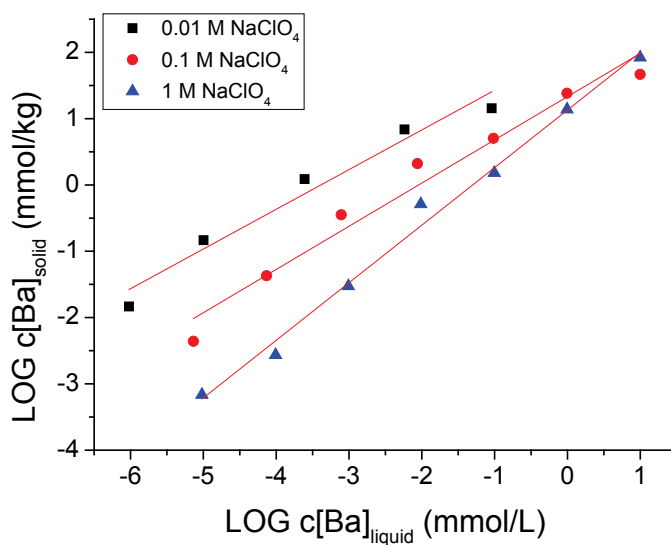


Figure 9. The Freundlich isotherm presentation of Ba retention on biotite in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH 8. The initial Ba carrier concentration in the experiments was 10⁻² M – 10⁻⁸ M.

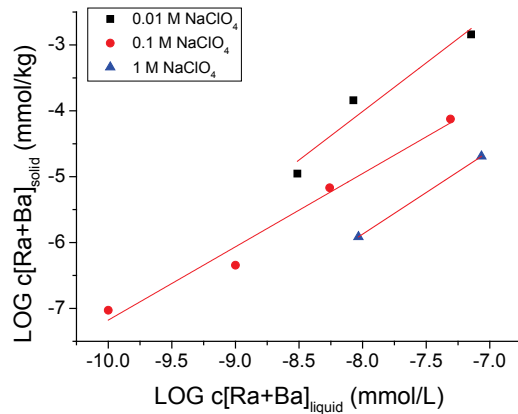


Figure 10. The Freundlich isotherm presentation of Ra retention on biotite in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH 8. Ba was used as a carrier at concentrations of 10⁻⁵ M – 10⁻⁹ M in the absence of stable Ra carrier. No carrier was used in the experiments with 10⁻¹⁰ M and 10⁻¹¹ M ²²⁶Ra concentration.

The logarithms of alkaline earth cations Ca, Sr, Ba and Ra K_d values as calculated from the isotherm experiments were plotted against the logarithm of equilibrium concentration in the solution ($c[M^{2+}]_{eq,liquid}$; Figures 11–14 and Appendix 2). The K_d values decrease in the order of Ra > Ba > Sr > Ca, which follows an increase in the hydrated radius of the cations (Ra smallest – Ca largest). This observation implies that no changes in the hydration of the cations takes place during sorption, meaning that the retention follows an outer sphere complexation mechanism (i.e. ion exchange). Thus, no inner sphere complexation (i.e. chemical bond formation) is expected to occur.

Two different features can be seen from Figures 11–14; (1) decreasing selectivity with increasing $LOG c[M^{2+}]_{eq,liquid}$ value and (2) decrease in the K_d values when the concentration of NaClO₄ solution increases. These both are expected results.

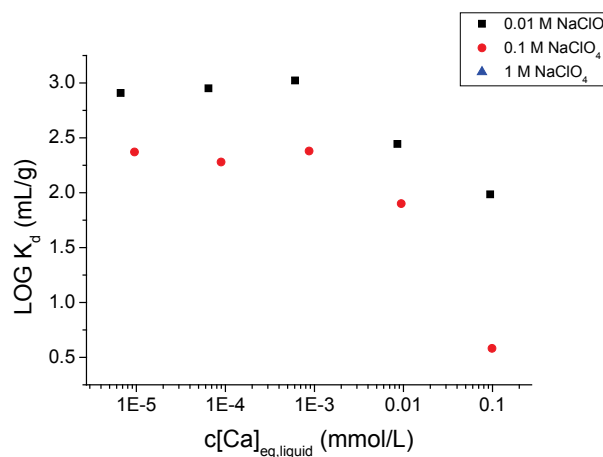


Figure 11. The K_d values of Ca as a function of equilibrium Ca concentration in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH value of 8. Ca concentration in the experiments was 10⁻² M – 10⁻⁸ M. Data points for 1 M NaClO₄ solution are not shown because no sorption took place in this solution.

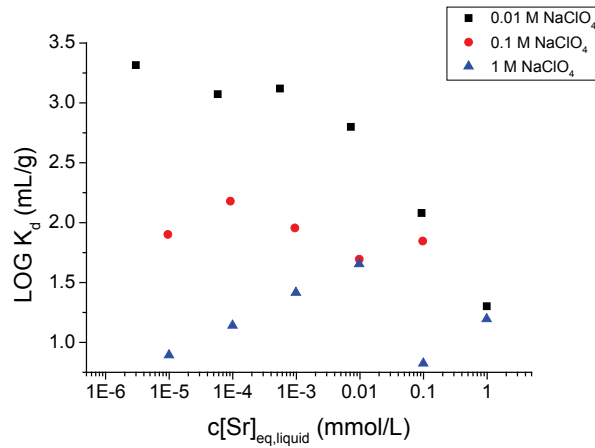


Figure 12. The K_d values of Sr as a function of equilibrium Sr concentration in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH value of 8. Sr concentration in the experiments was $10^{-2} \text{ M} - 10^{-8} \text{ M}$.

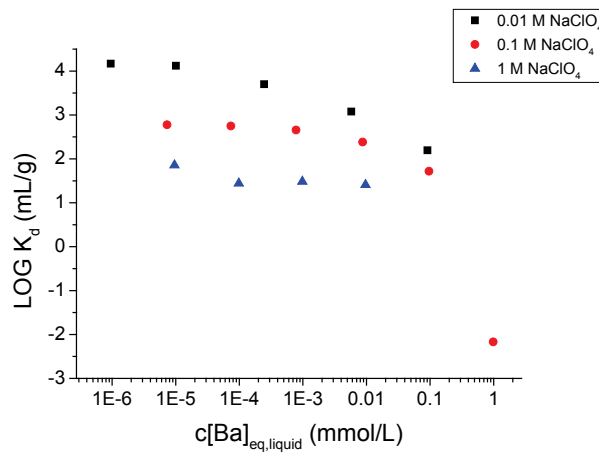


Figure 13. The K_d values of Ba as a function of equilibrium Ba concentration in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH value of 8. Ba concentration in the experiments was $10^{-2} \text{ M} - 10^{-8} \text{ M}$.

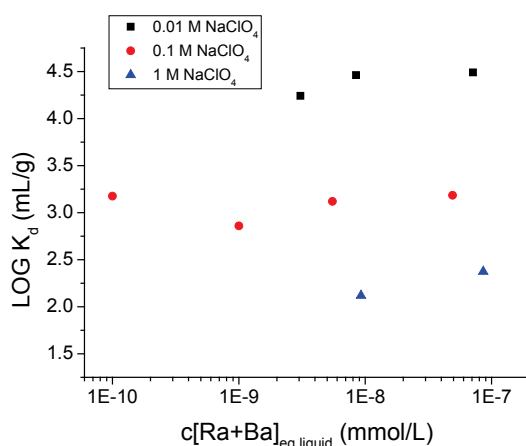


Figure 14. The K_d values of Ra as a function of equilibrium Ba concentration in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH value of 8. Ba concentration in the experiments was 10^{-5} M – 10^{-9} M. No carrier was used in the experiments with 10^{-10} M and 10^{-11} M ^{226}Ra concentration.

4.2.2 Reference groundwaters

The retention of alkaline earth cations Ca, Sr, Ba and Ra on biotite in Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA are depicted in Table 4. The highest sorption of Ca, Sr, Ba and Ra among the studied waters is observed in OLGA, where the respective K_d values are 126 ± 22 mL/g, 341 ± 53 mL/g, 4130 ± 120 mL/g and 8340 ± 2700 mL/g. Alkaline earth cation retention is also observed in ALLMR, whereas no sorption of Ca, Sr or Ra took place in OLSR or OLBA. Ba was slightly retained in OLBA (K_d 96 ± 9 mL/g). As was noticed in the isotherm experiments, the K_d values of Ca, Sr, Ba and Ra increased in the order of $\text{Ca} < \text{Sr} < \text{Ba} < \text{Ra}$ for both OLGA and ALLMR.

The retention behaviour of alkaline earth cations Ca, Sr, Ba and Ra in ALLMR, OLSR, OLGA and OLBA can be explained by the differences in solution composition; solutions having higher concentration of competing cations, such as OLSR and OLBA at solution ionic strengths of 515 and 91.4 mmol/L, are more than likely to have a negative effect on Ca, Sr, Ba and Ra retention through increased competition on the sorption sites. The competition is even more pronounced when it takes place between isotopes of the same element behaving similarly to each other – as is the case for Ca in all the studied Olkiluoto reference groundwaters. Thus, expectedly all the elements exhibited the highest retention in the most dilute solution OLGA, followed by the second dilute ALLMR. Speciation is not likely to participate significantly on the sorption reaction, since M^{2+} cation was modelled to be the dominant form in all the Olkiluoto reference groundwaters at the expected solution pH.

Table 4. The K_d values of ^{45}Ca , ^{85}Sr , ^{133}Ba and ^{226}Ra on monoionic Na–biotite in Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA.

Reference water	Alkaline earth metal concentration			
	tracer		carrier (10^{-8} M)	
	$K_d \pm \text{STDEV}$ (mL/g)	pH	$K_d \pm \text{STDEV}$ (mL/g)	pH
^{45}Ca				
ALLMR	47.3 ± 1.4	8.45	–	–
OLSR	0	7.67	–	–
OLGA	126 ± 22	6.46	–	–
OLBA	0	7.9	–	–
^{85}Sr				
ALLMR	105 ± 56	8.39	101 ± 9	8.26
OLSR	0	7.44	–	–
OLGA	341 ± 53	6.71	302 ± 22	6.22
OLBA	0	7.84	–	–
^{133}Ba				
ALLMR	4032 ± 21	8.30	4337 ± 32	8.30
OLSR	0	7.48	0	7.74
OLGA	4131 ± 122	6.53	4015 ± 468	5.92
OLBA	96 ± 9	7.85	88 ± 11	7.83
^{226}Ra				
ALLMR	4377 ± 177	7.79	4984 ± 1027	7.96
OLSR	0	7.23	0	7.13
OLGA	8338 ± 2689	7.44	9892 ± 1653	6.75
OLBA	0	7.45	0	7.94

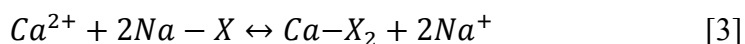
4.3 Sorption modelling

The sorption modelling of the alkaline earth cations Ca, Sr, Ba and Ra was based on cation exchange reactions using a three-site model developed for Cs sorption on biotite (Kyllönen et al., 2008; Kyllönen et al., 2014). The site occupancy of the planar ion exchange sites (site X) was adjusted to 95% of the cation exchange capacity of the biotite (CEC $16.7 \mu\text{eq/g}$), 5% for the intermediate sites (Z) and 0.02% for the FES sites (R) (Kyllönen et al., 2014). These fractions corresponded to 1.59×10^{-5} eq/g, 8.36×10^{-7} eq/g and 3.34×10^{-9} eq/g from the cation exchange capacity of 1.0 g KR2 biotite, and were used in the model as sorption site concentrations. The selectivity coefficients (k^{\prime} s) for Na^+ cations for sites X, Z and R were included in the model due to the competition of this cation from the sorption sites in 0.01 M, 0.1 M and 1 M NaClO_4 solutions and Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. In ALLMR, OLSR, OLGA and OLBA also the k values determined previously for K^+ (Kyllönen et al., 2014) on biotite, and the respective determined for Ca in this work, were included in the model at every modelling time. The respective was done also for Sr in the modellings of OLSR and OLBA, and Ba in Ra modellings at 10^{-8} M Ba carrier concentrations. The k value for

R sites were kept constant at the value of 2 throughout the modellings of Ca, Sr, Ba and Ra because of its low contribution to the overall results.

From the aforementioned sites, the planar ion exchange sites situate on the basal surfaces of biotite particles and arise from the isomorphic substitution of Si^{4+} with Al^{3+} in the Si-tetrahedral sheet during mineral crystallization. At the crystal edges lay broken bonds of Si/Al-tetrahedral and Fe/Mg-octahedral sheets forming $-\text{OH}$ ion exchange groups. Isomorphic substitution leading to permanent negative structural charge is balanced by exchangeable cations, K^+ for biotite, in mica interlayers and on basal planes. When this exchangeable cation is lost from the interlayer, FES sites (frayed edge site) can be formed between the collapsed space (containing exchangeable cation – thickness of 1.0 nm) and expanded layer part (thickness of 1.4 nm and containing strongly hydrated cation, e.g. Ca^{2+}). FES sites are considered as high affinity sites towards easily dehydrated cations such as Cs^+ , Rb^+ , K^+ and NH_4^+ , but strongly hydrated cations such as Na^+ and Ca^{2+} are easily replaced (Cornell, 1993; Essington, 2004; Kyllönen et al., 2014; Sawhney, 1972). Unfortunately the physical background of the intermediate sites remains to be unclear (Brouwer, 1983; Kyllönen et al., 2014; Sawhney, 1972).

The selectivity coefficients of exchange reactions are divided into half reactions in PHREEQC (Appelo and Postma, 1993). For example, $\text{Ca}^{2+}/\text{Na}^+$ exchange reaction can be written as:



where $-X$ denotes the sorption site. The selectivity coefficient for this reaction is $\log k = \log(1/\text{K}_{\text{Na/Ca}}^2) = \log(1/0.4^2) = 0.8$. One half reaction, for sodium in our case, needs to be defined as the point of reference:



By adding Reaction [3] twice to Reaction [4], we obtain the equation used in the database:



The selectivity coefficients of each site (X, Z and R) for Ca, Sr, Ba and Ra were obtained through iteration for the best fit for the sorption result of the sample having the lowest alkaline earth cation concentration in the isotherm experiments. For Ca, Sr and Ba this was the sample having 10^{-8} M carrier concentration, whereas for Ra carrier-free sample at 10^{-10} M ^{226}Ra concentration was applied. After finding the best fit for the specified sample in 0.01 M, 0.1 M and 1 M NaClO_4 solutions, the whole sorption isotherms were modelled to verify the goodness of the model in K_d form.

In case of the Olkiluoto reference groundwaters, the averages of the selectivity coefficients determined in 0.01 M, 0.1 M and 1 M NaClO_4 solutions were used to model the distribution coefficients of the studied radionuclides. In addition, the selectivity coefficients were also iterated in the case of the reference groundwaters to find the best fit for each element (Ca, Sr, Ba and Ra) and sorption site (X, Z and R) in the given conditions.

4.3.1 Modelling of Ca sorption

Figures 15–17 present the results from Ca sorption isotherm experiments and their K_d modelling outcomes in 0.01 M, 0.1 M and 1 M NaClO_4 solutions, and in Table 9 for Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. The model describes rather well Ca sorption in 0.01 M and 0.1 M NaClO_4 solutions at initial Ca concentrations of 10^{-8} M – 10^{-4} M. At higher Ca concentrations of 10^{-3} M and 10^{-2} M the model overestimates the retention, because no sorption took place in the experiments. Also in 1 M NaClO_4 solution (Figure 17) and Olkiluoto reference groundwaters OLSR and OLBA (Table 9) the model slightly overestimates Ca sorption (modelled values <1 mL/g) in the absence of experimental sorption. The model gave a very good fit in ALLMR and OLGA. Table 5 summarizes the logarithms for the selectivity coefficient of Ca for sites X, Z and R in all the modelled solutions.

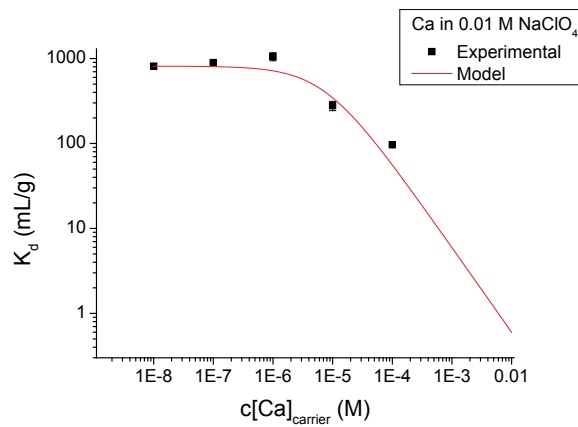


Figure 15. The experimental results from Ca sorption isotherm as determined in 0.01 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 1.00, 1.66 and 2.00, respectively.

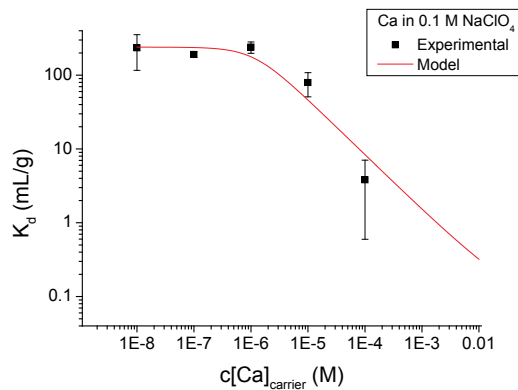


Figure 16. The experimental results from Ca sorption isotherm as determined in 0.1 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 1.00, 3.94 and 2.00, respectively.

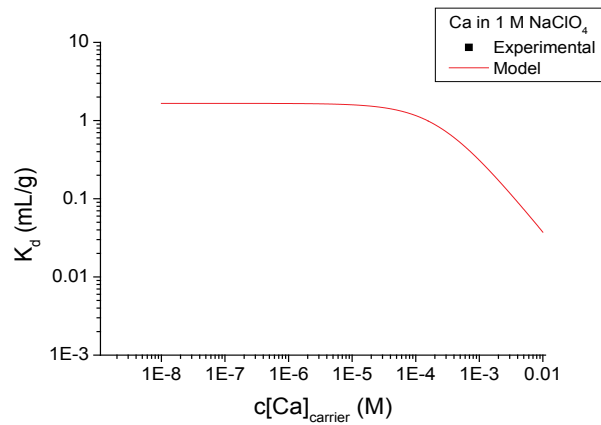


Figure 17. The experimental results from Ca sorption isotherm as determined in 1 M NaClO₄ solution at pH 8 and the data points modelled with three-site cation exchange model. Experimental data points are not shown since no Ca retention was observed in the sorption tests. Logarithms of the selectivity coefficient for X, Z and R were 1.00, 3.94 and 2.00, respectively.

Table 5. The logarithms of the best fit selectivity coefficients of sorption sites X (planar sites), Z (intermediate sites) and R (FES sites) obtained in Ca sorption modellings.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄	1.00	1.66	2.00
0.1 M NaClO ₄	1.00	3.94	2.00
1 M NaClO ₄	1.00	3.94	2.00
ALLMR	2.10	1.90	2.00
OLSR	1.00	3.94	2.00
OLGA	-1.30	-1.30	2.00
OLBA	1.00	3.94	2.00

4.3.2 Modelling of Sr sorption

Figures 18-20 present the results from Sr sorption isotherm experiments and their K_d modelling outcomes in 0.01 M, 0.1 M and 1 M NaClO₄ solutions, and Table 9 for Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. The model describes rather well Sr sorption in 0.01 M and 0.1 M NaClO₄ solutions at initial Sr concentrations of 10^{-8} M – 10^{-4} M / 10^{-3} M. In more concentrated Sr solutions the model overestimates the retention, since no sorption took place in the sorption tests. The fit between the modelled and experimental K_d values in 1 M NaClO₄ solution (Figure 20) is not very good due to nonsystematic behavior in the experimental values. However, the model does manage to describe the retention at some concentrations (at 10^{-8} M, 10^{-6} M, 10^{-4} M and 10^{-3} M) in the limits of experimental K_d uncertainties.

The modelled K_d values for Olkiluoto reference groundwaters ALLMR and OLGA (Table 9) gave a good fit. When the best fit k values determined for sorption sites X, Z

and R at Sr tracer level (10^{-14} M) were applied to model sorption at 10^{-8} M Sr carrier concentration, the model gave a good fit in ALLMR in the limits of experimental K_d uncertainty. However, in OLGA the model overestimated the retention at 10^{-8} M Sr carrier concentration and the k values needed to be iterated again to receive the best fit. As a comment it can be said that the same operation was also performed to ALLMR to get the best possible fit. In OLSR and OLBA groundwaters the model overestimated Sr retention (modelled values <1 mL/g) in the absence of experimental sorption. Table 6 summarizes the logarithms for the selectivity coefficient of Sr for sites X, Z and R in all the modelled solutions.

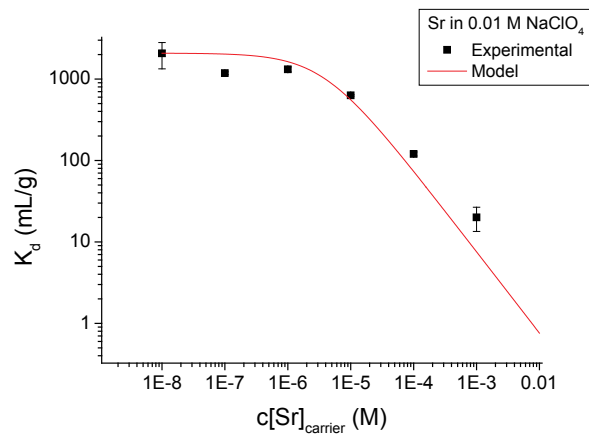


Figure 18. The experimental results from Sr sorption isotherm as determined in 0.01 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 1.5, 1.0 and 2.0, respectively.

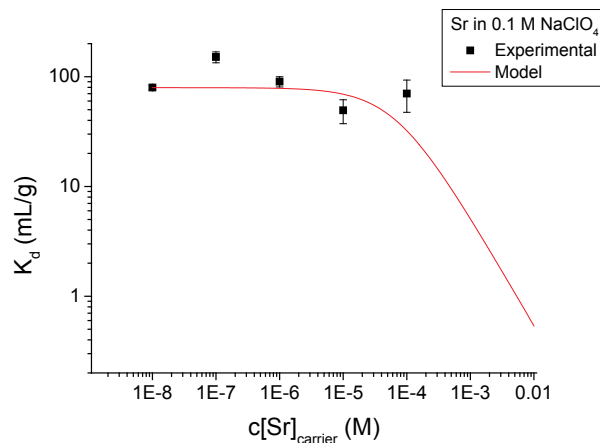


Figure 20. The experimental results from Sr sorption isotherm as determined in 0.1 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 2.2, 2.0 and 2.0, respectively.

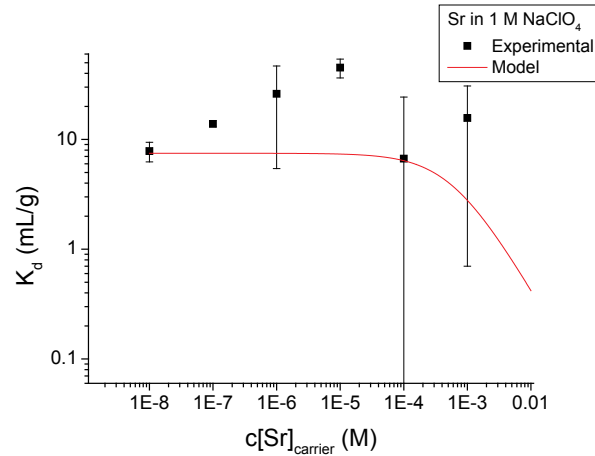


Figure 21. The experimental results from Sr sorption isotherm as determined in 1 M NaClO₄ solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 3.4, 2.0 and 2.0, respectively.

Table 6. The logarithms of the best fit selectivity coefficients of sorption sites X (planar sites), Z (intermediate sites) and R (FES sites) obtained in Sr sorption modellings.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄	1.50	1.00	2.00
0.1 M NaClO ₄	2.20	2.00	2.00
1 M NaClO ₄	3.40	2.00	2.00
ALLMR tracer ^A	1.37	0.80	2.00
ALLMR 10 ⁻⁸ M carrier ^B	1.34	1.00	2.00
OLSR	2.00	4.68	2.00
OLGA tracer ^A	1.68	1.20	2.00
OLGA 10 ⁻⁸ M carrier ^B	1.63	1.10	2.00
OLBA	1.00	2.00	2.00

^A : the experimental sorption tests conducted by adding only ⁸⁵Sr tracer at 10⁻¹⁴ M concentration level

^B : the experimental sorption tests conducted by adding Sr carrier at 10⁻⁸ M concentration level

4.3.3 Modelling of Ba sorption

The K_d results from Ba isotherm experiments and their K_d modelling outcomes in 0.01 M, 0.1 M and 1 M NaClO₄ solutions are presented in Figures 22-24. Table 9 gives the experimental and modelled Ba K_d values for Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. The model gave a good fit to experimental values in 0.01 M and 0.1 M NaClO₄ solutions at initial Ba concentrations of 10⁻⁸ M – 10⁻⁴ M. In more concentrated Ba solutions of 10⁻³ M and 10⁻² M the model overestimates the retention, since no experimental sorption was observed. There is also discrepancy between the modelled and experimental Ba K_d values in 1 M NaClO₄ solution (Figure 24), partly because of non-existing sorption at 10⁻² M – 10⁻⁴ M Ba concentrations.

The modelled K_d values for Olkiluoto reference groundwaters ALLMR, OLGA and OLBA (Table 9) gave a good fit. As was the case for Sr, the best fit k values determined for X, Z and R sites determined at Ba tracer level (10^{-12} M) needed to be iterated again to receive the best fit for Ba sorption at 10^{-8} M carrier concentration. In OLSR the model overestimated Ba retention (modelled values <1.5 mL/g) in the absence of experimental sorption. Table 7 summarizes the logarithms for the selectivity coefficient of Ba for sites X, Z and R in all the modelled solutions.

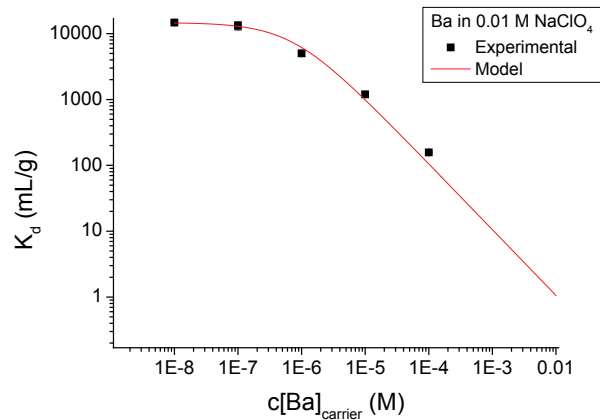


Figure 22. The experimental results from Ca sorption isotherm as determined in 0.01 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 2.0, 3.4 and 2.0, respectively.

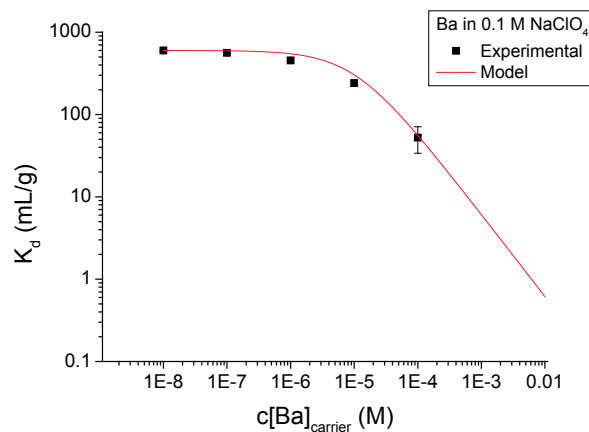


Figure 23. The experimental results from Ba sorption isotherm as determined in 0.1 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 3.07, 3.00 and 2.00, respectively.

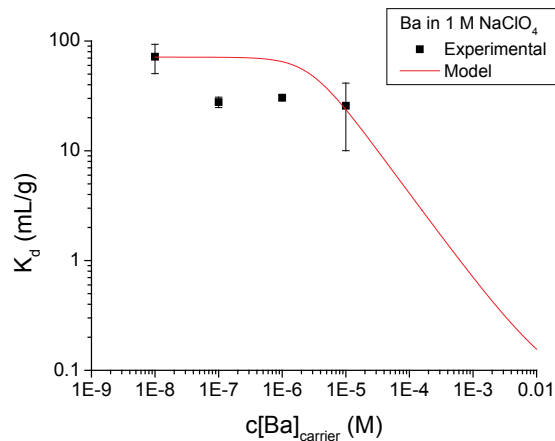


Figure 24. The experimental results from Ba sorption isotherm as determined in 1 M NaClO₄ solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 2.00, 5.64 and 2.00, respectively.

Table 7. The logarithms of the best fit selectivity coefficients of sorption sites X (planar sites), Z (intermediate sites) and R (FES sites) obtained in Ba sorption modellings.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄	2.00	3.40	2.00
0.1 M NaClO ₄	3.07	3.00	2.00
1 M NaClO ₄	2.00	5.64	2.00
ALLMR tracer ^A	2.86	3.42	2.00
ALLMR 10 ⁻⁸ M carrier ^B	2.90	3.41	2.00
OLSR tracer ^A	2.00	5.64	2.00
OLSR 10 ⁻⁸ M carrier ^B	2.00	5.64	2.00
OLGA tracer ^A	2.60	3.38	2.00
OLGA 10 ⁻⁸ M carrier ^B	2.60	3.35	2.00
OLBA tracer ^A	3.00	5.56	2.00
OLBA 10 ⁻⁸ M carrier ^B	3.00	5.20	2.00

^A : the experimental sorption tests conducted by adding only ¹³³Ba tracer at 10⁻¹² M concentration level

^B : the experimental sorption tests conducted by adding Ba carrier at 10⁻⁸ M concentration level

4.3.4 Modelling of Ra sorption

The K_d results from Ra isotherm experiments and their K_d modelling outcomes in 0.01 M, 0.1 M and 1 M NaClO₄ solutions are presented in Figures 25–27. Table 9 gives the experimental and modelled Ra K_d values for Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA. The model gave a satisfactory fit to the experimental values in 0.01 M and 0.1 M NaClO₄ solutions throughout the studied concentration range of 10⁻¹⁰ M – 10⁻⁷ M (notice; Ba carrier addition to gain concentrations 10⁻⁹ M – 10⁻⁷ M). In 1 M NaClO₄ solution (Figure 30) the model slightly underestimates the retention even in the

uncertainty limits of the experimental K_d values; the model predicts a steady K_d of 131 mL/g at Ra (and Ba) concentrations of 10^{-10} M – 10^{-8} M, whereas the range of the experimental values is 131–254 mL/g.

The modelled K_d values for Olkiluoto reference groundwaters ALLMR and OLGA (Table 9) gave a good fit. The best fit k values determined for X, Z and R sites at Ra tracer level of 10^{-10} M managed to produce a modelled K_d value to the limits of the experimental K_d values uncertainty in 10^{-8} M Ba carrier concentration, but to get a better fit the k values were iterated again. In OLSR and OLBA the model overestimated Ra retention (modelled values <1 mL/g) in the absence of experimental sorption. Table 8 summarizes the logarithms for the selectivity coefficient of Ra for sites X, Z and R in all the modelled solutions.

As a general trend in the k values of the sorption sites X for Ca, Sr, Ba and Ra, the values for X sites increased with increasing solution concentration for a certain element and increased in the order of $\text{Ca} < \text{Sr} < \text{Ba} < \text{Ra}$. All the models used in to produce modelled K_d values for Ca, Sr, Ba and Ra in 0.01 M, 0.1 M and 1 M NaClO_4 solutions are presented in Appendix 3.

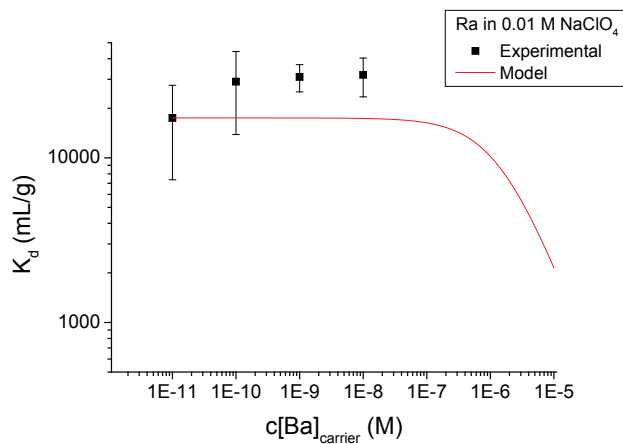


Figure 25. The experimental results from Ra sorption isotherm as determined in 0.01 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 2.41, 2.34 and 2.00, respectively.

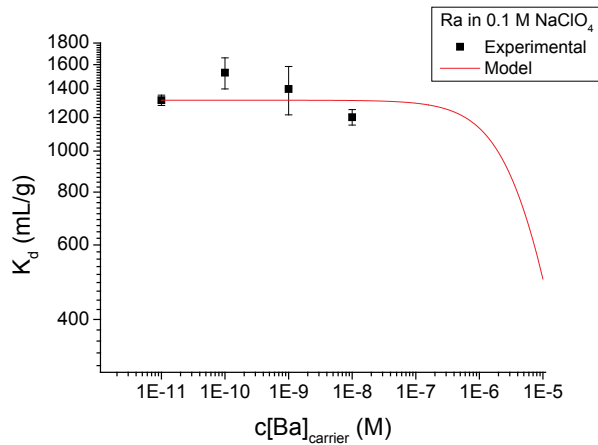


Figure 26. The experimental results from Ra sorption isotherm as determined in 0.1 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 3.4, 3.5 and 2.0, respectively.

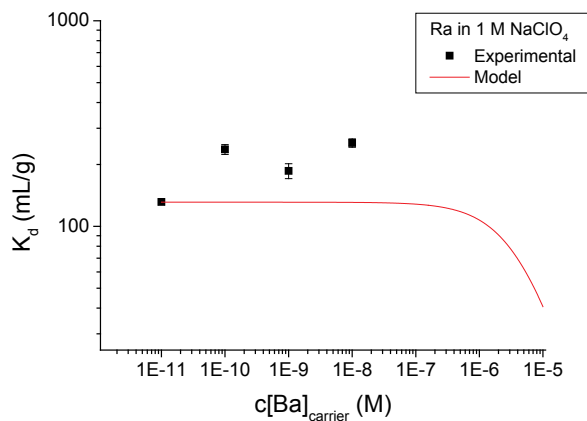


Figure 27. The experimental results from Ra sorption isotherm as determined in 1 M NaClO_4 solution at pH 8 and the data points modelled with three-site cation exchange model. Logarithms of the selectivity coefficient for X, Z and R were 4.6, 3.8 and 2.0, respectively.

Table 8. The logarithms of the best fit selectivity coefficients of sorption sites X (planar sites), Z (intermediate sites) and R (FES sites) obtained in Ra sorption modellings.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄	2.41	2.34	2.00
0.1 M NaClO ₄	3.40	3.50	2.00
1 M NaClO ₄	4.60	3.80	2.00
ALLMR tracer ^A	2.87	2.99	2.00
ALLMR 10 ⁻⁸ M carrier ^B	2.90	3.36	2.00
OLSR tracer ^A	2.00	5.88	2.00
OLSR 10 ⁻⁸ M carrier ^B	2.00	5.88	2.00
OLGA tracer ^A	3.00	3.39	2.00
OLGA 10 ⁻⁸ M carrier ^B	3.09	3.39	2.00
OLBA tracer ^A	1.00	3.00	2.00
OLBA 10 ⁻⁸ M carrier ^B	1.00	3.00	2.00

^A : the experimental sorption tests conducted by adding only ²²⁶Ra tracer at 10⁻¹¹ M concentration level

^B : the experimental sorption tests conducted by adding Ba carrier at 10⁻⁸ M concentration level

4.3.5 Modelled K_d value in reference ground waters

Table 9 gives the modelled K_d values for the four reference ground waters. Modelling was done using the averages of the selectivity coefficients determined for each element (Ca, Sr, Ba and Ra) and sorption site (X, Z and R) in 0.01 M, 0.1 M and 1 M NaClO₄ solutions. The modelled results were in good agreement with the experimental results. However, the model slightly overestimated the sorption in OLSR and OLBA reference ground waters, where no experimental sorption was discovered.

Table 9. The modelled K_d values of ^{45}Ca , ^{85}Sr , ^{133}Ba and ^{226}Ra on monoionic Na–biotite in Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA.

Reference water	Alkaline earth metal concentration			
	<i>tracer</i>		<i>carrier (10^{-8} M)</i>	
	K_d (mL/g)	Ratio: modelled/observed	K_d (mL/g)	Ratio: modelled/observed
^{45}Ca				
ALLMR	23	0.48	-	-
OLSR	0.055	-	-	-
OLGA	710	5.6	-	-
OLBA	0.92	-	-	-
^{85}Sr				
ALLMR	1520	14	1520	15
OLSR	0.0005	-	-	-
OLGA	1080	3.2	57	0.19
OLBA	0.0024	-	-	-
^{133}Ba				
ALLMR	9200	2.3	9180	2.1
OLSR	0.98	-	0.98	-
OLGA	7030	1.7	6880	1.7
OLBA	19	0.20	19	0.22
^{226}Ra				
ALLMR	5820	1.3	5060	1.0
OLSR	11	-	11	-
OLGA	9400	1.1	8400	0.85
OLBA	212	-	212	-

5 SUMMARY

The sorption of alkaline earth cations Ca, Sr, Ba and Ra was investigated in batch experiments on Na-converted biotite, the main sorbing mineral in granitic bedrock at the nuclear waste disposal site in Olkiluoto, Finland. The experiments were conducted in anoxic conditions of a glovebox by varying the concentration of the alkaline earth cation (Ca, Sr and Ba 10^{-8} M– 10^{-5} M; Ra 10^{-10} M– 10^{-7} M) or pH 8 buffered NaClO₄ solutions from 0.01 M to 0.1 M and 1 M. Additional experiments were conducted with Olkiluoto reference groundwaters ALLMR, OLSR, OLGA and OLBA.

The speciation of alkaline earth cations was modelled to be dominated by the presence of M²⁺ cation in all the solutions. In NaClO₄ solutions M²⁺ was the sole important form. Considerable fractions of M²⁺SO₄ and M²⁺CO₃ complexes were present in ALLMR, but their concentration was lower than that of M²⁺. In OLBA, the fraction of M²⁺CO₃ complexes almost reached the respective value of M²⁺ cation at high pH value of 12, but their significance at nominal OLBA pH of 7.6 is insignificant.

The retention of Ca, Sr, Ba and Ra followed a Freundlich representation of an adsorption isotherm as the linear fits to the experimental data were good with R² values ranging from 0.968 to 0.999. The values of *N* (a variable related to surface site heterogeneity) ranged from 0.599 to 1.33. The sorption of Ca, Sr, Ba and Ra showed dependence on the ionic strength of the NaClO₄ solutions. As a general trend, the retention of alkaline earth cations decreased upon (i) increasing $LOG c[M^{2+}]_{eq,liquid}$ value and (ii) increasing NaClO₄ solution concentration. The *K_d* values of Ca, Sr, Ba and Ra decrease in the order of Ra > Ba > Sr > Ca.

The highest retention of Ca, Sr, Ba and Ra among the Olkiluoto reference groundwaters was observed in OLGA, where the respective *K_d* values were 126±22 mL/g, 341±53 mL/g, 4130±120 mL/g and 8340±2700 mL/g. Retention was also observed in ALLMR (Ca 47±1 mL/g, Sr 105±56 mL/g, Ba 4030±10 mL/g and Ra 4380±200 mL/g). The *K_d* values increased in the order of Ca < Sr < Ba < Ra for both solutions. No retention of Ca, Sr or Ra took place in relatively high ionic strength OLSR and OLBA, whereas Ba was slightly retained in OLBA (96±10 mL/g). The sorption behavior of alkaline earth cations in Olkiluoto reference groundwaters is plausibly explained by the effect of increased competition on the sorption sites upon solution having higher ionic strength, that is in the order of OLGA < ALLMR < OLBA < OLSR.

The sorption of Ca, Sr, Ba and Ra was modelled in 0.01 M, 0.1 M and 1 M NaClO₄ solutions and Olkiluoto reference groundwaters using mechanistic three-site cation exchange model developed by Kyllönen et al. (2008, 2014) for Cs sorption on biotite. The model gave generally a good fit to experimental results in 0.01 M and 0.1 M NaClO₄ solutions and ALLMR and OLGA, whereas in 1 M NaClO₄ solutions and OLSR and OLBA it gave slightly overestimated values in the absence of experimentally proven sorption. Ranges of selectivity coefficients for the three sites of the studied elements were obtained in conditions ranging from fresh to saline water, which can be utilized in future modelling.

As a general trend in the k values of the planar sorption sites termed as X for Ca, Sr, Ba and Ra, its values increased with increasing NaClO₄ solution concentration for a certain element and increased in the order of Ca < Sr < Ba < Ra.

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APPENDIX 1 The linear fits of Freundlich isotherms of alkaline earth cations Ca, Sr, Ba and Ra in 0.01 M , 0.1 M and 1 M NaClO_4 solutions (Figures A1–A4).

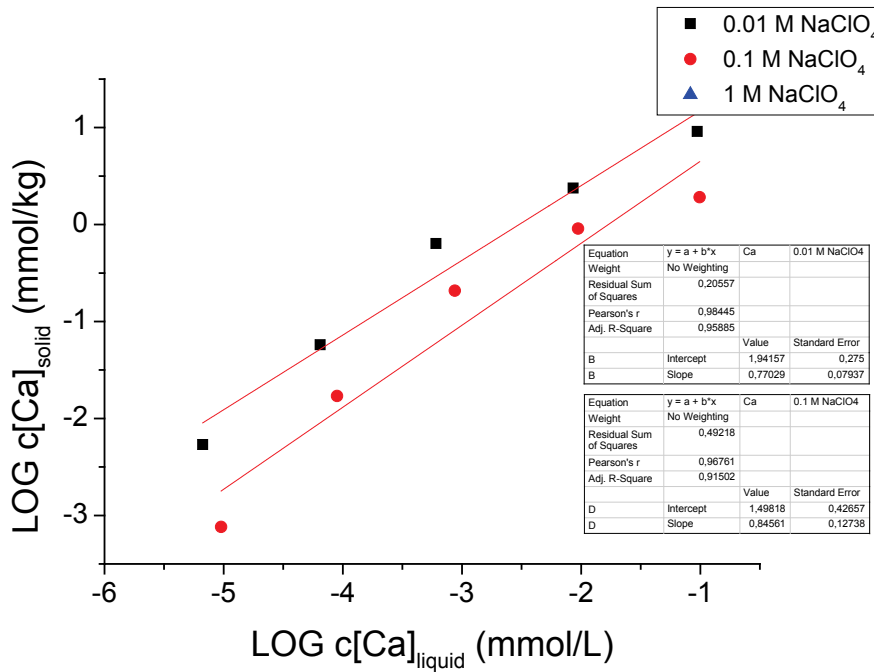


Figure A1. The linear fits to Freundlich Ca isotherm determined in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH 8.

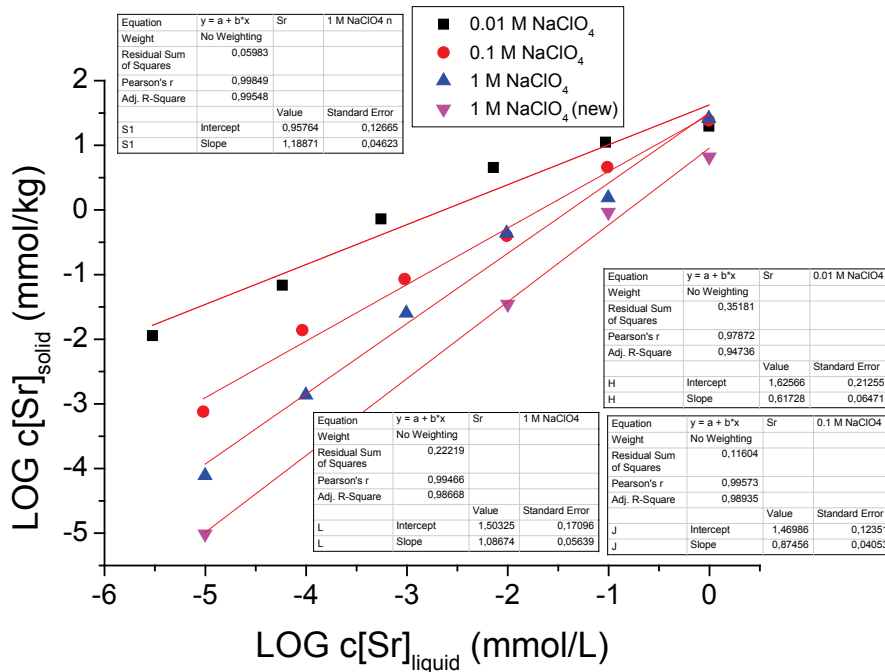


Figure A2. The linear fits to Freundlich Sr isotherm determined in 0.01 M, 0.1 M and 1 M NaClO_4 solutions at pH 8.

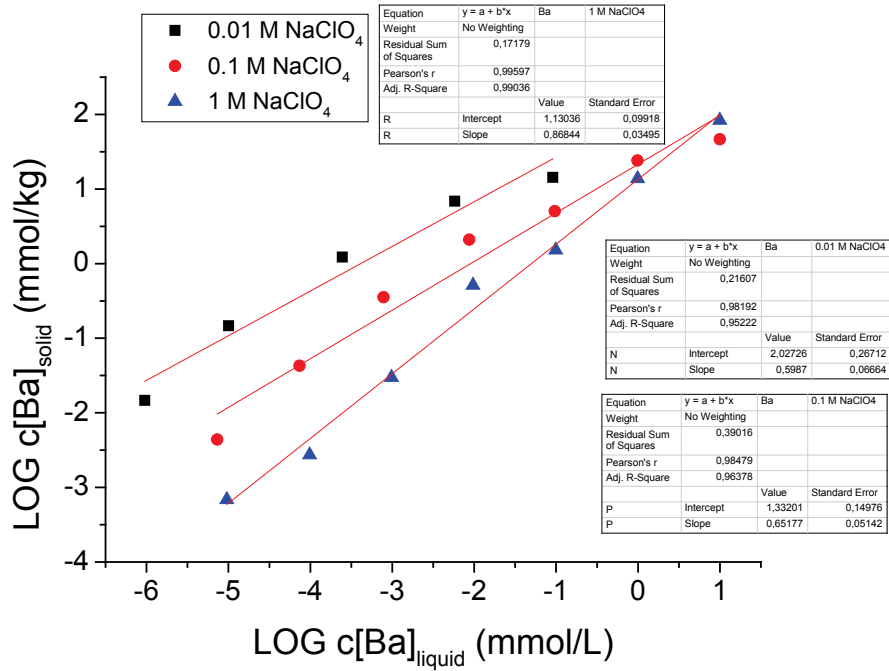


Figure A3. The linear fits to Freundlich Ba isotherm determined in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH 8.

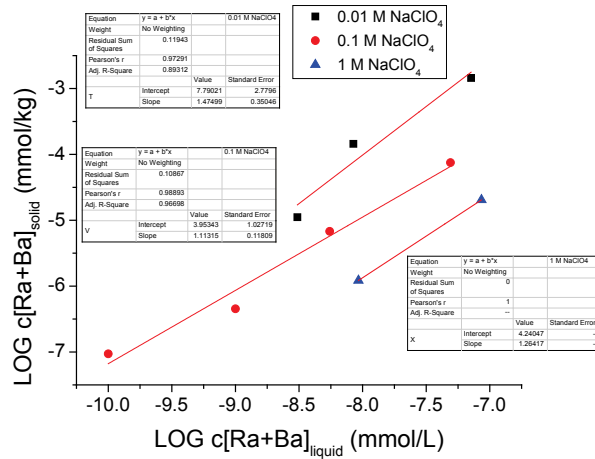


Figure A4. The linear fits to Freundlich Ra isotherm determined in 0.01 M, 0.1 M and 1 M NaClO₄ solutions at pH 8.

APPENDIX 2 The K_d values of ^{45}Ca , ^{85}Sr , ^{133}Ba and ^{226}Ra on monoionic Na-biotite as determined in the isotherm experiments (Tables A2-1 – A2-4).

Table A2-1. The K_d values of ^{45}Ca on monoionic Na-biotite.

[Ca] (M)	$K_d \pm \text{STDEV}$ (mL/g)	pH
0.01 M NaClO ₄		
10 ⁻⁸	811±61	8.41
10 ⁻⁷	894±26	8.56
10 ⁻⁶	1055±113	8.38
10 ⁻⁵	278±35	8.26
10 ⁻⁴	97±1	8.49
10 ⁻³	0	8.44
10 ⁻²	0	8.15
0.1 M NaClO ₄		
10 ⁻⁸	235±119	8.67
10 ⁻⁷	191±17	8.65
10 ⁻⁶	240±42	8.51
10 ⁻⁵	80±29	8.74
10 ⁻⁴	3.8±3	8.66
10 ⁻³	0	8.56
10 ⁻²	0	8.43
1 M NaClO ₄		
10 ⁻⁸	0	8.65
10 ⁻⁷	0	8.87
10 ⁻⁶	0	8.86
10 ⁻⁵	0	8.87
10 ⁻⁴	0	8.83
10 ⁻³	0	8.68
10 ⁻²	0	8.38

Table A2-2. The K_d values of ^{85}Sr on monoionic Na-biotite.

[Sr] (M)	$K_d \pm \text{STDEV}$ (mL/g)	pH
0.01 M NaClO ₄		
10 ⁻⁸	2069±734	8.30
10 ⁻⁷	1182±47	8.48
10 ⁻⁶	1317±92	8.49
10 ⁻⁵	630±14	8.56
10 ⁻⁴	120±7	8.67
10 ⁻³	20±7	8.69
10 ⁻²	0	8.44
0.1 M NaClO ₄		
10 ⁻⁸	80±3	8.56
10 ⁻⁷	151±17	8.63
10 ⁻⁶	90±10	8.69
10 ⁻⁵	50±12	8.68
10 ⁻⁴	70±23	8.59
10 ⁻³	0	8.64
10 ⁻²	0	8.48
1 M NaClO ₄		
10 ⁻⁸	7.8±2	8.80
10 ⁻⁷	14±1	8.92
10 ⁻⁶	26±21	8.91
10 ⁻⁵	45±9	8.83
10 ⁻⁴	6.7±18	8.77
10 ⁻³	16±15	8.77
10 ⁻²	0	8.72

Table A2-3. The K_d values of ^{133}Ba on monoionic Na-biotite.

[Ba] (M)	$K_d \pm \text{STDEV (mL/g)}$	pH
0.01 M NaClO ₄		
10 ⁻⁸	14740±248	8.55
10 ⁻⁷	13231±1853	8.47
10 ⁻⁶	5011±464	8.48
10 ⁻⁵	1196±111	8.39
10 ⁻⁴	157±3	8.52
10 ⁻³	0	8.36
10 ⁻²	0	8.44
0.1 M NaClO ₄		
10 ⁻⁸	600±8	8.74
10 ⁻⁷	561±13	8.72
10 ⁻⁶	455±33	8.59
10 ⁻⁵	241±18	8.59
10 ⁻⁴	53±19	8.73
10 ⁻³	0.007±0.4	8.68
10 ⁻²	0	8.64
1 M NaClO ₄		
10 ⁻⁸	72±22	8.79
10 ⁻⁷	28±3	8.69
10 ⁻⁶	30±2	8.74
10 ⁻⁵	26±16	8.79
10 ⁻⁴	0	8.83
10 ⁻³	0	8.69
10 ⁻²	0	8.44

Table A2–4. The K_d values of ^{226}Ra on monoionic Na–biotite.

[Ra] (M)*	$K_d \pm \text{STDEV (mL/g)}$	pH
0.01 M NaClO ₄		
10 ⁻¹¹	17463±10107	8.24
10 ⁻¹⁰	29024±15169	8.29
10 ⁻⁹	30969±5837	8.19
10 ⁻⁸	31896±8448	8.43
10 ⁻⁷	20460±16144	8.18
10 ⁻⁶	11648±2764	7.60
10 ⁻⁵	3719±645	8.36
0.1 M NaClO ₄		
10 ⁻¹¹	1319±37	8.58
10 ⁻¹⁰	1532±129	8.16
10 ⁻⁹	1401±184	8.53
10 ⁻⁸	1202±51	8.58
10 ⁻⁷	605±397	8.58
10 ⁻⁶	1052±172	8.51
10 ⁻⁵	705±330	8.57
1 M NaClO ₄		
10 ⁻¹¹	131±0	8.85
10 ⁻¹⁰	237±13	8.08
10 ⁻⁹	186±16	8.40
10 ⁻⁸	255±12	8.58
10 ⁻⁷	141±49	8.40
10 ⁻⁶	257±125	8.50
10 ⁻⁵	335±38	8.80

*The Ra concentrations of 10⁻¹¹ M and 10⁻¹⁰ M were achieved by ^{226}Ra addition. Concentrations 10⁻⁹ M – 10⁻⁵ M were gained from Ba carrier addition.

APPENDIX 3 The different sorption models (i.e. the same model with different k values for X, Z and R sites) used in the modelling of Ca (Figures A4–1 – A4–2, $\text{LOG } k$ values Table A4–1), Sr (Figures A4–3 – A4–5, $\text{LOG } k$ values Table A4–2), Ba (Figures A4–6 – A4–8, $\text{LOG } k$ values Table A4–3) and Ra (Figures A4–9 – A4–11, $\text{LOG } k$ values Table A4–4) retention on biotite in 0.01 M, 0.1 M and 1 M NaClO_4 solutions.

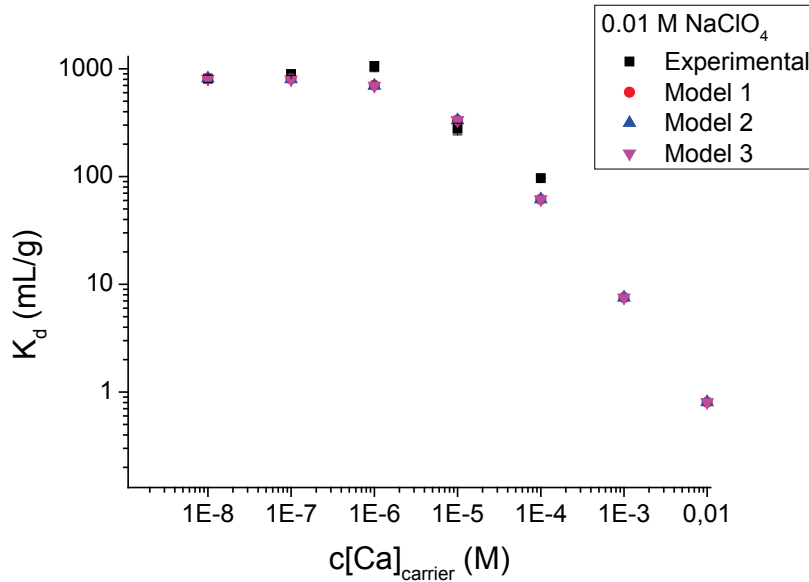


Figure A3–1. The fit between sorption models used to describe Ca retention on biotite in 0.01 M NaClO_4 solution and experimental K_d values.

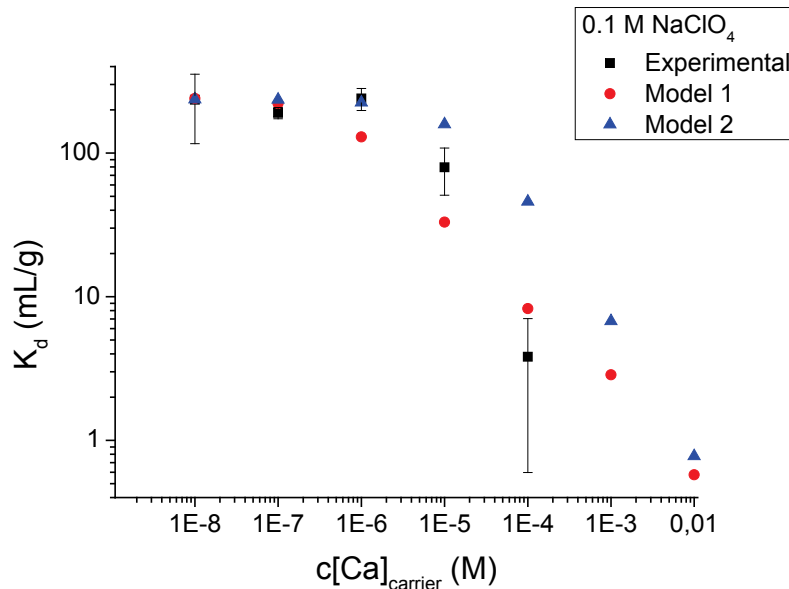


Figure A3–2. The fit between sorption models used to describe Ca retention on biotite in 0.1 M NaClO_4 solution and experimental K_d values.

Table A3–1. The logarithms of the best fit selectivity coefficients of sorption sites *X* (planar sites), *Z* (intermediate sites) and *R* (FES sites) obtained in Ca sorption modellings in 0.01 M, 0.01 M and 1 M NaClO₄ solutions.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄			
Model 1	1.08	1.00	2.00
Model 2	1.00	1.66	2.00
Model 3	1.00	1.65	2.00
0.1 M NaClO ₄			
Model 1	1.00	3.94	2.00
Model 2	2.66	1.00	2.00
1 M NaClO ₄			
Model 1	1.00	3.94	2.00

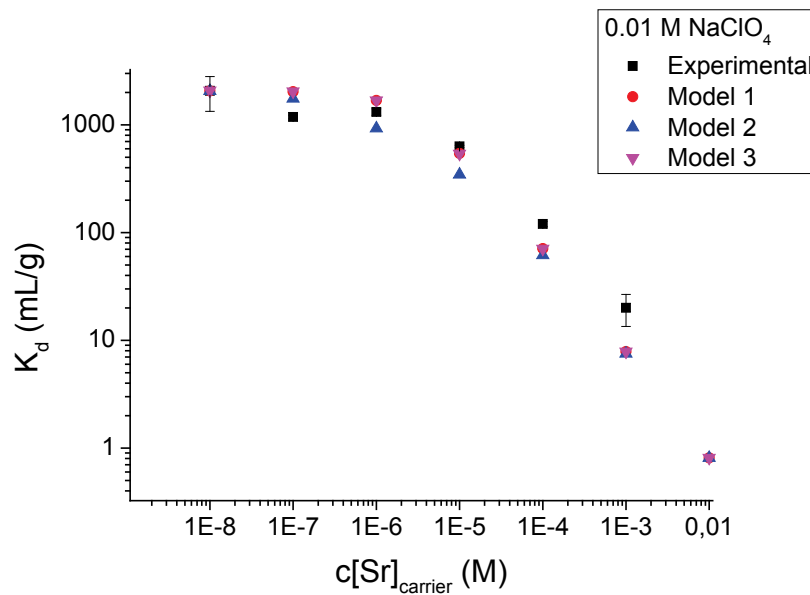


Figure A3–3. The fit between sorption models used to describe Sr retention on biotite in 0.01 M NaClO₄ solution and experimental K_d values.

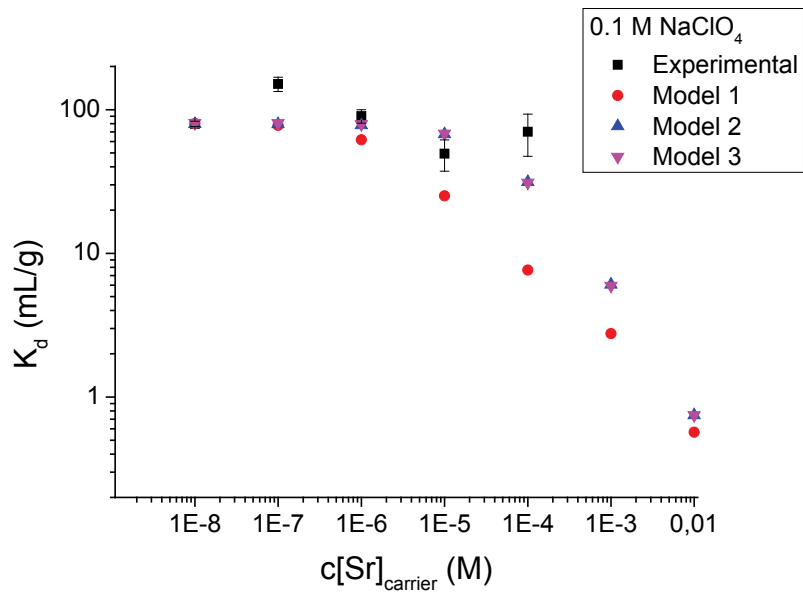


Figure A3–4. The fit between sorption models used to describe Sr retention on biotite in 0.1 M NaClO₄ solution and experimental K_d values.

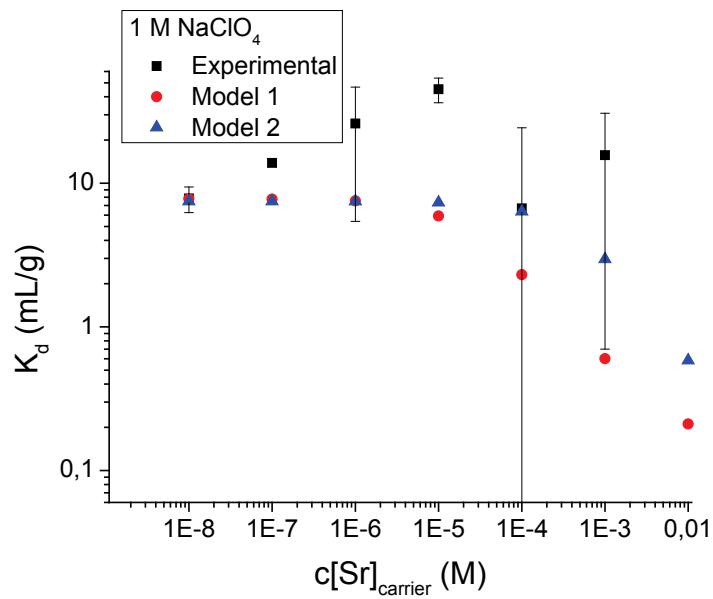


Figure A3–5. The fit between sorption models used to describe Sr retention on biotite in 1 M NaClO₄ solution and experimental K_d values.

Table A3–2. The logarithms of the best fit selectivity coefficients of sorption sites *X* (planar sites), *Z* (intermediate sites) and *R* (FES sites) obtained in Sr sorption modellings in 0.01 M, 0.01 M and 1 M NaClO₄ solutions.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄			
Model 1	1.48	1.49	2.00
Model 2	1.00	2.63	2.00
Model 3	1.50	1.00	2.00
0.1 M NaClO ₄			
Model 1	1.00	3.47	2.00
Model 2	2.20	2.00	2.00
Model 3	2.22	1.00	2.00
1 M NaClO ₄			
Model 1	2.00	4.68	2.00
Model 2	3.40	2.00	2.00

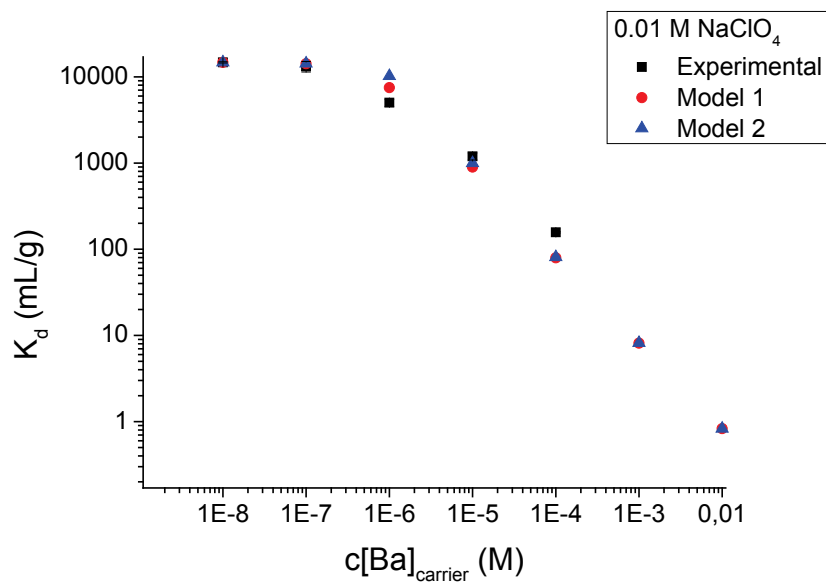


Figure A3–6. The fit between sorption models used to describe Ba retention on biotite in 0.01 M NaClO₄ solution and experimental K_d values.

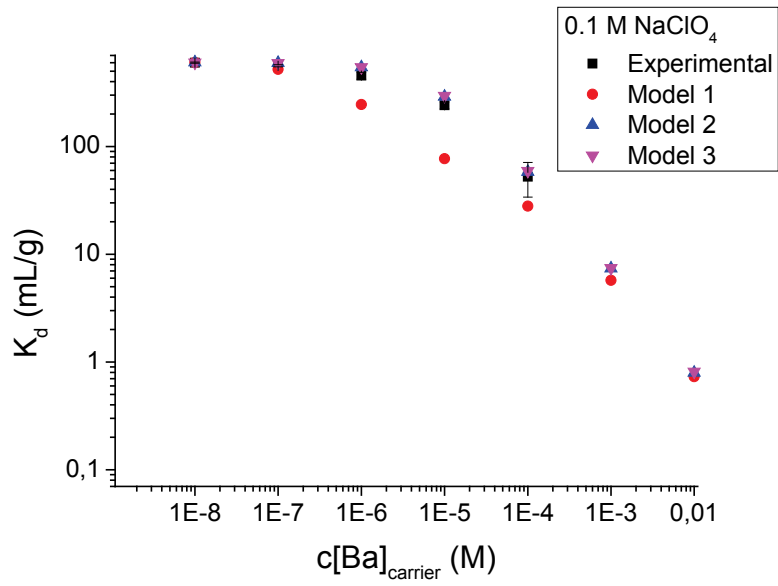


Figure A3–7. The fit between sorption models used to describe Ba retention on biotite in 0.1 M NaClO₄ solution and experimental K_d values.

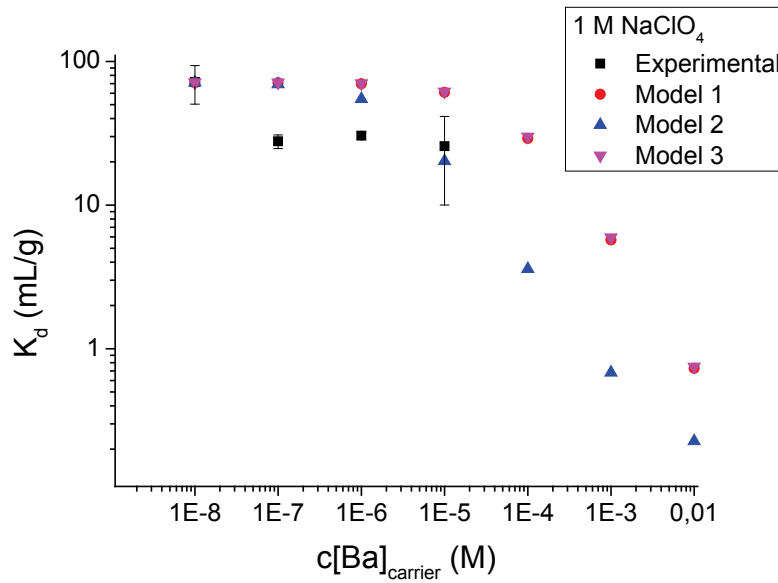


Figure A3–8. The fit between sorption models used to describe Ba retention on biotite in 1 M NaClO₄ solution and experimental K_d values.

Table A3–3. The logarithms of the best fit selectivity coefficients of sorption sites *X* (planar sites), *Z* (intermediate sites) and *R* (FES sites) obtained in Ba sorption modellings in 0.01 M, 0.01 M and 1 M NaClO₄ solutions.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄			
Model 1	2.00	3.40	2.00
Model 2	2.34	2.24	2.00
0.1 M NaClO ₄			
Model 1	2.00	4.34	2.00
Model 2	3.09	2.00	2.00
Model 3	3.07	3.00	2.00
1 M NaClO ₄			
Model 1	4.36	2.00	2.00
Model 2	2.00	5.64	2.00
Model 3	4.34	4.34	2.00

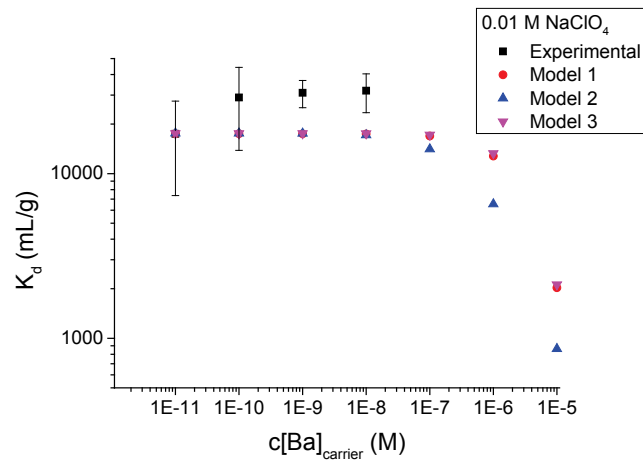


Figure A3–9. The fit between sorption models used to describe Ba retention on biotite in 0.01 M NaClO₄ solution and experimental K_d values.

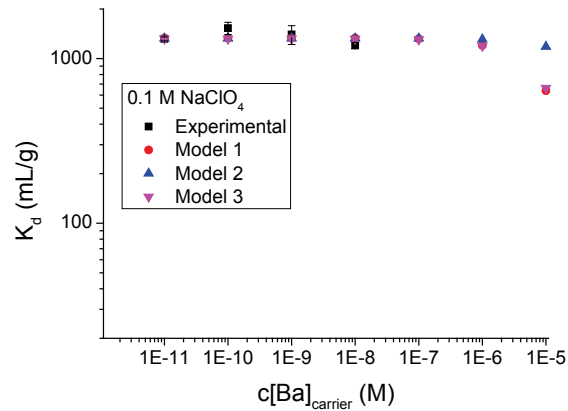


Figure A3–10. The fit between sorption models used to describe Ra retention on biotite in 0.1 M NaClO₄ solution and experimental K_d values.

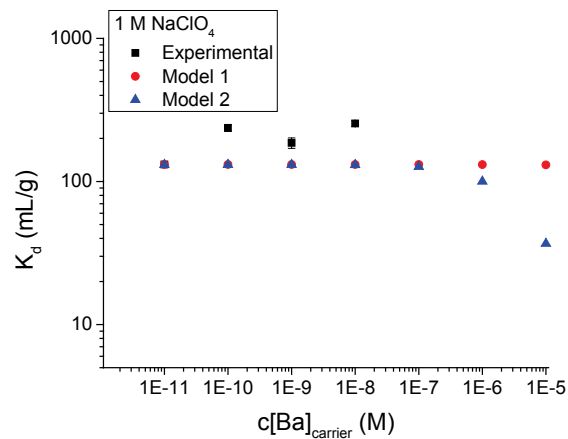


Figure A3–11. The fit between sorption models used to describe Ra retention on biotite in 1 M NaClO₄ solution and experimental K_d values.

Table A3–4. The logarithms of the best fit selectivity coefficients of sorption sites *X* (planar sites), *Z* (intermediate sites) and *R* (FES sites) obtained in Ra sorption modellings in 0.01 M, 0.01 M and 1 M NaClO₄ solutions.

Solution	LOG k		
	X	Z	R
0.01 M NaClO ₄			
Model 1	2.41	2.34	2.00
Model 2	2.00	3.51	2.00
Model 3	2.43	1.00	2.00
0.1 M NaClO ₄			
Model 1	3.43	1.00	2.00
Model 2	2.00	4.69	2.00
Model 3	3.40	3.50	2.00
1 M NaClO ₄			
Model 1	4.60	3.80	2.00
Model 2	2.00	5.88	2.00

