# SORPTION OF TRACE CONSTITUENTS FROM AQUEOUS SOLUTIONS ONTO SECONDARY MINERALS. II. RADIUM

## L. L. Ames, J. E. McGarrah, and B. A. Walker

### Battelle, Pacific Northwest Laboratories, P.O. Box 999, Richland, Washington 99352

Abstract—Radium sorption efficiencies as a function of temperature, Ra concentration, and secondary mineral sorbate were determined in a 0.01 M NaCl solution. Radium sorption on a characterized clinoptilolite, montmorillonite, nontronite, opal, silica gel, illite, kaolinite, and glauconite under comparable experimental conditions allowed determination of Ra sorption efficiency curves for each, through use of Freundlich constants, over the same temperature and initial Ra solution concentration range. Similar sorption efficiencies for Ra and U. Clinoptilolite, and nontronite were the most efficient Ra sorbents, while opal and silica gel were the poorest Ra sorbents. Generally, Ra sorption on secondary minerals was much greater than U sorption under the same experimental conditions.

Key Words-Cation exchange, Clinoptilolite, Freundlich isotherm, Glauconite, Illite, Montmorillonite, Opal, Radium, Sorption.

## INTRODUCTION

The separation of U from its daughter Ra<sup>226</sup> through migration of one or both is common in sandstone-type uranium deposits; however, little has been reported on radium sorption under comparable conditions on the same minerals. According to Starik (1936), radium is rapidly removed from waters of low salinity by sorption on sediments, greatly limiting its migration. Titayeva and Veksler (1977) reported that lack of experimental data on the causes regulating Ra sorptiondesorption processes necessitated the use of suppositions concerning them. Granger et al. (1961) and Granger (1963) showed that Ra had migrated from the Ambrosia Lake, New Mexico, ore bodies into surrounding sandstones for distances of up to a few meters. Barite, cryptomelane, and mudstone lenses adjacent to the ore bodies were enriched in Ra<sup>2+</sup> which substituted for  $Ba^{2+}$  in the barite and for  $Mn^{2+}$  in the cryptomelane. From extensive sampling of Ra-contaminated groundwaters in the Grants, New Mexico, area, Kaufmann et al. (1976) found that Ra was separated from the U initially due to U milling operations and continued to migrate with the groundwater.

Korner and Rose (1977) suggested that the increase of Ra with depth was due primarily to reduction of ferric hydroxides, removing a major site for radium sorption. Dyck (1978) reviewed the several factors involved in Ra migration including sorption on clays and iron and manganese oxyhydroxides. Langmuir and Cheatham (1980) reported displacement of Ra in the direction of groundwater flow at Oakville, Texas, uranium deposits.

The goal of the present work was to provide experimental data to allow comparisons of the sorption efficiencies of various secondary minerals for radium and uranium under the same conditions and on the same minerals.

## MATERIALS AND METHODS

## Characterization of the secondary minerals

Chemical analyses, cation exchange capacities, surface area measurements and X-ray diffraction results were given in Part I of this study (Ames *et al.*, 1983). The secondary minerals used in this study are the same as those used in the above study of uranium sorption on secondary minerals.

## Solutions

NaCl solutions (0.01 M) containing three Ra concentrations were used with the secondary minerals. The radium concentrations are given in Tables 1-3. Our prior experimentation showed that 0.01 M NaHCO<sub>2</sub> had little, if any, affect on radium sorption, and hence, only 0.01 M NaCl was used in this work. Radiochemically pure Ra<sup>226</sup> as RaCl<sub>2</sub> was used to trace Ra sorption on the minerals. Counting was done three weeks after taking the samples to allow radon to reach equilibrium with the radium. Because all radium isotopes are radioactive, the range of concentrations was limited to about  $5 \times 10^{-7}$  to  $5 \times 10^{-9}$  M or an initial Ra concentration of from about 105 to 1 ppb Ra. It was impractical to extend the range very much in either direction because counting statistics were poor at lower concentrations and a health hazard existed at higher concentrations.

#### Method

Twenty milliliters of each solution were added per gram of mineral contained in polypropylene tubes. Three aliquots of the original solutions were set aside

Secondary mineral	Initial solution Ra (M)	Equilibrium solution Ra (M)	Mineral loading, (mole Ra/g)	
Illite	$3.413 \times 10^{-7} 3.541 \times 10^{-8} 3.840 \times 10^{-9}$	$3.067 \times 10^{-9} 3.225 \times 10^{-10} 3.879 \times 10^{-11}$	$3.382 \times 10^{-9} \\ 3.509 \times 10^{-10} \\ 3.801 \times 10^{-11}$	
Kaolinite	$\begin{array}{c} 3.413 \times 10^{-7} \\ 3.541 \times 10^{-8} \\ 3.840 \times 10^{-9} \end{array}$	$\begin{array}{c} 7.820 \times 10^{-9} \\ 7.950 \times 10^{-10} \\ 8.540 \times 10^{-11} \end{array}$	$3.335 \times 10^{-9}$ $3.462 \times 10^{-10}$ $3.754 \times 10^{-11}$	
Montmorillonite	$\begin{array}{c} 3.413 \times 10^{-7} \\ 3.541 \times 10^{-8} \\ 3.840 \times 10^{-9} \end{array}$	$\begin{array}{c} 2.770 \times 10^{-9} \\ 2.966 \times 10^{-10} \\ 3.781 \times 10^{-11} \end{array}$	$3.385 \times 10^{-9}$ $3.512 \times 10^{-10}$ $3.802 \times 10^{-11}$	
Nontronite	$3.413 \times 10^{-7}$ $3.541 \times 10^{-8}$ $3.840 \times 10^{-9}$	$\begin{array}{c} 6.750 \times 10^{-10} \\ 8.460 \times 10^{-11} \\ 1.940 \times 10^{-11} \end{array}$	$3.406 \times 10^{-9}$ $3.533 \times 10^{-10}$ $3.820 \times 10^{-11}$	
Glauconite	$3.413 \times 10^{-7}$ $3.541 \times 10^{-8}$ $3.840 \times 10^{-9}$	$\begin{array}{c} 3.589 \times 10^{-10} \\ 5.055 \times 10^{-11} \\ 1.234 \times 10^{-11} \end{array}$	$3.409 \times 10^{-9}$ $3.536 \times 10^{-10}$ $3.827 \times 10^{-11}$	
Clinoptilolite	$3.413 \times 10^{-7}$ $3.541 \times 10^{-8}$ $3.840 \times 10^{-9}$	$\begin{array}{c} 6.700 \times 10^{-11} \\ 2.312 \times 10^{-11} \\ 9.210 \times 10^{-12} \end{array}$	$3.412 \times 10^{-9}$ $3.539 \times 10^{-10}$ $3.831 \times 10^{-11}$	
Opal	$3.413 \times 10^{-7}$ $3.541 \times 10^{-8}$ $3.840 \times 10^{-9}$	$\begin{array}{c} 4.330 \times 10^{-9} \\ 5.085 \times 10^{-10} \\ 6.600 \times 10^{-11} \end{array}$	$3.369 \times 10^{-9}$ $3.490 \times 10^{-10}$ $3.774 \times 10^{-11}$	
Silica gel	$3.413 \times 10^{-7}$ $3.541 \times 10^{-8}$ $3.840 \times 10^{-9}$	$2.042 \times 10^{-7}$ $2.201 \times 10^{-8}$ $2.096 \times 10^{-9}$	$1.371 \times 10^{-9}$ $1.340 \times 10^{-10}$ $1.744 \times 10^{-11}$	

Table 1. Mean experimental values for sorption of radium on secondary minerals at 65°C from 0.01 M NaCl.

Table 2. Mean experimental values for sorption of radium on secondary minerals at 25°C from 0.01 M NaCl.

Secondary mineral	Initial solution Ra (M)	Equilibrium solution Ra (M)	Mineral loading, (mole Ra/g)
Illite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$\begin{array}{c} 3.174 \times 10^{-10} \\ 4.153 \times 10^{-11} \\ 6.465 \times 10^{-12} \end{array}$	$2.602 \times 10^{-9}$ $2.649 \times 10^{-10}$ $2.791 \times 10^{-11}$
Kaolinite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$2.433 \times 10^{-9}$ $2.433 \times 10^{-10}$ $2.958 \times 10^{-11}$	$\begin{array}{c} 2.580 \times 10^{-9} \\ 2.626 \times 10^{-10} \\ 2.767 \times 10^{-11} \end{array}$
Montmorillonite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$1.395 \times 10^{-9}$ $1.469 \times 10^{-10}$ $1.822 \times 10^{-11}$	$5.180 \times 10^{-9}$ $5.280 \times 10^{-10}$ $5.560 \times 10^{-11}$
Nontronite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$\begin{array}{c} 3.142 \times 10^{-10} \\ 3.331 \times 10^{-11} \\ 4.898 \times 10^{-12} \end{array}$	$5.210 \times 10^{-9}$ $5.300 \times 10^{-10}$ $5.590 \times 10^{-11}$
Glauconite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$5.080 \times 10^{-10}$ $5.130 \times 10^{-11}$ $4.506 \times 10^{-12}$	$2.600 \times 10^{-9}$ $2.648 \times 10^{-10}$ $2.793 \times 10^{-11}$
Clinoptilolite	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$8.305 \times 10^{-11}$ $1.881 \times 10^{-11}$ $3.331 \times 10^{-12}$	$2.604 \times 10^{-9}$ $2.651 \times 10^{-10}$ $2.794 \times 10^{-11}$
Opal	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$2.757 \times 10^{-9}$ $3.068 \times 10^{-10}$ $2.743 \times 10^{-11}$	$2.577 \times 10^{-9}$ $2.622 \times 10^{-10}$ $2.770 \times 10^{-11}$
Silica gel	$2.605 \times 10^{-7}$ $2.653 \times 10^{-8}$ $2.797 \times 10^{-9}$	$1.384 \times 10^{-7}$ $1.969 \times 10^{-8}$ $2.118 \times 10^{-9}$	$\begin{array}{c} 1.139 \times 10^{-9} \\ 1.142 \times 10^{-10} \\ 6.945 \times 10^{-12} \end{array}$

for sampling at temperature and later counting with the equilibrium solution aliquots. Each mineral-solution equilibrium experiment was triplicated in sealed, polypropylene tubes, and mean values were used to determine the U remaining in solution and sorbed on the mineral. Tube-wall sorption was checked to be certain that large corrections were not required to compensate for this.

Equilibration of solutions and minerals was for 30 days at 5°, 25° or 65°C in environmental chambers with gentle agitation. Solutions plus liquid scintillation agent were sealed and set aside for three weeks to allow radon buildup and equilibrium. From the scintillation counting efficiency, initial and equilibrium solution counts, and Ra specific activity (0.988 Ci/g), concentrations of Ra in the equilibrium solution and on the mineral were calculated.

Dissolved oxygen measurements on final solutions yielded an average 8.3 mg  $O_2$ /liter on a computed Eh of +650 mV. Final solution pH measurements ranged between 6 and 7 and averaged near 6.5. There was no pH change between initial and final solution pH.

#### RESULTS

Tables 1-3 give the mean Ra sorption results at 65°, 25°, and 5°C, respectively, and include the various solution Ra concentrations in ppb. The initial solution Ra concentration represents the Ra in solution before

Table 3. Mean experimental values for sorption of radium on secondary minerals at 5°C from 0.01 M NaCl.

Secondary mineral	Initial solution Ra (M)	Equilibrium solution Ra (M)	Mineral loading, mole Ra/g	
Illite	$2.349 \times 10^{-7}$ $2.517 \times 10^{-8}$ $2.556 \times 10^{-9}$	$\begin{array}{c} 1.136 \times 10^{-10} \\ 1.888 \times 10^{-11} \\ 2.686 \times 10^{-12} \end{array}$	$\frac{2.348 \times 10^{-9}}{2.515 \times 10^{-10}}$ 2.553 $\times 10^{-11}$	
Kaolinite	2.349 × 10 <sup>-7</sup> 2.517 × 10 <sup>-8</sup> 2.556 × 10 <sup>-9</sup>	$\begin{array}{c} 4.795 \times 10^{-9} \\ 4.181 \times 10^{-10} \\ 5.100 \times 10^{-11} \end{array}$	$\begin{array}{c} 2.301 \times 10^{-9} \\ 2.475 \times 10^{-10} \\ 2.501 \times 10^{-11} \end{array}$	
Montmorillonite	$\begin{array}{c} 2.349 \times 10^{-7} \\ 2.517 \times 10^{-8} \\ 2.556 \times 10^{-9} \end{array}$	$\begin{array}{c} 1.445 \times 10^{-9} \\ 1.442 \times 10^{-10} \\ 1.737 \times 10^{-11} \end{array}$	$\begin{array}{c} 4.669 \times 10^{-9} \\ 5.001 \times 10^{-10} \\ 5.075 \times 10^{-11} \end{array}$	
Nontronite	$\begin{array}{c} 2.349 \times 10^{-7} \\ 2.517 \times 10^{-8} \\ 2.556 \times 10^{-9} \end{array}$	$\begin{array}{c} 3.749 \times 10^{-10} \\ 6.590 \times 10^{-11} \\ 1.074 \times 10^{-11} \end{array}$	$\begin{array}{c} 4.691 \times 10^{-9} \\ 5.025 \times 10^{-10} \\ 5.090 \times 10^{-11} \end{array}$	
Glauconite	$2.349 \times 10^{-7}$ $2.517 \times 10^{-8}$ $2.556 \times 10^{-9}$	$\begin{array}{c} 9.840 \times 10^{-9} \\ 9.650 \times 10^{-10} \\ 1.330 \times 10^{-10} \end{array}$	$2.251 \times 10^{-9}$ $2.420 \times 10^{-10}$ $2.423 \times 10^{-11}$	
Clinoptilolite	$2.349 \times 10^{-7}$ $2.517 \times 10^{-8}$ $2.556 \times 10^{-9}$	$\begin{array}{c} 4.752 \times 10^{-10} \\ 8.855 \times 10^{-11} \\ 9.845 \times 10^{-12} \end{array}$	$\begin{array}{c} 2.344 \times 10^{-9} \\ 2.508 \times 10^{-10} \\ 2.546 \times 10^{-11} \end{array}$	
Opal	$2.349 \times 10^{-7}$ $2.517 \times 10^{-8}$ $2.556 \times 10^{-9}$	$5.330 \times 10^{-9}$ $5.770 \times 10^{-10}$ $5.280 \times 10^{-11}$	$2.476 \times 10^{-9}$ $2.459 \times 10^{-10}$ $2.503 \times 10^{-11}$	
Silica gel	$\begin{array}{c} 2.349 \times 10^{-7} \\ 2.517 \times 10^{-8} \\ 2.556 \times 10^{-9} \end{array}$	$\begin{array}{c} 1.250 \times 10^{-7} \\ 1.569 \times 10^{-8} \\ 2.111 \times 10^{-9} \end{array}$	$1.099 \times 10^{-9}$ 9.480 × 10 <sup>-11</sup> 4.454 × 10 <sup>-12</sup>	

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Secondary mineral	Temperature (°C)	К	n	r	Sy x (In units)
Illite	5	2054.1	1.2081	+0.9998	±0.041344
	25	287.65	1.1665	+0.9998	$\pm 0.049704$
	65	1.8761	1.0273	+0.9999	$\pm 0.026168$
Kaolinite	5	0.41042	0.9891	+0.9987	$\pm 0.122764$
	25	1.8952	1.0290	+0.9998	$\pm 0.048752$
	65	0.36198	0.9911	+0.9999	$\pm 0.006091$
Montmorillonite	5	5.1507	1.0217	+0.9994	$\pm 0.083007$
	25	8.9065	1.0434	+0.9998	$\pm 0.042943$
	65	2.7114	1.0413	+0.9998	$\pm 0.046401$
Nontronite	5	4112.3	1.2760	+0.9999	$\pm 0.012204$
	25	115.96	1.0893	+0.9991	$\pm 0.103709$
	65	1038.47	1.2559	+0.9956	$\pm 0.233288$
Glauconite	5	0.57335	1.0483	+0.9984	$\pm 0.137991$
	25	2.2539	0.9615	+0.9998	$\pm 0.054233$
	65	8400.7	1.3180	+0.9963	$\pm 0.212130$
Clinoptilolite	5	119.55	1.1587	+0.9976	$\pm 0.166543$
	25	308234.0	1.4112	+0.9987	$\pm 0.121241$
	65	$1.1530  imes 10^{14}$	2.2488	+0.9985	$\pm 0.103498$
Opal	5	0.29462	0.9802	+0.9999	$\pm 0.033083$
	25	0.88563	0.9966	+0.9991	$\pm 0.101975$
	65	2.9439	1.0714	+0.9999	$\pm 0.027498$
Silica gel	5	1.9129	1.3469	+0.9972	$\pm 0.221318$
	25	0.23799	1.2209	+0.9998	$\pm 0.048952$
	65	$3.16670  imes 10^{-3}$	0.9534	+0.9986	$\pm 0.125640$

Table 4. Freundlich constants for radium sorption on secondary minerals.

the experiment began; the equilibrium concentration represents the Ra concentration remaining in solution after 30 days of mineral-solution continuous contact. The data of Tables 1–3 can be fitted to a linearized Freundlich sorption isotherm. The Freundlich equation,  $(x/m) = KC^n$ , where K and n are constants, C is the equilibrium solution concentration of the sorbed component in molarity, and (x/m) is the equilibrium

Secondary mineral	Temperature (℃)	L	р	r	Sy·x (In units)
Illite	5 25 65	$\begin{array}{c} 9.9518 \times 10^{-3} \\ 1.0362 \times 10^{-2} \\ 1.0257 \times 10^{-2} \end{array}$	1.0000 1.0022 1.0022	+1.000 +1.000 +1.000	$\pm 0.000003$ $\pm 0.003093$ $\pm 0.003082$
Kaolinite	5 25 65	$9.7548  imes 10^{-3}$ $1.0259  imes 10^{-2}$ $9.7548  imes 10^{-3}$	1.0000 1.0022 1.0000	+1.000 +1.000 +1.000	$\pm 0.000006 \\ \pm 0.003090 \\ \pm 0.000006$
Montmorillonite	5 25 65	$\begin{array}{c} 1.9841 \times 10^{-2} \\ 1.9841 \times 10^{-2} \\ 1.0257 \times 10^{-2} \end{array}$	1.0000 1.0000 1.0022	+1.000 +1.000 +1.000	$\pm 3.677 \times 10^{-7} \\ \pm 3.677 \times 10^{-7} \\ \pm 0.003082$
Nontronite	5 25 65	$\begin{array}{c} 2.0659 \times 10^{-2} \\ 2.0724 \times 10^{-2} \\ 1.0710 \times 10^{-2} \end{array}$	1.0022 1.0022 1.0045	+1.000 +1.000 +1.000	$\pm 0.003152 \\ \pm 0.003139 \\ \pm 0.000057$
Glauconite	5 25 65	$\begin{array}{c} 9.8927 \times 10^{-3} \\ 1.0362 \times 10^{-2} \\ 1.0359 \times 10^{-2} \end{array}$	1.0022 1.0022 1.0022	+1.000 +1.000 +1.000	$\pm 0.003071 \\ \pm 0.003093 \\ \pm 0.003111$
Clinoptilolite	5 25 65	$\begin{array}{c} 9.9518 \times 10^{-3} \\ 1.0362 \times 10^{-2} \\ 1.0359 \times 10^{-2} \end{array}$	1.0000 1.0022 1.0022	+1.000 +1.000 +1.000	$\pm 0.000003$ $\pm 0.003093$ $\pm 0.003111$
Opal	5 25 65	$\begin{array}{c} 9.7548 \times 10^{-3} \\ 1.3070 \times 10^{-2} \\ 1.0186 \times 10^{-2} \end{array}$	1.0000 1.0155 1.0022	+1.000 +1.000 +1.000	$\pm 0.000006 \\ \pm 0.021703 \\ \pm 0.003150$
Silica gel	5 25 65	0.120693 0.028972 2.74562 × 10 <sup>-3</sup>	1.2173 1.1245 0.9756	+0.999 +0.998 +1.000	$\pm 0.164004$ $\pm 0.168283$ $\pm 0.078355$

Table 5. Freundlich-like constants for radium sorption on secondary minerals.



Figure 1. Linearized Freundlich equation sorption isotherms of the natural logarithm of the equilibrium Ra concentration in solution (C) versus the natural logarithm of equilibrium Ra loading on illite (x/m).

concentration of the sorbed component on the solid in mole/g, is an empirical relationship (Freundlich, 1922), but very similar equations have been derived from basic parameters (Adamson, 1976). As example of a linearized sorption isotherm, a plot of ln(x/m) vs. In C is given in Figure 1 for illite at three temperatures. Note that three straight lines result for the three isotherms. The slope of the lines is n, and the Y intercept is K. The Freundlich constants for the sorption data in Tables 1–3 are given in Table 4 in addition to r, the correlation coefficient, and Sy·x, the standard deviation from regression.

In addition to the usual Freundlich sorption isotherms, the Ra sorption data also fit a modified Freundlich sorption isotherm equation,  $(x/m) = LC_1^p$ , where  $C_t$  is the initial Ra solution concentration in molarity. The Freundlich-like constants given in Table 5, and the associated r and Sy x values allow a Ra distribution coefficient to be computed that indicates comparative Ra sorption efficiencies for the secondary minerals under identical experimental conditions. For example, at 25°C for illite in 0.01 M NaCl, ln(x/m) = ln L + p ln $C_1$ , or from Table 5 at  $1.00 \times 10^{-8}$  M Ra, ln(x/m) =



Figure 2. Natural logarithm of the initial Ra concentration in solution ( $C_1$ ) vs. the Ra equilibrium distribution coefficient (D) for illite in 0.01 M NaCl.

 $(-4.5696) + (1.002212)(-18.421) = 9.9452 \times 10^{-11}$ mole Ra/g. From the data of Table 4,  $\ln(x/m) = \ln K + n \ln C \text{ or } -23.0313 = (+5.6618) + (1.16650)(\ln C)$ , and  $(C) = 2.0768 \times 10^{-11}$  M. D, then, is (x/m)/(C)(0.001)



Figure 3. Natural logarithm of the initial Ra concentration in solution  $(C_1)$  vs. the Ra equilibrium distribution coefficient (D) for kaolinite in 0.01 M NaCl.



Figure 4. Natural logarithm of the initial Ra concentration in solution ( $C_1$ ) vs. the Ra equilibrium distribution coefficient (D) for montmorillonite in 0.01 M NaCl.

=  $(9.9452 \times 10^{-11})/(2.0768 \times 10^{-11})(0.001) = 4788.7$  ml/g, or the Ra contained in 4788.7 ml of solution is sorbed on one gram of illite. By computing many such D values within the range of experimental C<sub>1</sub> values, a curve can be generated that describes the response of Ra sorption efficiency (D) to changes in temperature, Ra concentration, and type of secondary mineral formed.

## DISCUSSION

The curves of ln C<sub>1</sub> vs. D for illite, kaolinite, montmorillonite, nontronite, glauconite, clinoptilolite, opal, and silica gel are shown in Figures 2–9, respectively, for 5°C, 25°C, and 65°C in 0.01 M NaCl. The approximate Ra-sorption efficiencies for the secondary minerals in decreasing order is clinoptilolite > nontronite > glauconite > montmorillonite > kaolinite = opal > silica gel in this simple Na system. In a general way, sorption efficiency is correlated with cation-exchange capacity. For the cation-exchange minerals, Raremoval efficiency generally exceeds that for uranyl



Figure 5. Natural logarithm of the initial Ra concentration in solution ( $C_1$ ) vs. the Ra equilibrium distribution coefficient (D) for nontronite in 0.01 M NaCl.



Figure 6. Natural logarithm of the initial Ra concentration in solution ( $C_1$ ) vs. the Ra equilibrium distribution coefficient (D) for glauconite in 0.01 M NaCl.



Figure 7. Natural logarithm of the initial Ra concentration in solution  $(C_t)$  vs. the Ra equilibrium distribution coefficient (D) for clinoptilolite in 0.02 M NaCl.



Figure 8. Natural logarithm of the initial Ra concentration in solution  $(C_i)$  vs. the Ra equilibrium distribution coefficient (D) for opal in 0.01 M NaCl.



Figure 9. Natural logarithm of the initial Ra concentration in solution ( $C_1$ ) vs. the Ra equilibrium distribution coefficient (D) for silica gel in 0.01 M NaCl.

ions from 0.01 M NaCl systems. Comparable U sorption efficiency curves (D values) in 0.01 M NaCl were given by Ames et al. (1983) including those for illite, opal, silica gel, clinoptilolite, and montmorillonite. Uranium D values decrease with increasing U initial solution concentration, especially at 5°C. Radium D values, on the other hand, apparently increase with the increasing Ra initial solution concentration, as also reflected in Freundlich n values in excess of 1.0. It was likely that a precipitation reaction is responsible; however, the illite was previously contacted with NaCl solutions containing no radioactivity specifically to remove extraneous ions such as SO42- that might result in a direct Ra-precipitation reaction. It is unlikely that precipitation occurred in these systems below 20 ppb Ra because the minerals were thoroughly washed and based with NaCl solutions, the RaCl<sub>2</sub> was carrier-free and radiochemically pure, and only the RaCl<sub>2</sub> and reagent grade NaCl were added to the solution before contacting the mineral. In addition, equilibrium Ra concentrations were generally below those necessary to cause precipitation with SO42- or HPO42- solubilized from the minerals. Only the highest C<sub>1</sub> value exceeded the 20 ppb ( $8.85 \times 10^{-8}$  M) solubility limit for Ra in solution from RaSO<sub>4</sub> (Dyck, 1978). Because many of the secondary minerals yielded radium-sorption efficiency curves that increase with increasing radium initial solution concentration, the removal mechanisms

probably included direct precipitation of a radium compound at the highest Ra  $C_I$ . Radium D values on opal shown in Figure 8 are greater than those for U, but otherwise are quite similar, with temperature effects on sorption efficiency being nearly the same.

Silica gel Ra D values, shown in Figure 9, were much lower than comparable uranyl D values.

The radium-sorption efficiency on clinoptilolite as shown in Figure 7 was generally much higher than its comparable uranium sorption efficiency, as were those efficiencies on montmorillonite shown in Figure 4 for radium. Note the differences in radium D values between montmorillonite and nontronite, both dioctahedral smectites. The nontronite is a much more efficient sorbent for radium than montmorillonite under comparable conditions, perhaps due to the predominately tetrahedral substitutions exhibited by the nontronite.

Radium-sorption efficiency was generally greater on the crystalline secondary minerals than was the U-sorption efficiency under comparable conditions. The most efficient Ra sorbents tended to be those secondary minerals with the highest cation-exchange capacities, with the notable exception of montmorillonite.

This work was designed to ascertain the relative Ra and U sorption efficiencies of several well-characterized secondary minerals under comparable conditions. The conditions were obviously greatly simplified in comparison to natural systems. Nathwani and Phillips (1979), for example, have shown that the addition of comp. .ng alkaline earth cations to the system can greatly affect Ra sorption on the clay minerals. Hence, one should apply these results to more complex systems with great care.

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Резюме—Определены в растворе 0,01 М NaCl эффективности сорбции радия в зависимости от температуры, концентрации Ra и вторичных минералов. Сорбция радия на схарактеризованном клиноптилолите, монтмориллоните, нонтроните, опале, кремнеземном геле, иллите, каолините, и глауконите в аналогичных экспериментальных условиях позволяет определить кривые эффективности сорбции Ra, использу япостоянные фрейндлиха для каждого минерала для одинаковых диапазонов температуры и начальной концентрации Ra в растворе. Подобные данные по сорбции U на таких же вторичных минералах при одинаковых температурах позволяют сравнивать эффективности Ra и U. Клиноптилолит, иллит и нонтронит являлись наиболее эффективными сорбентами Ra, в то время как опал и кремнеземный гель были плохими сорбентами радия. В основном сорбция Ra на вторичных минералах была значительно больше, чем сорбция U при одинаковых значительно больше, чем сорбция U при

**Resümee**—Die Radiumadsorptionseffizienz wurde als Funktion der Temperatur, der Ra-Konzentration und des adsorbierenden sekundären Minerals in einer 0,01 M NaCl-Lösung bestimmt. Die Ra-Adsorption an genau bestimmtem Klinoptilolith, Montmorillonit, Nontronit, Opal, Silikagel, Illit, Kaolinit, und Glaukonit unter vergleichbaren experimentellen Bedingungen erlaubte die Bestimmung der Ra-Adsorptionseffizienzkurve für jedes Mineral, wozu die Freundlich-Konstanten für den gleichen Temperaturbereich und den ursprünglichen Ra-Konzentrationsbereich in der Lösung verwendet wurden. Änliche Adsorptionsdaten für U an den gleichen sekundären Mineralen im gleichen Temperaturbereich ermöglichten den Vergleich der Adsorptionseffizienzen für Ra und U. Klinoptilolith, Illit, und Nontronit waren die wirksamsten Ra-Adsorbenten, während Opal und Silikagel am schlechtesten Ra adsorbierten. Im allgemeinen war die Ra-Adsorption an sekundäre Minerale viel stärker als die U-Adsorption unter sonst gleichen experimentellen Bedingungen. [U.W.]

**Résumé** – Les efficacités de sorption de radium, en fonction de la température, de la concentration de Ra, et de sorbate minéral secondaire, ont été déterminées dans une solution 0,01 M NaCl. La sorption de radium sur des clinoptilites, montmorillonites, nontronites, opals, gels silices, illites, kaolinites, et glauconites caracterisés sous des conditions expérimentales comparables a permis la détermination de courbes d'efficacité de sorption de Ra pour chacun, par l'emploi des constantes de Freundlich, sur la même gamme de températures et de concentrations initiales de Ra. Des données de sorption pareilles pour U sur les mêmes minéraux secondaires aux mêmes températures ont permis la comparaison des efficacités de sorption pour Ra et U. La clinoptilolite, l'illite, et la nontronite étaient les sorbants de Ra les plus efficaces, tandis que l'opal et le gel silice étaient les sorbants de Ra les moins efficaces. Généralement, la sorption de Ra sur les minéraux secondaires était plus grande que la sorption d'U sous les mêmes conditions expérimentales. [D.J.]