

INTERACTION OF RADIUM WITH FRESHWATER SEDIMENTS AND THEIR MINERAL COMPONENTS

III. MUSCOVITE AND FELDSPAR

P. BENEŠ,* Z. BOROVEC,** P. STREJC*

**Department of Nuclear Chemistry, Technical University of Prague,
Břehová 7, 115 19 Prague (Czechoslovakia)*

***Department of Petrology, Charles University,
Albertov 6, 128 43 Prague (Czechoslovakia)*

(Received March 11, 1985)

Radiotracer method has been used for investigation of the adsorption and desorption of traces of radium on muscovite and feldspar (albite) under conditions similar to those prevailing in waste and surface waters. The effects of pH, liquid to solid ratio, time, ionic strength (Na^+) and presence of Ca^{2+} or SO_4^{2-} ions have been studied. It has been concluded that both minerals can significantly affect the fate and migration of radium in surface waters if present as major components of bottom sediments or as suspended solids in concentrations of several milligrams per liter or higher. Muscovite can adsorb radium even from moderately acidic waters. Radium adsorbed on muscovite and albite cannot be easily released upon an increase of the salinity of ambient water. However, almost complete desorption can be achieved with 1M HCl. Mechanisms of radium adsorption on both minerals and character of the adsorption sites are discussed.

Introduction

The aim of this series of studies is to elucidate the mechanisms and laws of radium interaction with freshwater sediments.¹ It is believed that the aim can be achieved by the study of the effect of principal factors on radium adsorption by freshwater sediments and by model solids, representing components of these sediments.² In previous papers of this series we discussed the interaction of radium with four model solids: ferric hydroxide and quartz,¹ kaolinite and montmorillonite.² The present paper contains data on the adsorption and desorption of radium by muscovite and albite. Muscovite is an important component of suspended solids in many uranium mine effluents and of bottom sediments in adjacent surface waters. Albite represents the group of feldspars, often present in freshwater sediments. It belongs to the most reactive feldspars. Literature data on

the interaction of radium with albite are virtually nonexistent, analogous data for other feldspars and for muscovite or other micas are very scarce.^{3,4}

Experimental conditions during the study were chosen so as to closely resemble those prevailing in waste and surface waters. In order to facilitate precise determination of radium distribution at concentrations of radium typical for waste waters, ²²⁴Ra was used for the study instead of ²²⁶Ra.

Experimental

Muscovite 2M₁ used in this work was separated from pegmatite found at Baba hill near Domažlice, Czechoslovakia. The large crystal was split to thin sheets, cut into small pieces and ground in an agate mortar. The fraction containing grains in the size range 0.05 – 0.08 mm was obtained by sieving and used for experiments without further pretreatment. Its specific surface area was 8.09 m² · g⁻¹, as determined by the low temperature (liquid N₂) adsorption⁵ of nitrogen from a mixture of hydrogen and nitrogen at a ratio of 3:1. Crystallochemical density of the sample was 2.814 g · cm⁻³, value of the tetrahedral twist was 14° 07', excess of negative charge in tetrahedral sheet -1.752, in octahedral sheet -0.180 and total charge per unit cell of the muscovite was -1.932. The structural crystallochemical formula of the muscovite was (Si_{6.248} Al_{1.752}) (Al_{3.694} Fe_{0.126}³⁺ Fe_{0.045}²⁺ Mg_{0.135}) (K_{1.670} Na_{0.262}) O₂₀ ◯ (OH, F)₄, as calculated from chemical analysis.

Albite Ab_{91.8} An_{8.2} from Dolní Bory near Velké Meziříčí (Czechoslovakia) was analyzed by SKŘIVAN and CHÁB.⁶ It contained 85.5% of the albite component, 7.6% of the anortite component, 6.9% of the orthoclase component and less than 0.1% of very fine-grained white mica. Its ordering index was ~95 and crystallochemical formula was (Na_{0.853} K_{0.068} Ca_{0.076}) (Al_{1.090} Fe_{0.008}³⁺ Si_{2.908} O₈). After grinding in agate mortar and sieving, fraction in the size range of 0.02 – 0.05 mm was used for experiments. The sample had a specific surface area of 1.96 m² · g⁻¹ (nitrogen adsorption)⁵ and its CEC was 1 meq/100 g.

The preparation of stock and experimental solutions used in this work was the same as described in detail earlier.¹ Distilled water and p.a. reagents were used throughout. The experimental solutions were labelled with carrier-free ²²⁴Ra (3.64 d), total concentration of radium amounted to 8–40 pg · l⁻¹. Variations in this range did not exert any significant influence on the results. When experiments with higher concentrations of radium were to be carried out, ²²⁶Ra was added as carrier for ²²⁴Ra.

Adsorption and desorption of radium were studied in a similar experimental arrangement. Ten milliliters of experimental solution were shaken at room

temperature with a known amount of muscovite or albite in 30 ml polythene bottles for 17 hours. Preliminary experiments had shown that the distribution of radium between the solid phase and solution did not change substantially after 17 hour contact. The distribution was determined, after separation of the solid phase by centrifugation (3000 r.p.m., 10 min), from the radioactivity of the solution, measured with a well-type NaI(Tl) scintillation crystal. Adsorption (in %) was calculated from the difference between radioactivities of the solution before and after the adsorption, desorption was evaluated in % from the same radioactivities and from the radioactivity of the desorption solution. Suitable corrections were made for the adsorption of radium on the walls of polyethylene bottles. This adsorption was, however, generally lower than 5%. Details of the experimental procedures and of the evaluations of results were given earlier.^{1,2}

Results and discussion

Muscovite

Adsorption of radium on muscovite is characterized by the data given in Figs 1, 2 and Table 2; desorption is shown in Table 1. Points in the figures represent the results of single experiments, values in the tables are averages from 3 — 4

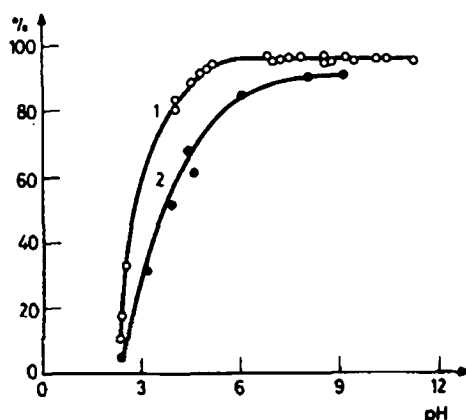


Fig. 1. Adsorption of radium (in %, after 17 hours contact) on muscovite from aqueous 0.01M Na⁺ solutions as a function of pH of the solution and liquid to solid ratio (V/m). Curve 1 — V/m = 500 cm³ · g⁻¹, curve 2 — V/m = 5000 cm³ · g⁻¹

experiments. As can be seen, the adsorption steeply increases with pH in the pH region 2.2 — 6 and levels off at higher pH values. Sulfate and calcium ions at concentrations typical for fresh waters and changes in the concentration of sodium

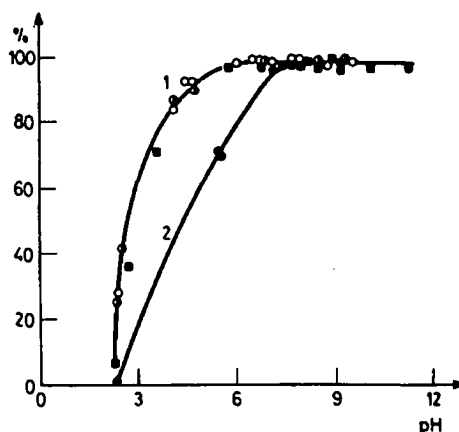


Fig. 2. Adsorption of radium (in %, after 17 hours contact) on muscovite ($V/m = 500 \text{ cm}^3 \cdot \text{g}^{-1}$) as a function of the pH and composition of solution. Curve 1 – 0.01M Na^+ , $60 \text{ mg} \cdot \text{l}^{-1} \text{ SO}_4^{2-}$ (○); 0.01M Na^+ , $30 \text{ mg} \cdot \text{l}^{-1} \text{ Ca}^{2+}$ (●); 0.001M Na^+ (■); curve 2 – 0.1M Na^+ (●)

Table 1

Desorption and reversibility of adsorption (both in %) of radium from/on muscovite as a function of the pH during the preliminary adsorption and of the composition of desorbing solution ($V/m = 500 \text{ cm}^3 \cdot \text{g}^{-1}$ during adsorption and desorption, 17 hrs contact, adsorption from the solution of 0.01M Na^+)

pH	4.0	4.8	6.8	7.2	7.8	8.5	9.2	
0.1M NaCl	21.4	18.9	6.1	4.1	6.2	5.3	2.1	
pH	2.7	4.1	4.5	6.8	7.1	8.6	10.3	
1M HCl	91.5	94.2	93.1	95.5	95.8	95.2	95.5	
pH	2.5	4.6	5.2	6.0	6.9	7.4	7.8	9.1
% REV	23.0	18.3	21.1	20.3	19.8	18.0	22.3	24.1

Table 2

Adsorption of radium (A) on muscovite from a solution of pH 7.50 ($0.005\text{M Na}_2\text{B}_4\text{O}_7$, 0.005M HCl) as a function of liquid to solid ratio (V/m)

$V/m, \text{cm}^3 \cdot \text{g}^{-1}$	A, %	$K_D, \text{cm}^3 \cdot \text{g}^{-1}$	$K'_D, \text{cm}^3 \cdot \text{g}^{-1}$
5000	92.8	64444	96667
3333	94.1	53159	89610
2000	95.6	43455	95600
1000	96.5	27571	87727
833	96.6	23667	80468
666	96.9	20818	92193
500	97.6	20333	—
10–200	97.6	—	—
		Mean $K'_D =$	$90378 \pm 2422 \text{ cm}^3 \cdot \text{g}^{-1}$

ions from 0.001 to 0.01M do not significantly affect the adsorption. Sodium ions in 0.1M concentration suppress the adsorption, but only in the pH region of 2.2 – 7.5. As shown in Table 3, the adsorption is characterized by rather low reversibility. Only a small part of the adsorbed radium can be desorbed with 0.1M NaCl and the desorption is incomplete even with 1M HCl.

All these facts lead to the conclusion that muscovite is able to adsorb radium even from rather acidic waste waters and can substantially affect the migration and fate of radium in surface waters, if present in sufficient concentrations as suspended solids in the waters (corresponding to at least $1 \text{ mg} \cdot \text{l}^{-1}$ muscovite) or as a major component of bottom sediments. Radium adsorbed on muscovite cannot be easily released by an increase in the salinity of water.

The pH-dependence of the adsorption, the small effect of the cations and the low desorption significantly distinguish the interaction of radium with muscovite from that with quartz, kaolinite and montmorillonite, described earlier.^{1,2} This is without doubt due to the different structure and composition of these minerals.

As known, muscovite as dioctahedral mica has a rather compact structure. Most of its isomorphously substituted atoms and, consequently, the deficit of positive charge (or, in other words, excess of negative charge) is in the tetrahedral sheet (Al^{3+} for Si^{4+}), whereas the substitution of Mg^{2+} and Fe^{2+} for Al^{3+} in the octahedral

Table 3
Adsorption of radium (in %)* on albite as a function of pH, concentration of radium, age** of the suspension (T), and composition of the solution

Conditions during the adsorption	pH			
	6.8 ± 0.2	7.5 ± 0.1	8.1 ± 0.1	9.0 ± 0.1
8–40 $\text{pg} \cdot \text{l}^{-1}$ Ra, T = 1 h, 0.01M Na ⁺	97.0 ± 0.9 n = 4	96.8 ± 0.5 n = 9	97.6 ± 0.2 n = 4	97.8 ± 0.2 n = 8
8–40 $\text{pg} \cdot \text{l}^{-1}$ Ra, T = 11 d, 0.01M Na ⁺	98.1 ± 0.3 n = 7	95.2 n = 2	95.0 n = 2	96.5 n = 1
6.8 $\text{ng} \cdot \text{l}^{-1}$ Ra, T = 1 h, 0.01M Na ⁺	98.2 n = 2	98.1 n = 1	97.8 n = 2	98.5 n = 2
8–40 $\text{pg} \cdot \text{l}^{-1}$ Ra, T = 1 h, 0.001M Na ⁺	98.6 ± 0.3 n = 6	99.2 n = 2	99.2 n = 1	99.6 n = 2

*The errors represent standard deviation of the mean.

**The age is the time interval between the first contact of dry albite with aqueous solution and addition of radium.

sheet accounts only for a minor part of the charge deficit. The charge deficit is compensated mostly by K^+ cations firmly bound in interlayer spaces of muscovite.

The interlayer cations in unexpanded micas are almost totally immobile (see, e.g. References^{7,8}) and virtually do not participate in exchange reactions. A higher exchange activity of the interlayer cations can result only from layer bending, rotation of the tetrahedra and shifting of adjacent layers.⁹ The bending is probable particularly in acidic media, when the ends of crystal layers situated on the surface of mica grains expand due to surface exchange of K^+ and Na^+ ions for H^+ ions. (Na^+ would exchange more readily than K^+). The expansion and ensuing interstratification can lead even to the splitting of muscovite grains. Under normal conditions, however, the crystal layers of muscovite are firmly bound together and do not allow penetration of water and ions into the interlayer spaces. Consequently, ion exchange can take place only on the external surface of muscovite grains.

Most of the radium is probably adsorbed on muscovite by ion exchange for ions compensating the charge deficit in the tetrahedral sheet. The distance between radium so bound and the negative charge in the tetrahedral sheet is rather small and therefore radium is bound very strongly, as reflected by the small effect of foreign cations on the adsorption, by the low reversibility of the adsorption and by the small desorption of radium with 0.1M NaCl. This also explains why the radium bond on muscovite is stronger than that on montmorillonite,² where the negative lattice charge (deficit of positive charges) is concentrated more in the octahedral sheet and hence at a greater distance from the adsorbed radium.

Only a small part of radium is adsorbed by muscovite on negative adsorption sites resulting from the isomorphous substitution in octahedral sheets, from dissociation of structural OH groups and from "broken bonds" (Al — OH or Si — O ruptured due to crushing or abrasion of muscovite grains). The latter facts follow from the pH dependence of the adsorption. As can be seen from Figs 1 and 2, the adsorption of radium on muscovite is rather high already below pH 5, where the dissociation of structural OH groups of muscovite is improbable. It has been shown earlier for kaolinite² that the adsorption of radium on the adsorption sites formed from "broken bonds" is significant only at pH >4. There is no reason why the similar sites on muscovite should be active at lower pH values. Consequently, the adsorption of radium by muscovite at pH ≤4 should almost entirely take place on the sites formed by the isomorphous substitution, whose activity does not depend on pH. It cannot be excluded that the structural OH groups and "broken bond" sites participate in the adsorption at pH >4 — 5, but no sudden increase on the pH curves of the adsorption indicating such a participation has been detected. The pH dependence found can be explained by the competition of H^+ ions with radium in the ion

exchange on the sites formed by substitution. Some effect is probably to be expected also from the decomposition of muscovite at $\text{pH} < 3$.

From Table 1 it follows that the reversibility of the adsorption is nearly independent of the pH. This can be considered as evidence that the adsorption sites derived from structural OH groups of muscovite and "broken bonds" play a small role in the adsorption. Were this not the case, the reversibility would have to increase at pH values corresponding to the onset of adsorption on these sites. It has been shown earlier that adsorption on such sites is quite reversible ($>63\%$ for kaolinite² and $>68\%$ for quartz)¹. As can further be seen from Table 1, radium adsorbed on muscovite at $\text{pH} < 5$ is more easily desorbed with 0.1M NaCl than that adsorbed at $\text{pH} > 5$. A similar finding was made with montmorillonite,² pointing to a lower strength of radium adsorption at low pH values. The incomplete desorption of radium with 1M HCl indicates either very strong bonding of radium at some sites or a significant adsorption of radium from 1M HCl. The effect depends little on pH during preliminary adsorption.

Study of the kinetics of radium adsorption on muscovite at pH 7.5 and 4.1 has shown that after about 30 minutes an adsorption value is attained which then remains constant (maximum contact time was 17 hours). Most of the radium is adsorbed during the first 10 min. The rapid course of adsorption indicates that radium is adsorbed only on the surface of muscovite and does not penetrate the interlayer spaces. In this connection it is interesting that radium is more adsorbed by muscovite than by montmorillonite, although the latter mineral has a large inner surface area available for the adsorption and cation exchange capacity usually higher than micas.¹⁰ In our case, the adsorption of radium on muscovite significantly exceeded that on montmorillonite² under the same conditions (pH, V/m), despite the lower specific surface area of the muscovite ($8.09 \text{ m}^2 \cdot \text{g}^{-1}$ compared to $750 \text{ m}^2 \cdot \text{g}^{-1}$ for montmorillonite). A similar conclusion can be derived from data obtained by AMES et al.^{4,11} under conditions different from ours. These findings corroborate that the adsorption is more dependent on the composition and/or structure of minerals than on their specific surface area. It is mainly the extent and quality of structural substitutions which determine radium adsorption. In our case the total charge deficit (-1.932 per unit cell for muscovite vs. -0.925 for montmorillonite) and its distribution (90.7% in tetrahedral sheet for muscovite compared to 9.5% for montmorillonite) were more favourable for muscovite.

No attempt was made in this paper to investigate the effect of the temperature and radium concentration on the adsorption. The adsorption isotherms are usually linear for the concentrations of radium commonly encountered in natural and contaminated surface waters ($0.1 - 100 \text{ pg} \cdot \text{l}^{-1}$), i.e. the percent adsorption should

not depend on radium concentration. The approximate linearity of adsorption isotherms for radium and muscovite was confirmed by AMES et al.⁴ in the concentration range $10^6 - 10^8 \text{ pg} \cdot \text{l}^{-1} \text{ Ra}$ ($V/m = 20 \text{ ml} \cdot \text{g}^{-1}$). The same authors found that adsorption increased with the temperature from 5 to 65 °C.

Comparison of curves 1 and 2 in Fig. 1 shows that the adsorption of radium on muscovite decreases with increasing liquid to solid ratio (V/m) in all the pH region studied. This effect was investigated in more detail at pH 7.50 and the results are presented in Table 2. It has been found that the adsorption (A) increases with decreasing V/m to the maximum value ($A_{\max}$) of 97.6% at $V/m \leq 500 \text{ cm}^3 \cdot \text{g}^{-1}$. The existence of a maximum adsorption of radium lower than 100% has already been observed with other minerals,¹⁻³ but no satisfactory explanation has been proposed.

The effect of V/m on ionic adsorption is usually expressed by means of the distribution coefficient K_D defined as

$$K_D = \frac{A}{100 - A} \cdot \frac{V}{m}$$

which is often considered as independent of V/m . However, in our case the value of K_D decreases with decreasing V/m and therefore K_D is not suitable for quantitative description of radium adsorption on muscovite. A similar finding has been made for other adsorbate – adsorbent systems, and may be due to a solid – solid interaction.^{1,2} As suggested earlier,³ the adsorption of radium on minerals and sediments can be better expressed by the modified distribution coefficient K'_D defined as

$$K'_D = \frac{A}{A_{\max} - A} \cdot \frac{V}{m}$$

It can be seen from Table 2 that K'_D is virtually independent of V/m and is therefore useful for comparison of adsorption ability of muscovite towards radium with analogous abilities of other minerals.¹⁻³ The following sequence of minerals follows from the comparison (mean K'_D values in $\text{cm}^3 \cdot \text{g}^{-1}$ are given in brackets): muscovite (90 000) > albite (32 000) > montmorillonite (8 700) > kaolinite (2 900) > quartz (1 700).

The sequence is valid for pH 7.4 – 8.1, for 0.01M Na^+ and for the mineral species studied in this series. Similar sequences of other minerals were published by MANSFELD and HANSLÍK,³ who found that the sequences depend on the composition of aqueous phase. It must be, however, emphasized that the minerals used for such studies need not exactly represent analogous minerals contained in freshwater sediments. The origin and pretreatment of mineral sample may significantly affect its adsorption properties. For instance mechanical crushing of minerals often

enhances the adsorption activity of minerals due to distortion of the crystal lattice.¹³ The effect is particularly pronounced for hard minerals and therefore the adsorption of radium on a sample of muscovite freshly prepared from a large crystal by grinding may be higher than the adsorption on muscovite grains of freshwater sediments, which have been in a long contact with water and/or are partially weathered. Consequently, the sequences of minerals found with pure minerals need not necessarily be representative for sediments.

Albite

The results of the study of radium interaction with albite are presented in Figs 3, 4 and Tables 3 – 5. Most of the results are averages from 2 – 9 independent measurements. Where 4 or more parallel experiments were carried out, standard deviation of the average is attached, if large enough to be shown in graph.

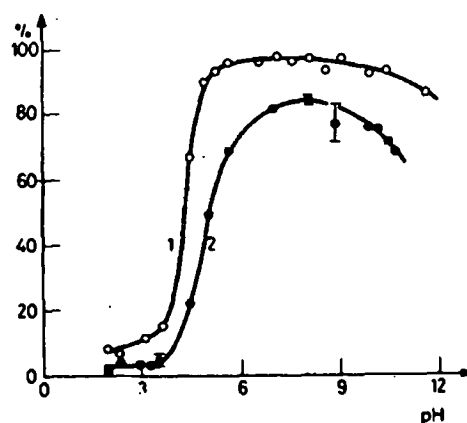


Fig. 3. Adsorption of radium on albite from aqueous 0.01M ($\text{Na}^+ + \text{H}^+$) solutions as a function of pH and liquid to solid ratio (V/m). Curve 1 – $V/m = 500 \text{ cm}^3 \cdot \text{g}^{-1}$, curve 2 – $V/m = 5000 \text{ cm}^3 \cdot \text{g}^{-1}$

Table 4
Desorption of radium (in %) from albite as a function of pH during the prior adsorption[†] and composition of the desorption solution

Desorption solution	pH		
	5.3	7.6	9.0
0.1M NaCl	9.2	2.1	2.1
1.0M HCl	96.5	99.0	98.3

[†]Prior adsorption from 0.01M ($\text{Na}^+ + \text{H}^+$).

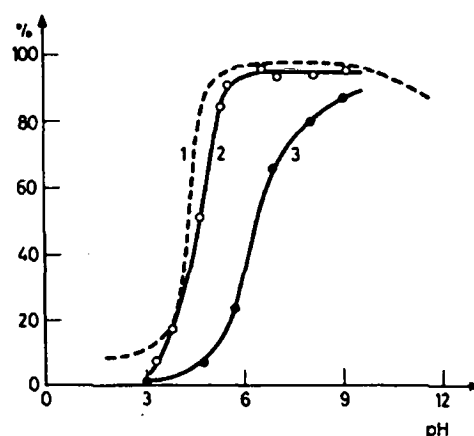


Fig. 4. Adsorption of radium on albite as a function of pH and composition of the solution ($V/m = 500 \text{ cm}^3 \cdot \text{g}^{-1}$). Curves: 1 – $0.01\text{M} (\text{Na}^+ + \text{H}^+)$, 2 – 0.01M Na^+ , $30 \text{ mg} \cdot \text{l}^{-1} \text{ Ca}^{2+}$, 3 – 0.1M NaCl

Table 5
Adsorption (A) of radium on albite from a solution of $\text{pH } 8.05 \pm 0.15$
($0.005\text{M Na}_2\text{B}_4\text{O}_7$, 0.005M HCl) as a function of liquid to solid ratio (V/m)

$V/m, \text{cm}^3 \cdot \text{g}^{-1}$	A, %	$K_D, \text{cm}^3 \cdot \text{g}^{-1}$	$K'_D, \text{cm}^3 \cdot \text{g}^{-1}$
5000	84.9	28113	29479
2000	94.7	35736	41174
1000	96.5	27571	34464
500	97.6	20333	28706
200	98.5	13133	33000
100	99.0	9900	24625
20	$99.3 = A_{\text{max}}$	2837	—
Mean $K'_D =$			$31908 \pm 2329 \text{ cm}^3 \cdot \text{g}^{-1}$

As can be seen from Fig. 3 adsorption of radium on albite depends relatively little on pH in the pH range common for natural waters ($\text{pH } 6 - 8$). The adsorption depends on liquid to solid ratio, V/m , but the decrease in the adsorption with increasing V/m is rather moderate. Below pH 5 the adsorption steeply decreases. Data presented in Fig. 4 show that calcium ions at a concentration typical for fresh waters exert only a small influence on radium adsorption by albite. The adsorption is, however, strongly suppressed by the addition of sodium ions at 0.1M concentration. In the latter case, the increase of adsorption with increasing pH is shifted to higher pH values. The effect of sodium ions (or of ionic strength) on the adsorption can also be seen in Table 3, where the adsorption is generally higher from a solution containing 0.001M Na^+ than from that containing 0.01M Na^+ .

The increase of the initial concentration of radium in the adsorption solution from $8 - 40 \text{ pg} \cdot \text{l}^{-1} {}^{224}\text{Ra}$ to $6.8 \text{ ng} \cdot \text{l}^{-1} \text{Ra}$ (mostly ${}^{226}\text{Ra}$) does not bring about any significant changes in the adsorption percentage (see Table 3). This indicates linearity of the adsorption isotherm in the range studied and suggests that radium adsorption on albite expressed in percent is independent of radium concentration.

It is known that when feldspars are in contact with water, their composition and properties slowly change due either to slow hydrolysis and/or to annealing of their crystall structure damaged by crushing. It seemed interesting to examine the possible effect of these processes on the adsorption of radium on albite. Therefore the adsorbent was stored for 11 days in contact with the solution before radium was added. The results shown in Table 3 seem to indicate that the storage resulted in a slightly decreased adsorption, except for the lowest pH value (6.8) studied.

As shown in Table 4 radium adsorbed at $\text{pH} \geq 5.3$ can be almost completely desorbed by 1M HCl. The analogous desorption with 0.1M NaCl is very low, which points to low reversibility of the adsorption, since 0.1M NaCl has normally a strong suppressing effect on the adsorption (see Fig. 4).

From these findings it can be concluded that feldspars can represent a significant component of freshwater sediments from the point of view of radium adsorption, particularly if composed mainly of plagioclase (albite and oligoclase). An increasing proportion of microcline will probably decrease the activity of the feldspar component as microcline is generally less reactive. Radium adsorbed on the albite component of the sediments cannot be easily released due to an increase in the salinity of ambient water.

For the interpretation of the results found with albite, it is important that the lattice of albite consists of tetrahedra SiO_4 and AlO_4 , so that bonds $\equiv \text{Si} - \text{O} - \text{Si} \equiv$, $\equiv \text{Si} - \text{O} - \text{Al} =$ and $= \text{Al} - \text{O} - \text{Al} =$ are present. Breaking of these bonds by mechanical crushing or abrasion of albite grains results in the formation of negatively and positively charged sites on the surface of albite. The negatively charged sites are capable of binding radium and other cations. The presence of aluminium instead of silicon in the tetrahedra of albite causes a deficit of positive charge which is compensated by incorporation in the lattice of cations, mainly Na^+ . The cations, if sited on the surface of albite, can dissociate from the surface and exchange for other cations from the solution in contact with albite. About one exchangeable Na^+ ion occurs for 4 tetrahedra in unhydrolyzed albite. Hydrolysis of albite in contact with aqueous solution leads to the replacement of Na^+ ions with H^+ ions, which dissociate less easily and are thus less exchangeable for cations. This is for instance reflected in a decrease of negative charge of albite with the age of its aqueous suspension⁶ at $\text{pH } 3.85 - 4.27$.

It can be assumed that at pH 5 – 9 the hydrolysis of albite is very slow (see Table 3) and radium is adsorbed mainly via exchange with structural cations (mostly Na^+) of albite. This interpretation is supported by the strong effect of Na^+ ions on the adsorption, which is due to suppression of the exchange, and by the low desorption of radium with 0.1M NaCl. The divalent radium compensating the deficit of positive charge in the crystal lattice of albite is obviously held very firmly and cannot be easily replaced by Na^+ ions. Previous studies with quartz¹ and kaolinite² have shown that radium adsorbed predominantly on adsorption sites formed from "broken bonds" is readily desorbed by 0.1M NaCl.

The decrease of radium adsorption on albite at pH <5 can be due to competition of H^+ ions in the exchange, or the hydrolysis of albite and the release of Al^{3+} ions, which compete with Ra^{2+} ions in the adsorption. All these effects also account for the easy desorption of radium with 1M HCl. Albite undergoes decomposition also in alkaline medium, where both aluminium and silicon compounds slowly dissolve. This decomposition is the most probable reason of the decrease in the adsorption of radium at pH >9, shown in Fig. 3.

In the presence of 0.1M NaCl, radium is probably adsorbed on the adsorption sites formed from "broken bonds", mainly on $\equiv \text{Si} - \text{O}^-$ groups. Curve 2 in Fig. 4 closely resembles radium adsorption on quartz¹ and the increase of negative charge on albite with increasing pH.⁶

The interpretation given above is further supported by the large adsorption affinity of albite for radium. As shown in Table 5, the affinity is characterized by a high K_D value, distinguishing albite as better adsorbent for radium than montmorillonite and kaolinite (see above), although these minerals under comparable conditions have higher specific surface areas and cation exchange capacities² than albite. This fact cannot be due to the adsorption on "broken bond" groups, but reflects the high selectivity of the exchange reaction $\text{Ra}^{2+} \rightleftharpoons \text{Na}^+$ on albite.

*

Our thanks are due to the International Atomic Energy Agency for financial support of this work, to Dr. B. KŘÍBEK for providing the sample of muscovite and to Dr. P. SKŘIVAN for supplying and preparation of the sample of albite.

References

1. P. BENEŠ, P. STREJC, Z. LUKAVEC, J. Radioanal. Nucl. Chem., 82 (1984) 275.
2. P. BENEŠ, Z. BOROVEC, P. STREJC, J. Radioanal. Nucl. Chem., 89 (1985) 339.
3. A. MANSFELD, E. HANSLÍK, The Effect of Mining Radioactive Raw Materials on the Quality of Surface Waters. Final Report No. C16-331-112-03-04, Water Research Institute, Prague, 1980 (in Czech).

4. L. L. AMES, J. E. McGARRAH, B. A. WALKER, *Clays Clay Minerals*, 31 (1983) 343.
5. F. M. NELSEN, F. T. EGGERTSEN, *Anal. Chem.*, 30 (1958) 1387.
6. P. SKŘIVAN, J. CHÁB, *Acta Univ. Carolinae-Geologica*, 4 (1975) 311.
7. H. GRAF VON REICHENBACH, C. I. RICH, *Trans. 9th Intern. Congr. Soil Sci.* 1 (1968) 709.
8. K. NORISH, *Proc. of the Intern. Clay Conference, Madrid, 1973*, p. 417.
9. H. GRAF VON REICHENBACH, C. I. RICH, *Clays Clay Minerals*, 17 (1969) 23.
10. A. LERMAN, *Geochemical Processes. Water and Sediment Environments*, Wiley-Interscience, New York, 1979, p. 348.
11. L. L. AMES, J. E. McGARRAH, B. A. WALKER, *Clays Clay Minerals*, 31 (1983) 335.
12. D. J. O'CONNOR, J. P. CONNOLLY, *Water Res.*, 14 (1980) 1517.
13. K. G. TILLER, J. F. HODGSON, *Clays Clay Minerals, Proc. 9th Nat. Conf.* 1961, p. 344.

AR-030