

SORPTION OF URANIUM AND RADIUM BY BIOTITE, MUSCOVITE, AND PHLOGOPITE

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Abstract—The sorption of U and Ra on finely ground biotite, muscovite, and phlogopite was adequately described by the Freundlich adsorption equation, $(x/m) = KC^n$, at low U and Ra concentrations despite Ra precipitation at the higher temperature. Radium and U sorption-efficiency curves derived from the Freundlich constants generally showed decreased distribution coefficients in response to increasing temperature and increasing Ra or U concentrations. Temperatures investigated were 5°C, 25°C, and 65°C. Solution compositions used were 0.1 M NaCl and 0.01 M NaHCO₃ for U, and 0.01 M NaCl for Ra. Uranium initial solution concentrations ranged from 1.00×10^{-4} M to 4.00×10^{-7} M; the Ra initial solution concentration range was 6.80×10^{-7} M to 8.60×10^{-9} M.

In 0.01 M NaHCO₃ solutions, anionic uranyl carbonate complexes were prevalent, and because they are weakly sorbed relative to free uranyl ion and uranyl hydroxy complexes, the result was a relatively low U sorption efficiency on biotite and phlogopite and excellent sorption efficiency on muscovite. Uranyl carbonate complexes decreased in solubility with increasing temperature, so that U sorption efficiency on biotite increased with increasing temperature. Sorption of uranyl ion and uranyl hydroxy cations on biotite decreased with increasing temperature.

Key Words—Anion exchange, Biotite, Cation exchange, Muscovite, Phlogopite, Radium, Sorption, Uranium.

INTRODUCTION

Tieh *et al.* (1980) reported three modes of uranium occurrence in central Texas granite rocks: (1) uranium in accessory minerals (zircon, sphene, apatite), referred to by the above authors as resistate U; (2) uranium along crystal boundaries, particularly biotite, called intergranular U; and (3) uranium disseminated in primary quartz and feldspar as background U. Modes (1) and (2) were reported to be about equal in abundance, whereas mode (3) was much less abundant. According to the above authors, intergranular U was probably deposited as surface adsorptions during late-stage crystallization or shortly thereafter, and was readily mobilized during the initial decomposition of the granite. Uranium is concentrated in the finer weathering products, but its sorption onto secondary clay minerals (e.g., kaolinite) was not found by Tieh *et al.* (1980) to be an important mechanism for uranium concentration in the finer fraction of soils. At several meters from the original granite, the fine to very fine-sand weathering products and resistates consist of, in order of abundance, quartz, altered feldspar, biotite, leucoxene, microcline, hornblende, zircon, and plagioclase. Most, if not all, of the intergranular U has been desorbed from the biotite in less than one kilometer of sediment transport.

Merifield *et al.* (1980) investigated uranium distribution and fixation in relation to sedimentary facies within the Kern and Buena Vista Lake drainage basins, California. Here, uranium is also mainly associated

with the finer grained sediments and varies from 2 to 23 ppm for the whole sediment. The clay-size fraction contains 50 to 60 wt. % U, the sand fraction 13 to 23 wt. % U, and the silt fraction 26 to 32 wt. % U by difference. The unaltered biotite in the sand-size fraction contains 45 ppm U, whereas the U content of the altered biotite in the sand fraction is 35 ppm, suggesting that most of the U in the sand fraction, and perhaps the silt fraction, is present on the biotite flakes. Three modes of uranium occurrence were reported by Merifield *et al.* (1980): (1) uranium sorbed on minerals, e.g., biotite; (2) organically bound uranium which may also be sorbed on mineral surfaces; and (3) detrital, uranium-containing minerals such as zircon, sphene, and apatite. Together, the first two modes contain 50.3 to 82.3 wt. % of the U, with sorbed U predominating. The means of the sorbed U, organically complexed U, and detrital U were 5.17 ppm, 0.96 ppm, and 3.48 ppm, respectively.

These two papers demonstrate examples of probable late-stage sorption and transport of uranium on trioctahedral biotite. Noticeably missing are data on the U-sorption abilities of muscovite and phlogopite from these also common constituents of granitic rocks. To obtain more rigorous, comparative data on the U-sorption ability of mica minerals, a study was undertaken with fine-grained biotite, muscovite, and phlogopite at several temperatures and solution compositions. Radium sorption also was investigated to assess the possibility for U-Ra separation due to differential sorption on the micas.

Table 1. Characterization of muscovite, biotite, and phlogopite.

Constituent	Muscovite	Biotite	Phlogopite	Detection limit
Major components (wt. %)				
SiO ₂	45.50	38.10	42.20	0.5
Al ₂ O ₃	31.40	14.76	11.70	0.4
Fe ₂ O ₃	4.01	17.90	3.45	0.04
CaO	—	2.30	0.34	0.01
MgO	0.40	11.60	25.90	0.01
Na ₂ O	0.60	0.42	0.53	0.1
K ₂ O	12.10	11.20	10.10	0.01
Loss on ignition (900°C)	5.80	1.80	3.33	0.01
Total	99.81	98.08	98.22	
Trace components (ppm)				
Ba	—	760	1810	10
Mn	995	7170	1050	30
Sr	—	51	28	10
Ti	948	15,700	5650	50
U	—	6.5	—	0.5
Th	—	26.0	—	2.0
Surface area (m ² /g)	1.88	1.59	1.22	
Cs CEC (meq/100 g)	0.95 ± 0.06	15.3 ± 1.1	1.17 ± 0.15	
UO ₂ (CO ₃) ₂ ²⁻ AEC (meq/100 g)	10.02 ± 0.96	3.62 ± 0.40	4.44 ± 1.24	
<i>Structural formulae¹</i>				
<i>Muscovite</i>				
(Si _{6.48} Al _{1.52})(Al _{3.75} Fe _{0.43} Mg _{0.08})				
(K _{2.20} Na _{0.17})(OH _{4.94})				
<i>Biotite</i>				
(Si _{5.67} Al _{2.33})(Al _{0.26} Ti _{0.29} Fe _{2.00} Mg _{2.57} Mn _{0.12})				
(Ca _{0.37} K _{2.13} Na _{0.12})(OH _{3.60})				
<i>Phlogopite</i>				
(Si _{6.04} Al _{1.96})(Al _{0.01} Ti _{0.10} Mn _{0.02} Mg _{5.52})				
(Ca _{0.05} K _{1.84} Na _{0.15})(OH _{3.18})				

¹ Number of cations based on 24 O, OH, F.

METHODS OF INVESTIGATION

Biotite from Bancroft, Ontario, phlogopite also from Ontario, and muscovite from Stoneham, Maine, were purchased from Ward's Natural Science Establishment, Rochester, New York. Sheets of micas were separated by hand, cut into small pieces, and mechanically ground and screened to recover a 50 × 100 mesh-size fraction. This size fraction was treated with 0.01 M NaCl, washed, and dried at 60°C overnight. Chemical analyses and other characteristics of the 50 × 100 mesh (0.300 to 0.150 mm) micas are given in Table 1. Representative samples were dissolved in HF-H₂SO₄ in Teflon-lined digesters and analyzed by inductively coupled plasma, and atomic absorption spectroscopic techniques. Surface areas were determined by the standing multipoint B.E.T. method (Lowell, 1979) and cesium cation-exchange capacities were determined by a method proposed by Routson *et al.* (1973) for low-

capacity materials. The sodium-washing and cesium cation-exchange procedures removed very minor amounts of interlayer potassium from the biotite and none from the muscovite (Leonard and Weed, 1970; Feigenbaum *et al.*, 1981). An anion-exchange capacity was measured with the divalent uranyl carbonate complex as shown in Table 1. In general, the micas with the low cation-exchange capacities tended to show the highest anion-exchange capacity. However, exchange capacity is to a large extent a function of the ion used to measure it. The chloride capacity, for example, was found to be very low for all three micas. X-ray powder diffraction tracings showed no mineral phases other than muscovite, biotite, and phlogopite. The trace Mn and Ti of the chemical analyses are well within the ranges for structural Mn and Ti listed in Deer *et al.* (1962). Scanning electron micrographs of the mica showed no other phases present, including ferric oxyhydroxides, on mica surfaces, but did show excessive edge fraying due to the mechanical grinding.

Radiochemically pure and carrier-free U²³³ as uranyl nitrate was added to 0.01 M NaCl solutions. U²³³ is an alpha particle emitter with a half-life of 1.61 × 10⁵ yr and a specific activity of 9.48 × 10⁻³ Ci/g, enabling accurate scintillation counting into the ppb-concentration range. Ra²²⁶ also is an alpha particle emitter with a half-life of 1602 yr and a specific activity of 0.988 Ci/g. U²³⁸ was used to extend the range of U concentration, but no such isotope of Ra exists. Hence, only Ra²²⁶ was used in the Ra solutions. There was, of necessity, an upper limit of Ra²²⁶ concentration that could be used in the experiments, due to the increasing radioactivity. In addition, as much as three weeks was required before scintillation counting for the Ra²²⁶ to reach equilibrium with its Rn²²² daughter.

Four aliquots of the original radioactive solution were set aside for later counting with the equilibrium solution aliquots. Ten milliliters of each radioactive solution was added for each gram of mica. All mica-solution equilibrium experiments were executed in triplicate in sealed polypropylene tubes, and mean values were used to determine U or Ra remaining in solution and on the mica. The tubes were later rinsed with methanol to remove all solids and recounted to determine tube-wall sorption. Only three instances of tube-wall sorption greater than 2% of the total tube activity were found and used in correcting solution counts.

The tubes containing the various solutions and micas were gently rotated for a continuous 30-day equilibrium period at the temperatures of the isotherms (5°, 25°, and 65°C). Both the original radioactive solution and equilibrium solution aliquots were pipeted at temperature to equalize volumes and count rates. The experiments were carried out in a New Brunswick incubator-rotator where the variation was ±1.0°C over the temperature range.

Table 2. Mean experimental values for sorption of U on muscovite and biotite.

Mica	Initial solution U (M)	Equilibrium solution U (M)	Mica loading (mole U/g)	Initial solution U (M)	Equilibrium solution U (M)	Mica loading (mole U/g)
5°C, 0.01 M NaCl						
Biotite	1.005×10^{-4}	8.578×10^{-5}	1.472×10^{-7}	1.005×10^{-4}	9.101×10^{-5}	9.493×10^{-8}
	1.038×10^{-5}	6.285×10^{-6}	4.095×10^{-8}	1.045×10^{-5}	6.915×10^{-6}	3.535×10^{-8}
	1.403×10^{-6}	7.093×10^{-8}	1.332×10^{-8}	1.434×10^{-6}	3.059×10^{-7}	1.128×10^{-8}
	3.928×10^{-7}	5.485×10^{-9}	3.873×10^{-9}	4.388×10^{-7}	1.526×10^{-8}	4.235×10^{-9}
Muscovite	1.005×10^{-4}	3.355×10^{-5}	6.695×10^{-7}	1.005×10^{-4}	8.448×10^{-5}	1.602×10^{-7}
	1.038×10^{-5}	1.136×10^{-6}	9.244×10^{-8}	1.045×10^{-5}	3.624×10^{-6}	6.826×10^{-8}
	1.403×10^{-6}	2.909×10^{-8}	1.374×10^{-8}	1.434×10^{-6}	5.571×10^{-8}	1.378×10^{-8}
	3.928×10^{-7}	2.544×10^{-9}	3.903×10^{-9}	4.388×10^{-7}	3.975×10^{-10}	4.384×10^{-9}
25°C, 0.01 M NaCl						
Biotite	1.004×10^{-4}	5.450×10^{-5}	4.590×10^{-7}	1.004×10^{-4}	9.209×10^{-5}	8.308×10^{-8}
	1.004×10^{-5}	1.936×10^{-6}	8.504×10^{-8}	1.044×10^{-5}	7.800×10^{-6}	2.640×10^{-8}
	1.438×10^{-6}	5.456×10^{-8}	1.383×10^{-8}	1.437×10^{-6}	4.360×10^{-7}	1.001×10^{-8}
	4.379×10^{-7}	7.900×10^{-9}	4.300×10^{-9}	4.374×10^{-7}	4.818×10^{-8}	3.892×10^{-9}
Muscovite	1.004×10^{-4}	8.115×10^{-6}	9.228×10^{-7}	1.004×10^{-4}	8.244×10^{-5}	1.796×10^{-7}
	1.044×10^{-5}	4.000×10^{-7}	1.004×10^{-7}	1.004×10^{-5}	2.827×10^{-6}	7.613×10^{-8}
	1.438×10^{-6}	3.061×10^{-8}	1.407×10^{-8}	1.437×10^{-6}	2.347×10^{-8}	1.414×10^{-8}
	4.379×10^{-7}	5.603×10^{-8}	3.819×10^{-9}	4.374×10^{-7}	1.250×10^{-9}	4.362×10^{-9}
Phlogopite	1.044×10^{-5}	3.208×10^{-6}	2.177×10^{-7}	1.045×10^{-5}	1.023×10^{-5}	6.381×10^{-9}
	1.441×10^{-6}	3.736×10^{-7}	3.192×10^{-8}	1.442×10^{-6}	1.385×10^{-6}	1.589×10^{-9}
	4.375×10^{-7}	1.049×10^{-7}	1.001×10^{-8}	4.422×10^{-7}	4.341×10^{-7}	2.401×10^{-10}
65°C, 0.01 M NaCl						
Biotite	1.005×10^{-4}	1.589×10^{-5}	8.461×10^{-7}	1.004×10^{-4}	4.724×10^{-5}	5.316×10^{-8}
	1.039×10^{-5}	1.022×10^{-6}	9.368×10^{-8}	1.041×10^{-5}	7.438×10^{-6}	2.972×10^{-8}
	1.393×10^{-6}	7.518×10^{-8}	1.318×10^{-8}	1.353×10^{-6}	3.600×10^{-7}	9.930×10^{-9}
	3.458×10^{-7}	2.083×10^{-8}	3.250×10^{-9}	3.508×10^{-7}	1.744×10^{-8}	3.334×10^{-9}
Muscovite	1.005×10^{-4}	2.830×10^{-6}	9.767×10^{-7}	1.004×10^{-4}	8.272×10^{-5}	1.770×10^{-7}
	1.039×10^{-5}	5.289×10^{-7}	9.861×10^{-8}	1.041×10^{-5}	3.727×10^{-6}	6.683×10^{-8}
	1.393×10^{-6}	7.913×10^{-8}	1.314×10^{-8}	1.353×10^{-6}	4.140×10^{-8}	1.312×10^{-8}
	3.458×10^{-7}	2.107×10^{-8}	3.247×10^{-9}	3.508×10^{-7}	7.583×10^{-10}	3.500×10^{-9}
Phlogopite	1.044×10^{-5}	1.708×10^{-6}	2.633×10^{-7}	1.045×10^{-5}	1.023×10^{-5}	6.843×10^{-9}
	1.441×10^{-6}	1.231×10^{-7}	3.938×10^{-8}	1.442×10^{-6}	1.385×10^{-6}	1.722×10^{-9}
	4.375×10^{-7}	2.748×10^{-8}	1.235×10^{-8}	4.422×10^{-7}	4.255×10^{-7}	5.617×10^{-10}
65°C, 0.01 M NaHCO ₃						
Biotite	1.005×10^{-4}	1.589×10^{-5}	8.461×10^{-7}	1.004×10^{-4}	4.724×10^{-5}	5.316×10^{-8}
	1.039×10^{-5}	1.022×10^{-6}	9.368×10^{-8}	1.041×10^{-5}	7.438×10^{-6}	2.972×10^{-8}
	1.393×10^{-6}	7.518×10^{-8}	1.318×10^{-8}	1.353×10^{-6}	3.600×10^{-7}	9.930×10^{-9}
	3.458×10^{-7}	2.083×10^{-8}	3.250×10^{-9}	3.508×10^{-7}	1.744×10^{-8}	3.334×10^{-9}
Muscovite	1.005×10^{-4}	2.830×10^{-6}	9.767×10^{-7}	1.004×10^{-4}	8.272×10^{-5}	1.770×10^{-7}
	1.039×10^{-5}	5.289×10^{-7}	9.861×10^{-8}	1.041×10^{-5}	3.727×10^{-6}	6.683×10^{-8}
	1.393×10^{-6}	7.913×10^{-8}	1.314×10^{-8}	1.353×10^{-6}	4.140×10^{-8}	1.312×10^{-8}
	3.458×10^{-7}	2.107×10^{-8}	3.247×10^{-9}	3.508×10^{-7}	7.583×10^{-10}	3.500×10^{-9}
Phlogopite	1.044×10^{-5}	1.708×10^{-6}	2.633×10^{-7}	1.045×10^{-5}	1.023×10^{-5}	6.843×10^{-9}
	1.441×10^{-6}	1.231×10^{-7}	3.938×10^{-8}	1.442×10^{-6}	1.385×10^{-6}	1.722×10^{-9}
	4.375×10^{-7}	2.748×10^{-8}	1.235×10^{-8}	4.422×10^{-7}	4.255×10^{-7}	5.617×10^{-10}

Table 3. Freundlich constants for U sorption on biotite, muscovite, and phlogopite.

Mica	Temperature (°C)	Solution	$(x/m) = KC^N$			
			K(mole ^{1-N} liter ^N /g)	N	r	Sy·x (ln units)
Biotite	5	NaCl	3.6304×10^{-6}	0.3544	+0.9908	±0.25778
	5	NaHCO ₃	2.5519×10^{-6}	0.3580	+0.9994	±0.05790
	25	NaCl	8.1524×10^{-5}	0.5240	+0.9994	±0.08460
	25	NaHCO ₃	3.1295×10^{-6}	0.3966	+0.9981	±0.09932
	65	NaCl	7.6675×10^{-3}	0.8208	+0.9982	±0.17652
	65	NaHCO ₃	2.2832×10^{-6}	0.3648	+0.9997	±0.03401
Muscovite	5	NaCl	1.6286×10^{-4}	0.5397	+0.9995	±0.08290
	5	NaHCO ₃	2.6693×10^{-6}	0.3014	+0.9950	±0.19800
	25	NaCl	6.3691×10^{-3}	0.7526	+1.0000	±0.02590
	25	NaHCO ₃	4.8508×10^{-6}	0.3370	+0.9966	±0.16808
	65	NaCl	2.13234	1.1541	+0.9979	±0.19535
	65	NaHCO ₃	4.4951×10^{-6}	0.3412	+0.9997	±0.05317
Phlogopite	25	NaCl	1.9182×10^{-2}	0.8998	+1.0000	±0.01148
	25	NaHCO ₃	7.3805×10^{-4}	1.0004	+0.9713	±0.54790
	65	NaCl	4.8590×10^{-3}	0.7388	+0.9998	±0.04835
	65	NaHCO ₃	5.3421×10^{-5}	0.7760	+0.9961	±0.15380

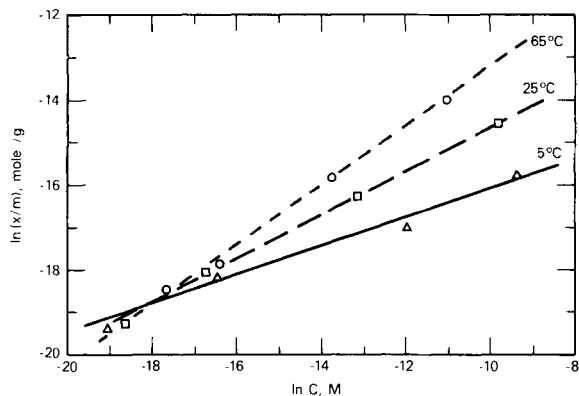


Figure 1. Equilibrium U-sorption isotherms on biotite in 0.01 M NaCl.

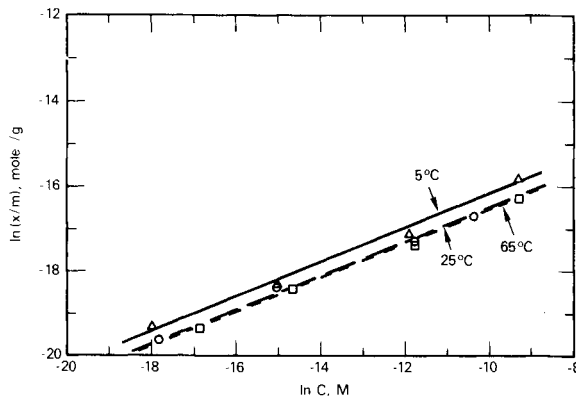


Figure 2. Equilibrium U-sorption isotherms on biotite in 0.01 M NaHCO₃.

After the 30-day contact period, solution aliquots were taken for counting along with the initial solution samples at their respective temperatures. From the counting efficiency, initial and equilibrium solution counts and specific activities of the Ra and U, the concentrations in the equilibrium solution and on the mica were calculated. A mean value was determined from triplicate experiments. Final pH values were measured at 25° with a standard calomel electrode and a pH range between 6.5 and 7.8 for the micas in 0.01 M NaCl and 8.1 to 9.2 for the micas in 0.01 M NaHCO₃. Dissolved oxygen measurements taken with a calibrated Orion oxygen probe averaging 8.3 mg O₂/liter at 25°C indicated an Eh environment of from +600 to +700 mV.

The simple sodium systems used in this study were designed to show the relative effects of bicarbonate ions, U and Ra concentration, and temperature on U and Ra sorption on micas and are obviously not rep-

resentative of many chemically complex natural systems.

RESULTS

Means of triplicate experimental values for the sorption of U on biotite, muscovite, and phlogopite are given in Table 2. The data fit a Freundlich sorption isotherm (Freundlich, 1922), or $(x/m) = KC^N$, where (x/m) is the equilibrium solids loading in moles of radionuclide/g of solid, K and N are constants, and C is the equilibrium solution radionuclide concentration in mole/liter. The units of K are $(\text{mole/g})/(\text{mole/liter})^N$ or $(\text{mole}^{1-N}/\text{g})\text{liter}^N$. The Freundlich equation is empirical in origin, but similar equations have been derived from theoretical considerations (Greenland and Hayes, 1981). An example of the Freundlich relationship between equilibrium biotite loading (x/m) and equilibrium solution concentration (C) of U is shown in Figure 1 from 0.01 M NaCl, and Figure 2 from 0.01

Table 4. Freundlich-like constants for U sorption on biotite, muscovite, and phlogopite.

Mica	Temperature °C	Solution	$(x/m) = \text{liter } C_i^N$			
			liter(mole ^{1-N} /liter ^N /g)	N	r	Sy-x (ln units)
Biotite	5	NaCl	5.7340×10^{-5}	0.6372	+0.9926	±0.23077
	5	NaHCO ₃	1.9202×10^{-5}	0.5631	+0.9917	±0.21519
	25	NaCl	1.3896×10^{-3}	0.8596	+0.9981	±0.15448
	25	NaHCO ₃	1.3674×10^{-5}	0.5482	+0.9954	±0.15402
	65	NaCl	7.0428×10^{-3}	0.9794	+1.0000	±0.02130
	65	NaHCO ₃	5.6649×10^{-6}	0.4833	+0.9739	±0.34067
Muscovite	5	NaCl	3.5948×10^{-3}	0.9274	+0.9996	±0.07608
	5	NaHCO ₃	9.2678×10^{-5}	0.6633	+0.9807	±0.38566
	25	NaCl	9.8765×10^{-3}	1.0048	+0.9998	±0.06160
	25	NaHCO ₃	1.3128×10^{-4}	0.6867	+0.9801	±0.40559
	65	NaCl	1.0218×10^{-2}	1.0059	+1.0000	±0.00546
	65	NaHCO ₃	2.1815×10^{-5}	0.5719	+0.9648	±0.36481
Phlogopite	25	NaCl	1.5041×10^{-2}	0.9714	+0.9999	±0.00536
	25	NaHCO ₃	7.4563×10^{-4}	1.0032	+0.9732	±0.53320
	60	NaCl	1.6875×10^{-2}	0.9647	+0.9999	±0.01508
	60	NaHCO ₃	5.5896×10^{-5}	0.7814	+0.9964	±0.15050

Table 5. Mean experimental values for sorption of Ra on muscovite and biotite in 0.01 M NaCl.

Muscovite	Initial solution Ra (M)	Equilibrium solution Ra (M)	Mica loading (mole Ra/g)
5°C			
Biotite	4.698×10^{-7}	5.806×10^{-10}	4.692×10^{-9}
	5.033×10^{-8}	7.602×10^{-11}	5.025×10^{-10}
	5.112×10^{-9}	8.951×10^{-12}	5.103×10^{-11}
Muscovite	4.698×10^{-7}	1.236×10^{-9}	4.686×10^{-9}
	5.033×10^{-8}	1.818×10^{-10}	5.015×10^{-10}
	5.112×10^{-9}	1.325×10^{-11}	5.099×10^{-11}
25°C			
Biotite	5.209×10^{-7}	7.076×10^{-10}	5.202×10^{-9}
	5.305×10^{-8}	7.522×10^{-11}	5.297×10^{-10}
	5.594×10^{-9}	9.404×10^{-12}	5.585×10^{-11}
Muscovite	5.209×10^{-7}	1.299×10^{-9}	5.196×10^{-9}
	5.305×10^{-8}	1.152×10^{-10}	5.293×10^{-10}
	5.594×10^{-9}	1.763×10^{-11}	5.576×10^{-11}
65°C			
Biotite	6.825×10^{-7}	2.758×10^{-10}	6.822×10^{-9}
	7.082×10^{-8}	7.365×10^{-11}	7.075×10^{-10}
	7.679×10^{-9}	1.920×10^{-11}	7.660×10^{-11}
Muscovite	6.825×10^{-7}	7.295×10^{-10}	6.817×10^{-9}
	7.082×10^{-8}	9.246×10^{-11}	7.073×10^{-10}
	7.679×10^{-9}	1.959×10^{-11}	7.659×10^{-11}

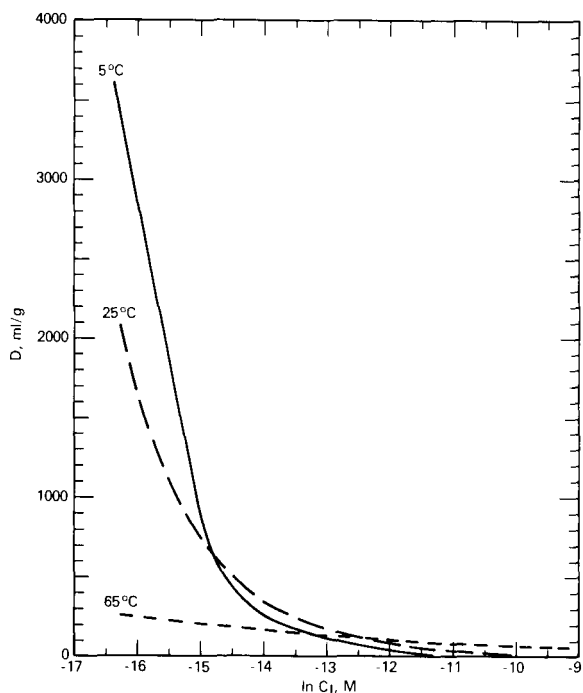


Figure 3. Equilibrium sorption of U on biotite in 0.01 M NaCl.

M NaHCO₃. Note the straight-line relationship between $\ln(x/m)$ and $\ln C$. The Freundlich constants for the isotherms are given in Table 3. The r is a correlation coefficient, or a geometric mean of the two regression coefficients, and varies between +1.00 and -1.00 as a function of regression line slope. $Sy \cdot x$ is a standard deviation from regression, a measure of dispersion applied to differences between measured and estimated values of $\ln(x/m)$ in linear regression. The Freundlich constants may be used to predict U loading within their specific temperature, solution-composition, and pH ranges via the equation $\ln(x/m) = \ln K + n \ln C$, where C is known. An additional constraint requires that such predictions remain within the U concentration range dealt with in the experiment.

A further variation of the Freundlich equations allows the substitution of the initial concentration (C_1)

of U in solution for the equilibrium concentration (C), and generation of a new set of Freundlich-like constants. These constants may be used to compare U-sorption efficiencies from the same initial U solution concentrations. The equation again is subject to use only within the temperature, pH, solution-composition, and U-concentration ranges for which it is valid. The very simple Freundlich isotherm is not useful for the modeling of complex natural geohydrologic systems because the range of variables is too large for efficient laboratory study. The Freundlich-like equation is $\ln(x/m) = \ln \text{liter} + m \ln C_1$.

The Freundlich-like constants for U are given in Table 4. The mean experimental values for sorption of Ra from 0.01 M NaCl solutions on the micas are given in Table 5. Only three experimental points were obtained, and these were obtained using initial solution

Table 6. Freundlich constants for Ra sorption on biotite and muscovite from 0.01 M NaCl.

Mica	Temperature, °C	$(x/m) = KC^N$			
		K (mole ^{1-N} liter ^N /g)	N	r	$Sy \cdot x$ (ln units)
Biotite	5	47.5825	1.0838	+0.9999	±0.0184
	25	21.8862	1.0506	+0.9999	±0.0402
	65	7964000.	1.6815	+0.9999	±0.0313
Muscovite	5	2.6416	0.9884	+0.9967	±0.1937
	25	11.5389	1.0483	+0.9977	±0.1707
	65	1375.19	1.2331	+0.9973	±0.1808

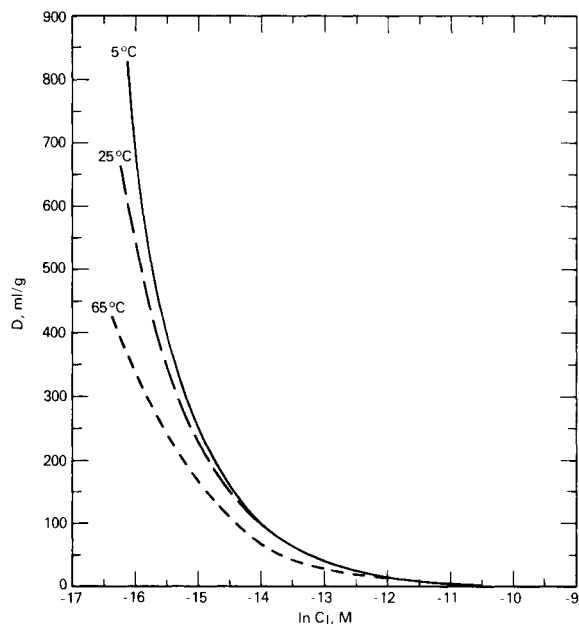


Figure 4. Equilibrium sorption of U on biotite in 0.01 M NaHCO_3 .

concentrations of Ra ranging from about 120 ppb to 1.2 ppb, considerably lower than the U concentrations. However, the lower Ra concentrations used here parallel the lower-than-U Ra concentrations found in some natural environments. The Ra-sorption data also fit the Freundlich sorption isotherm as shown in Figure 2. The comparable experimental sorption values for Ra are linear on a plot of $\ln(x/m)$ vs. $\ln C$, and the experimental values at 5° and 25°C are nearly the same. The Freundlich and Freundlich-like constants are given in Tables 6 and 7, respectively, for the Ra-sorption data of Table 5.

DISCUSSION

By utilizing the Freundlich and Freundlich-like constants given in Tables 3, 4, 6, and 7, curves were constructed of D, a measure of the efficiency of the mica for sorbing U or Ra from solution (x/m) vs. the initial U or Ra solution concentration (C_i) contacting the mica.

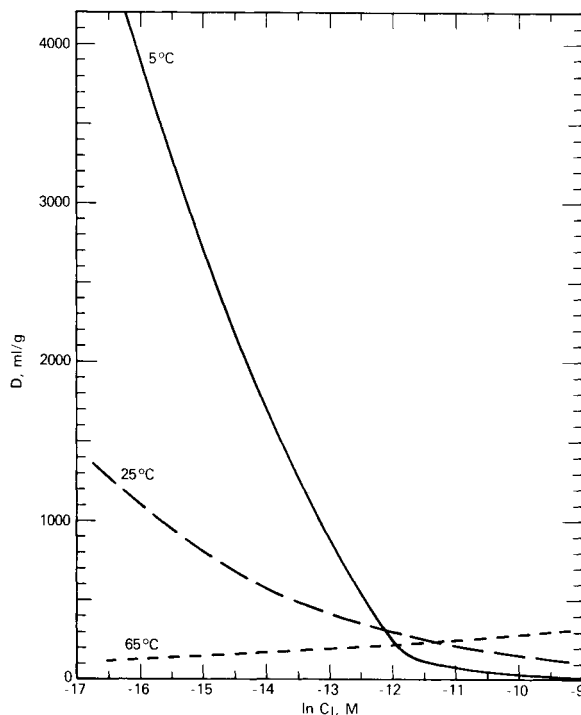


Figure 5. Equilibrium sorption of U on muscovite in 0.01 M NaCl.

For example, for a U C_i value of 1.00×10^{-4} M in 0.01 M NaCl at 5°C using the appropriate Freundlich-like constants from Table 4, (x/m) is 1.620×10^{-7} mole/g. Using this (x/m) value with the Freundlich constants for 5°C, 0.01 M NaCl for U given in Table 3, $C = 1.546 \times 10^{-4}$ N, and $D = (x/m)/C(0.001)$, or 1.05 ml/g. This computation was made for several C_i values resulting in curves for a given temperature and solution composition that show the difference in D values due to initial U or Ra solution concentrations. The D curves for U sorbed on biotite in 0.01 M NaCl at three temperatures are given in Figure 3. Each D value is based on means of 9–12 experimental equilibrium points, but is otherwise similar to a K_d .

Note that the sorption of U increased dramatically with decreasing initial U solution concentration and

Table 7. Freundlich-like constants for Ra sorption on biotite and muscovite from 0.01 M NaCl.

Mica	Temperature °C	$(x/m) = \text{liter } C_i^m$			
		liter(mole ⁻¹ liter ^M /g)	m	r	Sy·x (ln units)
Biotite	5	9.9518×10^{-3}	1.0000	+1.0000	$\pm 2.404 \times 10^{-7}$
	25	1.0362×10^{-2}	1.0022	+1.0000	± 0.0031
	65	1.0360×10^{-2}	1.0022	+1.0000	± 0.0031
Muscovite	5	9.9518×10^{-3}	1.0000	+1.0000	$\pm 2.404 \times 10^{-7}$
	25	9.9518×10^{-3}	1.0000	+1.0000	$\pm 2.404 \times 10^{-7}$
	65	1.0360×10^{-2}	1.0022	+1.0000	± 0.0031

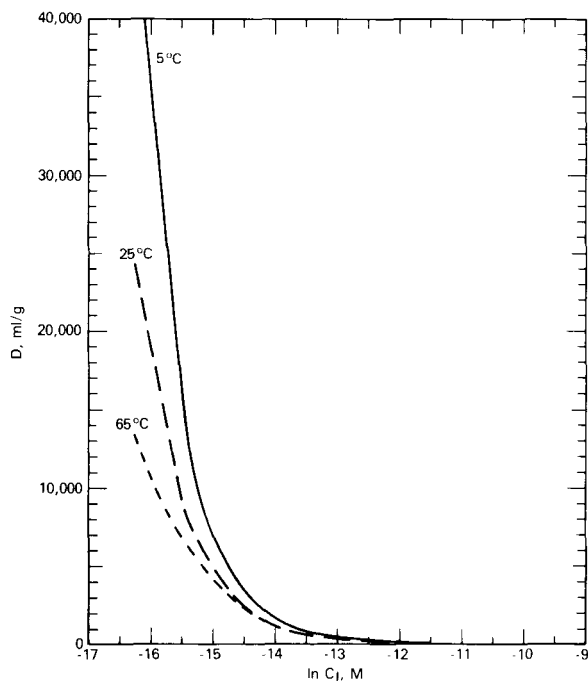


Figure 6. Equilibrium sorption of U on muscovite in 0.01 M NaHCO_3 .

temperature. D values exceed 3000 ml/g at the lower uranium C_1 values, or a gram of biotite at equilibrium has 3000 times the U concentration found in a milliliter of contacting solution. The effect of adding bicarbonate ions to the system on uranium D values is shown in Figure 4. The least effect is apparent on the 65°C curve. The 5°C and 25°C curves were considerably reduced in U sorption efficiency, presumably due to U carbonate complexing. The uranyl carbonate complexes are relatively heat-sensitive and resulted in nearly the same sorption at 65°C as for uranyl ions from 0.01 M NaCl with no carbonate complexing (Langmuir, 1978).

U sorption on muscovite from 0.01 M NaCl is shown in Figure 5. In general, these curves were similar to those for biotite in the same environment. In contrast, sorption of U on muscovite from 0.01 M NaHCO_3 was much more efficient than on biotite under comparable conditions, as shown in Figure 6. D values above 40,000 ml/g were common. As seen in Table 1, the muscovite was largely an anion-exchange material. Muscovite cation-exchange capacity was minimal. U sorption from a solution (0.01 M NaHCO_3) containing largely uranyl carbonate anionic complexes should exceed that of a cation-exchange material (biotite) from the same solution.

Ra-sorption efficiency curves on biotite muscovite in 0.01 M NaCl are shown in Figures 7 and 8, respectively. Little evidence was found for Ra complexing by bicarbonate at the 0.01 M NaHCO_3 concentration level. Hence, only 0.01 M NaCl was investigated. The

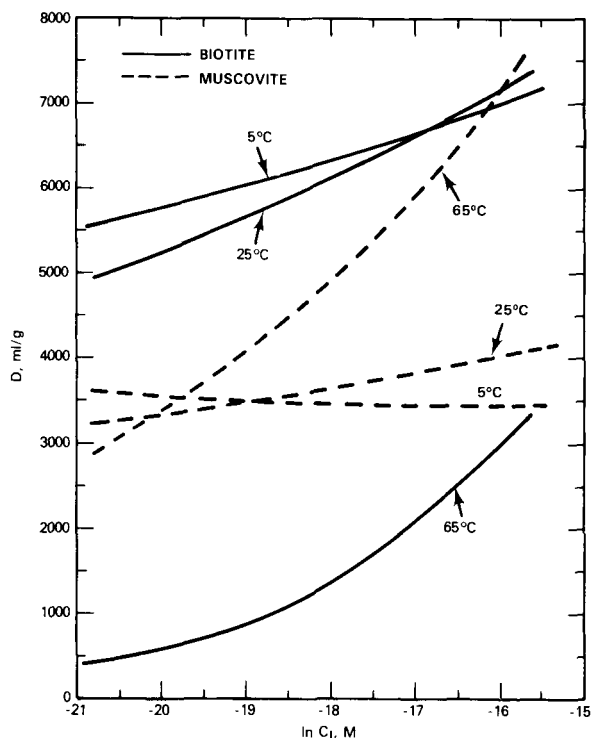


Figure 7. Equilibrium sorption of Ra on muscovite and biotite in 0.01 M NaCl.

65°C isotherm was below the 5° and 25°C isotherms for muscovite, mostly an anion exchanger. Ra sorption is mainly an ion-exchange reaction, and ion-exchange reactions from solution to solid are typically exothermic. As temperature increases, cation selectivity (for Ra in this case) should tend to decrease in aqueous solutions (Helferich, 1962). A Ra-removal reaction in addition to that of cation exchange is implied when

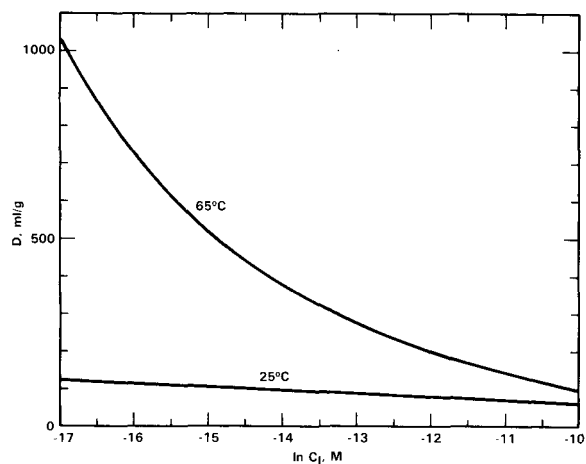


Figure 8. Equilibrium sorption of U on phlogopite in 0.01 M NaCl.

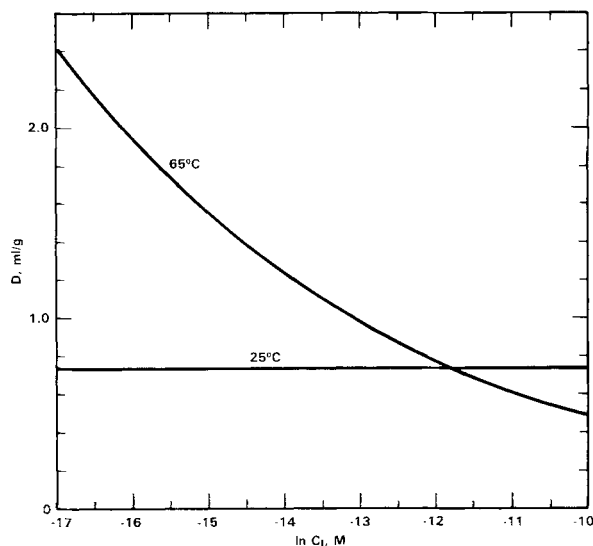


Figure 9. Equilibrium sorption of U on phlogopite in 0.01 M NaHCO₃.

the slope of the regression line (n in the Freundlich equation) exceeds a value of 1.0. The Ra is being removed from solution at a faster rate than it is being added. Radium precipitation obviously occurred at 65°C. It is not unusual for the removal reactions to include precipitation and still have the results produce a linear Freundlich or Langmuir plot (Vieth and Spisito, 1977).

U-sorption efficiency curves on phlogopite from 0.01 M NaCl and NaHCO₃ solutions are shown in Figures 8 and 9, respectively. Unlike biotite, more U was sorbed at 65°C than at 25°C, but the U-sorption results in 0.01 M NaCl were otherwise comparable to biotite and muscovite in the same system. However, U sorption by phlogopite from a 0.01 M NaHCO₃ system was much less than by either biotite or muscovite in comparable systems.

It is not difficult to understand how Ra and U could become separated during weathering and migration processes, especially in bicarbonate-containing groundwaters. Under such conditions, Ra migrates as a cation competing with other alkaline earth cations for sorption sites (Nathwani and Phillips, 1979), while U travels mainly as anionic carbonate and hydroxide complexes (Langmuir, 1978). U could be mainly sorbed on the edges and exposed basal sheets of muscovite whereas Ra could be transported as sorbed cations on secondary minerals, phlogopite, and biotite. U present along biotite crystal boundaries in a granite (Tieh *et al.*, 1980) may have accumulated by sorption from a hot, late-stage solution containing a small concentration of U. After cooling and the beginning of weathering, the U on biotite exterior surfaces would tend to be desorbed and to migrate in local groundwaters. Mus-

covite would not tend to sorb U from hot, late-stage solutions because of its preference for carbonate complexes. Uranyl carbonate complexes are heat-sensitive and largely revert to simple uranyl cations at higher temperatures (Langmuir, 1978). The high specificity of muscovite for U in the form of anionic uranyl carbonate complexes is only exceeded by uranyl cation sorption on ferric oxyhydroxides (Starik *et al.*, 1958; Hsi, 1981; Ames *et al.*, 1983). The selectivity of the mica for uranyl carbonate complexes is largely reflected in its ion-exchange capacity as measured with the same anion.

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Резюме—Сорбция U и Ra на мелкораздробленных биотите, мусковите и флогопите была соответственно описана уравнением адсорбции Фрейндлиха $(x/m) = KC^n$ при низких концентрациях U и Ra несмотря на осаждение Ra при повышенных температурах. Кривые эффективности сорбции Ra и U, полученные из постоянных Фрейндлиха, показывали в основном уменьшенные коэффициенты распределения при увеличении температуры и концентрации Ra или U. Опытные температуры были равны 5°, 25°, и 65°C. Составы растворов были 0,1 M NaCl и 0,01 M NaHCO₃ для U и 0,01 M NaCl для Ra. Начальные концентрации урановых растворов изменялись от $1,00 \times 10^{-4}$ M до $4,00 \times 10^{-7}$ M; для радовых растворов—от $6,80 \times 10^{-7}$ M до $8,60 \times 10^{-9}$ M.

В 0,01 M растворе NaHCO₃ доминировали анионные уранилово-карбонатные комплексы. В результате их слабой сорбции по отношению к свободным ионам урана и гидрокси-ураниловым комплексам была получена относительно слабая эффективность сорбции на биотите и флогопите и отличная эффективность сорбции на мусковите. Растворимость уранилово-карбонатных комплексов уменьшалась с увеличением температуры, так что эффективность сорбции на биотите увеличивалась с увеличением температуры. Сорбция ураниловых ионов и гидрокси-ураниловых катионов на биотите уменьшалась с увеличением температуры. [E.G.]

Resümee—Die Adsorption von U und Ra an feingemahlenem Biotit, Muskovit, und Phlogopit wurde durch die Adsorptionsgleichung von Freundlich, $(x/m) = KC^n$, bei niedrigen U- und Ra-Konzentrationen angemessen beschrieben, trotz der Ra-Ausfällung bei höheren Temperaturen. Die Adsorptionseffizienzkurven von Ra und U, die von den Freundlich-Konstanten abgeleitet wurden, zeigten im allgemeinen verringerte Verteilungskoeffizienten als Folge von zunehmender Temperatur und zunehmenden Ra- und U-Konzentrationen. Die untersuchten Temperaturen betragen 5°, 25°, und 65°C. Als Lösungen wurden für U 0,1 M NaCl sowie 0,01 M NaHCO₃, und für Ra 0,01 M NaCl verwendet. Die ursprüngliche Uranium-Konzentration in der Lösung reichte von $1,00 \times 10^{-4}$ M bis $4,00 \times 10^{-7}$ M; die ursprüngliche Radiumkonzentrationen in der Lösung betragen $6,80 \times 10^{-7}$ M bis $8,60 \times 10^{-9}$ M.

In 0,01 M NaHCO₃-Lösungen waren anionische Uranylkarbonatkomplexe vorherrschend. Da diese Komplexe im Vergleich zu freien Uranylionen und Uranylhydroxykomplexen schwach adsorbiert werden, war das Ergebnis eine relativ geringe U-Adsorptionseffizienz an Biotit und Phlogopit und eine ausgezeichnete Adsorptionseffizienz an Muskovit. Die Löslichkeit der Uranylkarbonatkomplexe nahm mit zunehmender Temperatur ab, so daß die U-Adsorptionseffizienz an Biotit mit zunehmender Temperatur zunahm. Die Adsorption von Uranylionen und Uranylhydroxykationen an Biotit nahm mit zunehmender Temperatur ab. [U.W.]

Résumé—La sorption d'U et de Ra sur de la biotite, de la muscovite, et de la phlogopite finement moulus a été décrite de façon adéquate par l'équation d'adsorption de Freundlich, $(x/m) = KC^n$, à de basses concentrations d'U et de Ra malgré la précipitation de Ra à la température plus élevée. Les courbes d'efficacité de sorption du radium et d'U dérivées des constantes de Freundlich montraient généralement des coefficients de distribution diminués en réponse à une hausse de température et à de plus fortes concentrations de Ra ou d'U. Les températures investiguées étaient 5°C, 25°C, et 65°C. Les compositions des solutions utilisées étaient 0,1 M NaCl et 0,01 M NaHCO₃ pour U, 0,01 M NaCl pour Ra. Les concentrations initiales de solutions d'uranium variaient de $1,00 \times 10^{-4}$ M à $4,00 \times 10^{-7}$ M; la variation de concentrations initiales de solutions de Ra était $6,80 \times 10^{-7}$ M à $8,60 \times 10^{-9}$ M.

Dans les solutions 0,01 M NaHCO₃, les complexes anioniques de carbonate uranyl étaient prévalents, et parcequ'ils sont sorbés faiblement relativement à l'ion d'uranyl libre et aux complexes hydroxy uranyl, le résultat était une efficacité de sorption d'U relativement basse sur la biotite et la phlogopite, et une efficacité de sorption excellente sur la muscovite. La solubilité des complexes de carbonate uranyl a diminué proportionnellement à une hausse de température, de telle sorte que l'efficacité de la sorption d'U a augmenté proportionnellement à une hausse de température. La sorption de l'ion uranyl et des cations hydroxy uranyl sur la biotite a diminué proportionnellement à une hausse de la température. [D.J.]