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Sorption of Strontium on Unconsolidated Glaciofluvial Deposits and Clay Minerals; Mutual Interference of Cesium, Strontium and Barium

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Abstract

In earlier studies we investigated the sorption behaviour of cesium and barium on size fractions of glaciofluvial materials and on the clay minerals montmorillonite, illite and chlorite. Here, we report on the sorption, desorption and exchange of strontium (concentration range: $1.5E-07$ to $1.0E-04$ M) in synthetic groundwater on the same materials. The experiments with strontium on glaciofluvial material were restricted to the $<32\text{-}\mu\text{m}$ size fraction. For this material the influence of its mineralogical composition and of the solution chemistry on the sorption of strontium was investigated. We also studied the interference of barium with the sorption of strontium on montmorillonite and on illite, and the mutual interference of cesium and barium on the $<32\text{-}\mu\text{m}$ material.

The isotherms of strontium on all materials investigated were nearly linear. The results suggest that reversible cation-exchange mechanisms on clay minerals are responsible for its sorption behaviour on the glaciofluvial material. Its dependence on the composition of the groundwater could be reproduced with a 3-site model based on two ion-exchange reactions.

1. Introduction

The fission product ^{90}Sr contributes significantly to the radiation hazard of irradiated fuel elements and reprocessing wastes during several hundred years of storage. Its sorption behaviour has therefore been investigated by numerous authors. To our knowledge, only nearly linear isotherms are reported in the literature (e.g. [1–5]). On the other hand in our earlier experiments with barium a linear isotherm was observed only for montmorillonite, whereas non-linear isotherms were obtained for illite, chlorite and the glaciofluvial materials [6]. We therefore decided to investigate also the sorption behaviour of strontium on the same materials. Quaternary glaciofluvial deposits abound in the pre-alpine countries and act as the final barrier before radionuclides released from an underground storage facility enter the biosphere. The glaciofluvial deposits consist of gravel, sand, silt and clay. Clay minerals are powerful sorbents and will be used as back-fill materials in nuclear waste repositories.

2. Experimental

Materials

The glaciofluvial materials investigated were obtained from the water-saturated part of a percussion drilled core at Glattfelden (20 km north of Zürich). This material had been deposited by the Rhine glacier during the ice ages and was subsequently rearranged by rivers. The $<32\text{-}\mu\text{m}$ size fraction was isolated from the section of the core which was 22 to 24 m below the surface. Its mineralogical composition was: 31% of quartz, 36% of calcite, 7% of dolomite, 11% of albite, 9% of illite, 5% of chlorite and 1% of montmorillonite (Tj. Peters, private communication). Experiments were also performed with $<32\text{-}\mu\text{m}$ material treated

- with sodium chloride solutions in order to reduce the amounts of exchangeable barium, strontium and possibly other interfering cations.
- to remove the carbonates, then the free iron and the manganese oxides, and finally the organics.

For details concerning the treatments see Ref. [6]. Experiments were also conducted with the following clay minerals: a montmorillonite from Crook County, Wyoming, USA, an illite from Puy-en-Velay, France, and a chlorite [7] from Grimsel, Switzerland.

The cation-exchange capacities C were determined by sodium saturation in 1 M sodium acetate (procedure of Chapman [8], adapted for small samples using ^{22}Na). The results are summarized in Table 1 of Ref. [6].

Synthetic groundwater

For the majority of the experiments synthetic groundwater (SGW) of the following composition (in meq/l) was used: Ca^{2+} , 4.50; Mg^{2+} , 1.69; Na^+ , 0.67; K^+ , 0.084; Cl^- , 6.52; alkalinity, 0.42; pH 7.9. This is a typical composition of groundwaters of calcite-rich aquifers. However, the bicarbonate ion was largely replaced by the chloride ion to allow investigations at ambient carbon dioxide pressure. This synthetic groundwater is slightly undersaturated with respect to calcite. In the experiments dealing with the influence of solution chemistry the composition of the synthetic

Table 1. Parameters of a 2nd order polynome fit to the experimental sorption data, range of strontium concentrations in solution (M) at equilibrium and mean values for the exponent *n* in the isotherm equation of Freundlich

Material	Synthetic groundwater (see text)	2nd order polynome fit**			Range of log([Sr])	<i>n</i>
		a	b	c		
glaciofluvial materials:						
<32 μm	SGW	-0.485	0.4826	-0.04093	-6.60/-4.05	0.92
<32 μm, NaCl-treated	SGW	-0.823	0.3747	-0.04566	-6.69/-4.03	0.86
<32 μm, free of carbonates*	SGW	-0.603	0.4005	-0.04232	-6.82/-4.04	0.86
<32 μm, free of carbonates, oxides and organics	SGW	-0.701	-0.3969	-0.04140	-6.82/-4.06	0.85
<32 μm, free of carbonates	SGW-1/3K	-0.602	0.4034	-0.04084	-6.82/-4.04	0.85
<32 μm, free of carbonates	SGW-1/2Ca	-0.134	0.4912	-0.03343	-7.10/-4.08	0.86
<32 μm, free of carbonates	SGW-2Ca	-0.815	0.3998	-0.04348	-6.53/-4.03	0.86
<32 μm, NaCl-treated	SGW-HCO3	-0.315	0.5654	-0.03053	-6.27/-4.01	0.88
clay minerals:						
montmorillonite	SGW	1.948	0.9492	-0.00368	-6.46/-4.37	0.99
illite	SGW	0.984	0.8063	-0.01340	-6.81/-4.08	0.95
<40-μm chlorite	SGW	-0.769	0.5790	-0.03009	-6.82/-4.02	0.90

* 3-site model used to calculate the isotherm for SGW from results with SGW's of various composition.

** Parameters obtained, if the experimental isotherms are fitted using the second order polynome $\log([Sr]_s) = a + b \cdot \log([Sr]) + c \cdot (\log([Sr]))^2$.

groundwater was changed. Details are given in the section "Influence of solution chemistry".

Procedure and calculations

The procedure used was the same as that described in Ref. [6]. In a batch method 100 to 200 mg of solid material were contacted with 20 ml of synthetic groundwater in a closed 40-ml centrifuge tube. The solid material remained within this tube throughout the sequence: (1) pretreatment, (2) sorption, (3) desorption and (4) 1 to 2 exchanges. For the sorption step, synthetic groundwater containing strontium labelled with ^{85}Sr was added (concentration range: 0.15–100 μmol/l). The lowest concentration of 0.15 μmol/l was due to impurities in the chemicals (calcium and magnesium chlorides). For the exchange experiments synthetic groundwater with a strontium concentration of 100 μmol/l was used. The sorption and desorption steps lasted 14 days and the exchange steps 21 days.

The concentration of strontium in the solid material (mmole/g) is denoted by $[Sr]_s$ and that in solution/mmole/ml) by $[Sr]$. The distribution ratio (ml/g) is defined by $R_D = [Sr]_s/[Sr]$ and the loading of the solid with strontium by $[Sr]_s \cdot 2/C$. *C* is the cation-exchange capacity (meq/g). The distribution ratios were calculated using Equations (1) to (5) in Ref. [9]. The concentrations of total strontium in the solutions ($[Sr]$) were determined independently of the Sr-85 determination using ICP-AES.

3. Results and discussion

General remarks

In the Figures we present the distribution ratios as a function of the loadings of the solid with strontium in

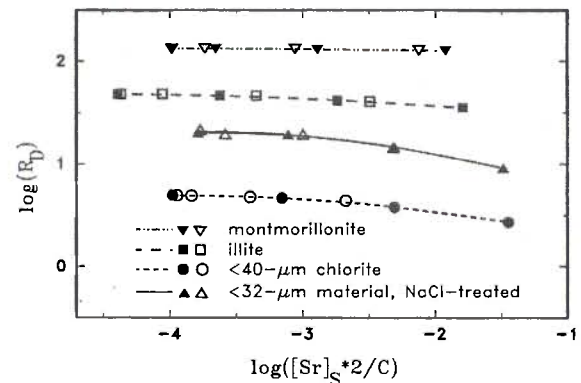


Fig. 1. Sorption (filled symbols) and desorption (open symbols) data for strontium in synthetic groundwater on clay minerals and on the NaCl-treated <32-μm material.

log-log plots. We call the resulting curves "sorption curves" to distinguish them from "isotherms" defined by $[Sr]_s = f([Sr])$. Similarity in shape of sorption curves is equivalent to similarity in shape of isotherms. A linear isotherm ($[Sr]_s = a \cdot [Sr]$) is characterized by a distribution ratio, which does not depend on loadings, i.e. a horizontal line in the Figures, and is equivalent to a Freundlich isotherm with an exponent of 1.0.

Table 1 summarizes some values characterizing the sorption of strontium. The values of $\log([Sr]_s)$ calculated with the parameters of the second order polynome fit do not deviate by more than 0.01 from those determined experimentally.

Influence of mineralogy

Figure 1 shows the sorption and desorption curves for strontium in synthetic groundwater obtained with the

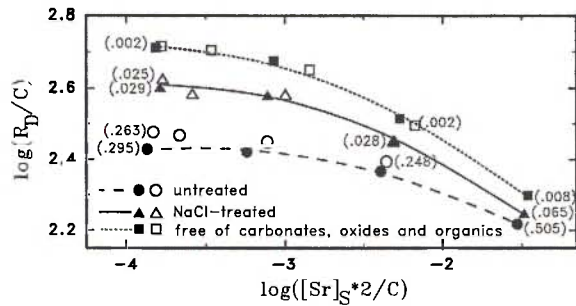


Fig. 2. Sorption (filled symbols) and desorption (open symbols) data for strontium in synthetic groundwater on $<32\text{-}\mu\text{m}$ materials subjected to different chemical treatments; the distribution ratios are normalized with the cation exchange capacity C . The data for the NaCl-treated material are those also shown in Figure 1. In parentheses: concentrations of barium ($\mu\text{mol/l}$) in the solutions.

clay minerals montmorillonite, illite and $<40\text{-}\mu\text{m}$ chlorite and with the NaCl-treated $<32\text{-}\mu\text{m}$ glaciofluvial material. All isotherms are nearly linear (see also Freundlich exponents given in Table 1). The sorption of strontium is almost completely reversible on all materials: sorption and desorption data do not differ significantly. The results of the exchange experiments showed, that the amount of Sr-85 'irreversibly' sorbed during the sorption step amounted to less than 1%.

The sorption curves of $<32\text{-}\mu\text{m}$ glaciofluvial materials with changed mineralogy move close together by normalizing the distribution ratios with the cation-exchange capacities (Figure 2). Since the shape of the sorption curves for all chemically treated glaciofluvial materials are very similar, we show only the two extremes: the NaCl-treated material and that free of carbonates, oxides and organics. This similarity demonstrates that neither the carbonates nor the iron and manganese oxides nor the organic substances contribute significantly to the sorption of strontium. Therefore, clay minerals must be the main sorbing component in the $<32\text{-}\mu\text{m}$ material from Glattfelden. On the other hand the sorption curve of the untreated glaciofluvial material has a flatter shape than that of the NaCl-treated material. Moreover, the desorption data for the untreated material lie above the sorption data, whereas they coincide with the sorption data of the treated materials. These effects can be explained in the following way: The sorption of strontium is sensitive to the amount of barium present (smaller distribution ratios with increasing barium concentration for a given strontium loading), the sensitivity increases with decreasing strontium loadings and it dominates over effects due to changes in the mineralogy of the $<32\text{-}\mu\text{m}$ material. The dependence of the sorption of strontium on the barium concentration will be discussed later.

Figure 3 shows the sorption curves measured for the sorption of cesium, strontium and barium on the clay minerals and on NaCl-treated $<32\text{-}\mu\text{m}$ material. Montmorillonite exhibits approximately linear isotherms and similar distribution ratios for all three ions.

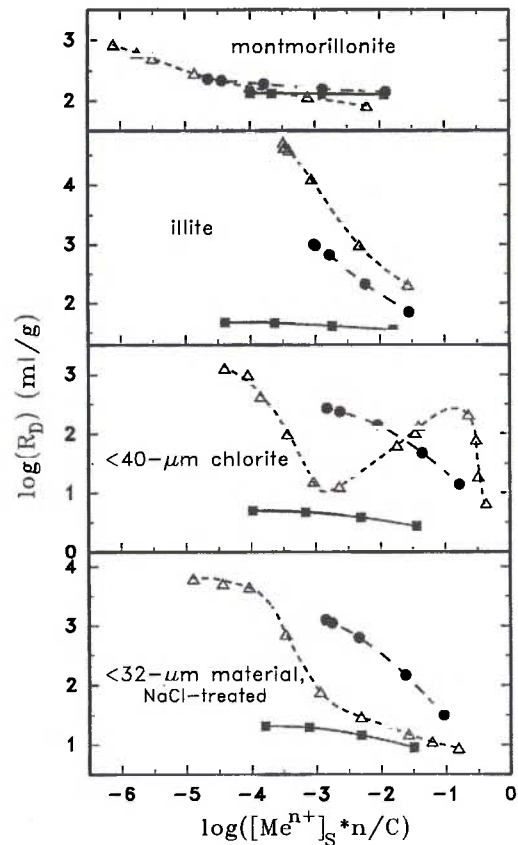


Fig. 3. Sorption data for cesium, strontium and barium in synthetic groundwater on clay minerals and on the NaCl-treated $<32\text{-}\mu\text{m}$ material. - - Δ cesium; — \blacksquare strontium; - - \bullet barium.

For the other solids the isotherms increase in non-linearity in the sequence from strontium (almost linear) to barium and cesium, the distribution ratios being lowest for strontium. In addition to the experiments reported in Ref. [9], the sorption of cesium on the treated $<32\text{-}\mu\text{m}$ materials was also investigated: The shapes of the isotherms for cesium on all $<32\text{-}\mu\text{m}$ materials, whether treated or untreated, were indistinguishable.

Influence of solution chemistry

Groundwaters of the Swiss pre-alpine plains vary in composition. In addition to variations in the concentrations of the major cations they contain much higher concentrations of bicarbonate ion and due to that have a lower pH than the synthetic groundwater (SGW) used in this study. In order to investigate these effects we measured sorption curves for the $<32\text{-}\mu\text{m}$ glaciofluvial material in synthetic groundwater with halved and doubled calcium and magnesium ion concentrations, denoted by SGW-1/2(Ca,Mg) and SGW-2(Ca,Mg) respectively, and with a potassium ion concentration of one third (SGW-1/3K). In an experiment performed in a glove box, the carbon dioxide pressure

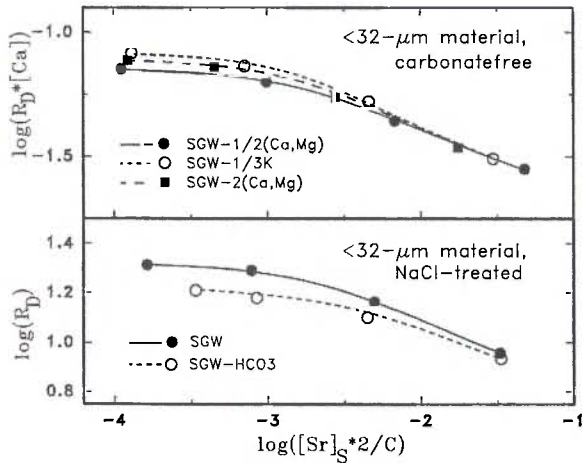


Fig. 4. Experimental data (symbols) for the sorption of strontium on $<32\text{-}\mu\text{m}$ material in synthetic groundwater of varying composition; they are compared with solid, dashed and dotted curves calculated using a 3-site model with two ion-exchange reactions. The names of the various solutions are explained in the section "Influence of solution chemistry".

was increased to 0.02 bar. In this synthetic groundwater (SGW-HCO₃) the concentrations of the major cations were identical to those in SGW. However, the alkalinity was increased to 4.23 meq/l and the pH decreased to 7.1.

Variations in the calcium and magnesium ion concentrations of the synthetic groundwater influence the sorption curves strongly, whereas changes in the potassium ion concentration cause minor effects. If the latter effects are ignored, a single curve should result when plotting the distribution ratios multiplied by the calcium concentration as a function of the loading with strontium [6]. In such a plot, at low loadings, the experimental data deviate only slightly from a single curve and coincide at higher loadings, as can be judged from Figure 4. The remaining differences are due to variations in the $[K]/[Ca]$ -ratio. The curves shown in Figure 4 were calculated using the model developed in Ref. [6] in which 3 types of sorption sites and ion-exchange reactions of strontium with two competing ions (here: calcium and potassium) are considered. The model reproduces the variations in the experimental values very well.

If the partial pressure of carbon dioxide is increased from atmospheric to 0.02 bar (SGW-HCO₃), the sorption of strontium is reduced at low loadings, but remains nearly unchanged at high loadings as shown in Figure 4. Using again the 3-site model with two ion-exchange reactions, a good fit (curves) to the experimental values (points) is again obtained. Here calcium and hydrogen ions are considered as competing ions. The agreement between experiment and model is a strong indication that the decreased sorption of strontium in SGW-HCO₃ compared to that in SGW is caused by an increased competition of hydrogen ions with strontium ions for sorption sites.

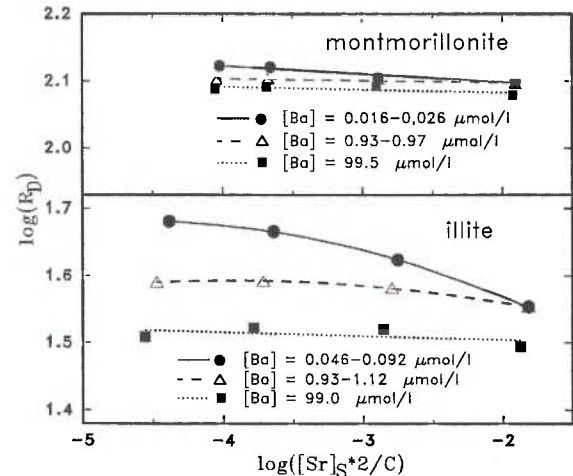


Fig. 5. Sensitivity of the sorption of strontium on montmorillonite and illite to the amounts of barium present in the system.

Mutual interference of barium, strontium and cesium

The sorption curves for strontium on the untreated and the NaCl-treated $<32\text{-}\mu\text{m}$ material differed significantly (Figure 2). The differences increased with decreasing loadings. Since the sorption curves for barium on these two materials coincided [6], variations in solution chemistry must be responsible for the effects observed with strontium. Differences in the concentrations of barium were the only major variations found. It was therefore of interest to investigate the sensitivity of the sorption of strontium to the presence of various amounts of barium. These experiments were performed with montmorillonite (linear isotherms and similar distribution ratios for both elements) and with illite (non-linear isotherm for barium, linear isotherm and lower distribution ratios for strontium). The experiments with the lowest barium concentrations were obtained with SGW to which no barium had been added. For the higher concentrations of about 1.0 and 100 $\mu\text{mol/l}$, barium chloride was added to the SGW and the solids had been pretreated with these solutions. The results are presented in Figure 5. The effects are significant for the illite whereas for the montmorillonite they are of the order of the experimental uncertainties. The results for montmorillonite can be understood if one recalls that the sorption sites are nearly monoenergetic, that the distribution ratios for strontium and barium, i.e. sorption energies of the sites for strontium and barium, are similar, and that the loadings with strontium and barium amount to less than 10 percent, i.e. sites not occupied by these ions are ample. In the case of the illite the sorption sites exhibit a large spectrum of sorption energies for barium, whereas they are nearly monoenergetic for strontium. The differences in sorption energies are largest at low loadings and smallest at high loadings. It is therefore not surprising that the influence of the barium concentration on the sorption of strontium is largest at low loadings of strontium and that, with increasing concentration of barium, the

Table 2. Influence of the concentration of strontium on that of barium at the end of sorption in the solutions resulting from the experiments with <32- μm materials

Material	Concentrations ($\mu\text{mol/l}$)			
untreated	[Sr] =	0.253		88.9
	[Ba] =	0.295		0.505
NaCl-treated	[Sr] =	0.204	8.54	92.2
	[Ba] =	0.029	0.031	0.064
free of carbonates, oxides and organics	[Sr] =	0.150	10.6	86.7
	[Ba] =	0.002	0.002	0.008

Table 3. Influence of cesium on the sorption of barium on NaCl-treated <32- μm material. Distribution ratios for barium (R_D) as a function of barium and cesium concentrations ($\mu\text{mol/l}$) at the end of the sorption

[Ba] =	0.041	0.170	3.73
	R_D		
no cesium added	1416.0	843.0	197.70
[Cs] = 0.0043	1390.0	841.0	195.0
[Cs] = 0.442	1371.0	836.0	194.5
[Cs] = 7.38	1358.0	824.0	200.9

sorption curve for strontium gets flatter, i.e. the isotherm more linear. At the highest concentration of barium, the more energetic sites are occupied by barium and therefore no longer available for the sorption of strontium. The highest concentrations of barium indicated in Figure 5 were measured for the highest loadings of strontium. They indicate that high concentrations of strontium are able to displace sorbed barium. This effect increases with decreasing concentrations of barium. Similar effects were also observed for the <32- μm materials as shown in Table 2. The sorption curves obtained for strontium on untreated and NaCl-treated <32- μm material (Figure 2) indicate that changes in the concentration of barium cause larger effects for this material than was observed for the illite. This higher sensitivity of the <32- μm material to changes in the barium concentration can be explained by the fact that at low loadings the <32- μm material exhibits larger differences in the distribution ratios for barium and strontium than does the illite (Figure 3).

Finally, we investigated the mutual influence of cesium and barium on NaCl-treated <32- μm material. In these experiments ^{137}Cs and ^{133}Ba tracers were added simultaneously. As can be seen from Figure 3, the isotherms for both elements are non-linear, but show distinctly different shapes of the sorption curves. The results are presented in Tables 3 and 4. Small corrections have been applied to the experimental data in order to be able to compare the distribution ratios at constant barium (Table 3) or cesium concentrations (Table 4). These Tables show that the distribution ratios vary at

Table 4. Influence of barium on the sorption of cesium on NaCl-treated <32- μm material. Distribution ratios for cesium (R_D) as a function of cesium and barium concentrations ($\mu\text{mol/l}$) at the end of the sorption

[Cs] =	0.0043	0.442	7.38
	R_D		
[Ba] = 0.041	2635.0	145.2	40.1
[Ba] = 0.170	2560.0	141.6	40.0
[Ba] = 3.73	2560.0	141.6	37.8

most by a few percent, if the concentration of the competing cations is changed by a factor of 100 for barium or 2000 for cesium with upper levels of approximately 5 $\mu\text{mol/l}$. The sorption of strontium at its lowest concentration was not influenced by the presence of cesium: no increase in the concentration of strontium, i.e. no displacement of sorbed strontium, could be observed even at a cesium concentration of 7.4 $\mu\text{mol/l}$.

Comparison with the sorption behaviour of barium

To conclude, we would like to summarize the similarities and differences observed for the sorption behaviour of the two homologous elements strontium and barium. The results obtained for barium were reported in Ref. [6].

- The isotherms for strontium and barium on the montmorillonite are nearly linear and the distribution ratios are similar.
- The isotherms for strontium on the illite, the <40- μm chlorite and the <32- μm materials are nearly linear; those for barium are strongly non-linear.
- The sorption process is reversible for both elements on all materials investigated.
- The sorption curves for barium and strontium on the chemically treated <32- μm materials (NaCl-treated; free of carbonates, of carbonates and oxides and of carbonates, oxides and organics) move close together, if the distribution ratios are normalized with the cation exchange capacities.
- Clay minerals are responsible for the sorption of both elements on the glaciofluvial material: removal of the carbonates, oxides and organics from the <32- μm material caused only minor changes in the sorption curves.
- The dependence of the sorption curves on solution chemistry, i.e. on calcium and magnesium or potassium ion concentrations and on pH, is very similar for both elements.
- Whereas the sorption data for barium on the untreated and on the NaCl-treated <32- μm materials coincide, those for strontium differ. The shape of the sorption curve for strontium on the untreated material is flatter. The different behaviour of barium and strontium is due to the fact, that the amount of barium in the sorption solutions decreases with

increasing chemical treatment of the <32- μm material, whereas that of strontium remains nearly unchanged, and that the sorption of strontium is sensitive to changes in barium level.

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