

## SURFACE CHARGE DENSITY DETERMINATION OF MICACEOUS MINERALS BY $^{235}\text{U}$ FISSION PARTICLE TRACK METHOD

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**Abstract**—The surface charge density of mica (001) cleavages was determined by counting the number of fission particle tracks in a given area of a 6-mm muscovite disc replica with optical and scanning electron microscopy after saturation of the layer charge by washing with 0.5 M  $\text{UO}_2(\text{NO}_3)_2$  solution, dilution of the excess salt by washing with 0.01 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.005 M  $\text{HNO}_3$  (pH 2.4), blotting off the excess liquid, thermal neutron activation in contact with the muscovite disc, etching the muscovite, and counting the  $^{235}\text{U}$  fission tracks/cm<sup>2</sup>. In initial studies, the uranyl cations were found to hydrolyze from the cleavage surface continuously during the washings with water, ethanol or acetone to remove excess salts, but the uranyl cations in the interlayers near broken edges and crystallographical steps were strongly retained even against washings with 0.5 M  $\text{CaCl}_2$  solution. The hydrolysis of  $\text{UO}_2^{2+}$  from the smooth portions of the flake surfaces was avoided by the use of three 1-hr final washings with the 0.01 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.005 M  $\text{HNO}_3$  solution. Each flake was pressed between filter papers three times to remove the excess solution. A negligible amount of excess salt remained on the cover glass controls. The  $\text{UO}_2^{2+}$  cations retained (mean,  $3.6 \pm 0.2 \times 10^{-7}$  mequiv./cm<sup>2</sup>) on the cleavage surfaces of various micas were nearly equivalent to the theoretical surface charge (cation exchange capacity,  $3.5 \times 10^{-7}$  mequiv./cm<sup>2</sup>), showing that hydrolysis was prevented. The uranium on the unblemished mica planar surfaces increased with increasing uranyl concentrations in the final washing solution, indicating that the excess salt remaining on the surfaces had become significant. With a given  $\text{UO}_2^{2+}$  salt concentration, the uranium on the surface increased on increasing the solution pH from 2.5 to 3.5, attributable to the formation of polymeric ions such as  $\text{U}_2\text{O}_5^{2+}$  and  $\text{U}_3\text{O}_8^{2+}$  with higher uranium retention per unit positive charge equivalent to the fixed negative charge of the mineral surface. Uranyl cations replaced much of the interlayer cations from vermiculites even after K, Rb and Cs presaturation and drying from 110°C were employed. Strong adsorption of uranyl cations (in a form not replaced by washings with a neutral salt solution), which occurred in the defects of micaceous minerals, is important in the interpretation of actinide element retention in soils and sediments wherein these minerals are abundant.

### INTRODUCTION

The objective of this paper is to present a method for determining the surface charge density of mica flakes by the  $^{235}\text{U}$  fission particle track method. Investigation of the hydrolysis behavior of uranyl cations from mica cleavage surfaces and adherence of uranyl cations to mica defects and in micaceous vermiculite minerals after collapse with fixing cations was necessary. Surface charge density of mica flakes can be computed from the unit cell formula and dimensions (van Olphen, 1963). The unit cell formula has been determined by total chemical analysis and the unit cell dimensions, determined by the X-ray powder diffraction technique (Jackson, 1974), although considerable error arises from the presence of impurities. Surface charge has been determined by direct measurement of cation exchange capacity and surface area of large (3-cm) flakes (Mokma *et al.*, 1970); however, the excess quantities of exchange sites over the expected from the geometric (001) cleavage surface area of muscovite flakes was attributed to

flaws that permitted adsorption of additional cations. The adsorption sites of the uranyl ion on unflawed and flawed parts of mica surfaces were examined directly by the  $^{235}\text{U}$  fission track method.

Fluorescence studies of aqueous solution of uranyl nitrate has shown the presence of four different species, namely  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{NO}_3^+$ ,  $\text{U}_2\text{O}_5^{2+}$  and  $\text{UO}_2(\text{NO}_3)_2$  as functions of concentration and pH (Sutton, 1949; Cordfunke, 1969). Generally, the  $\text{UO}_2^{2+}$  is the dominant ion at concentrations of 0.5 M  $\text{UO}_2(\text{NO}_3)_2$  and lower and pH values below 2.5 (equivalent to 0.005 M  $\text{HNO}_3$ ) at room temperature (Rabinowitch and Belford, 1964). The surface charge density of micaceous minerals and the behavior of uranium ions in solution-mineral systems are of particular interest in soil, geological and environmental sciences (Lee *et al.*, 1974).

### MATERIALS AND METHODS

About 100  $\mu\text{m}$  thick flakes were selected from two muscovites, one from Mitchell Co., NY and the other, No. 2, of an unknown source, biotite (Bancroft, Ontario), lepidomelane (Faraday Twp., Ontario), lepidolite (Western Australia), and phlogopite (Herimer

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Co., NY). Naturally weathered micaceous vermiculite macroflakes were selected from Libby, MT, Kenya, and Transvaal, South Africa.

Circular discs 6.5 mm in diameter were made from the selected mica flakes with a paper punch. The fresh cleavage surfaces were made by cleaving surfaces with Scotch tape. The micaceous vermiculites were saturated with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  and dried overnight in an oven at  $110^\circ\text{C}$ . The mica discs were then saturated with  $\text{Ca}^{2+}$ . The mica disc and micaceous vermiculites were transferred in a 0.5 M uranyl nitrate solution at pH 2. The solution was changed 3 times after 1 hr contact with each fresh solution.

The muscovite discs (No. 2) saturated with  $\text{UO}_2^{2+}$  were washed with 100% ethanol, 100% acetone, distilled water, and 0.5 M  $\text{CaCl}_2$  solution from 1 to 8 times with 4 min equilibration for each time. The washed discs were dried at room temperature on filter paper. Some of the  $\text{UO}_2^{2+}$  saturated muscovite were transferred in 0.01 M  $\text{HNO}_3$  solutions (pH 2) containing 0.1, 0.01, 0.001 and 0.0001 M  $\text{UO}_2(\text{NO}_3)_2$ ; in 0.005 M  $\text{HNO}_3$  containing 0.01 M (pH 2.4) and 0.02 M (pH 2.3)  $\text{UO}_2(\text{NO}_3)_2$ ; and in 0.02 M  $\text{UO}_2(\text{NO}_3)_2$  at pH 3.0 and 0.02 M  $\text{UO}_2(\text{NO}_3)_2$  solution at pH 3.5, the pH values having been adjusted with 0.005 M  $\text{NaOH}$ . Other micas and micaceous vermiculites were transferred in 0.005 M  $\text{HNO}_3$  containing 0.01 and 0.02 M  $\text{UO}_2(\text{NO}_3)_2$ . The solutions were changed 3 times after 1 hr of contact with each fresh solution. Each disc was removed and gently pressed between filter paper to remove excess solution on the mica surface.

One side of the prepared samples were cleaved off with Scotch tape and the other side (the fission tracks of which were to be replicated; Seitz and Taylor, 1974; Jackson *et al.*, 1977) was covered with an untreated muscovite disc flake 6-mm dia. and 0.1 mm thick (No. 2) and then covered with Scotch tape. The replication provided for a standard muscovite etching time for the various micaceous samples, which varied greatly in etching rate. Several cover glass control background count discs were prepared in the same way. The samples were activated in a nuclear reactor ( $3 \times 10^{12}$  neutrons/cm<sup>2</sup>/sec) for 1 min for micas and 30 sec for micaceous vermiculites. The Scotch tape was then cut with scissors along the edge of the disc and removed. The activated muscovite replica discs were etched with 16% HF solution for 18 hr. The induced track density (number of tracks/cm<sup>2</sup>) of  $^{235}\text{U}$  on the muscovite surface was computed from micrographs from scanning electron and optical microscopes. The layer charge density,  $L$ , as mequiv./cm<sup>2</sup> on the cleavage face, was calculated by the equation,

$$L = 2 \times 10^3 \rho/\eta\sigma IA, \quad (1)$$

in which  $\rho$  is the  $^{235}\text{U}$  track density (cm<sup>-2</sup> after subtraction of background track density of muscovite),  $\eta$  is the thermal neutron dose (neutrons/cm<sup>2</sup>/sec  $\times$  activation time in sec),  $\sigma$  is the cross-section of  $^{235}\text{U}$  for thermal neutrons ( $580 \times 10^{-24}$  cm<sup>2</sup>),  $I$  is the iso-

topic ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$  ( $7.26 \times 10^{-3}$ ),  $A$  is the Avogadro number ( $6.02 \times 10^{23}$  mole<sup>-1</sup>), 2 is the  $\text{UO}_2^{2+}$  valence, and  $10^3$  is the conversion factor from equivalents to mequiv., giving

$$L = 789 \times \rho/\eta. \quad (2)$$

## RESULTS AND DISCUSSION

### Results with micas

The uranyl cations ( $\text{UO}_2^{2+}$ ) on the muscovite cleavage surfaces were hydrolyzed to values much below theoretical by washing with water, acetone or ethanol (Figure 1). The amount of uranyl cation retained on the surface after the first washings (except for that with ethanol) was already smaller than the theoretical surface charge of the muscovite,  $3.5 \times 10^{-7}$  mequiv./cm<sup>2</sup>. The uranyl cations on the surface were continuously depleted by successive washings. After five washings, the uranyl cation retained on the surface were highest with ethanol washings and lowest with water washings. After eight washings with 0.5 M  $\text{CaCl}_2$  and the other solutions, small amounts ( $0.5$  to  $1.2 \times 10^{-7}$  mequiv./cm<sup>2</sup>) of uranium were retained on the muscovite surface, presumably within structural defects.

The hydrolysis of the uranyl cation ( $\text{UO}_2^{2+}$ ) may lead to the formation of neutral complex molecules such as  $\text{U}_3\text{O}_8(\text{OH})_2$  at pH 6-7 (Rabinowitch and Belford, 1964). The product of hydrolysis,  $\text{H}^+$ , may occupy the cation exchange sites. Because  $\text{UO}_2(\text{NO}_3)_2$  is very soluble in the water, acetone and ethanol, the excessive removal of uranyl cations by acetone and ethanol may be attributed partially to some hydrolysis of exchangeable  $\text{UO}_2^{2+}$  in the thin layer of water on the muscovite surface. Analogous results were obtained when the cation exchange capacity (CEC) of muscovite was determined by Na saturation (Mokma *et al.*, 1970).

When the muscovite was saturated with uranyl cations in 0.5 M  $\text{UO}_2(\text{NO}_3)_2$  solution, then washed with varying, low concentrations of  $\text{UO}_2(\text{NO}_3)_2$  solution, and the excess solution on the surface removed by filter paper, the uranyl cations remaining on the muscovite planar surface decreased with decreasing

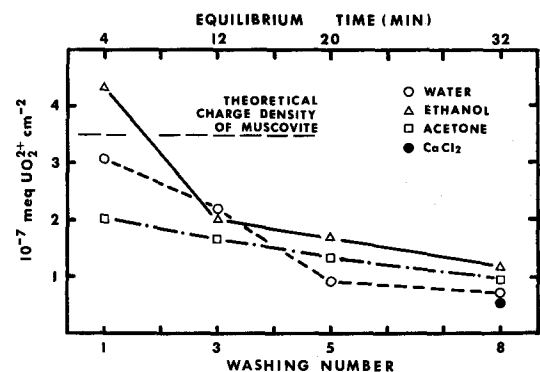


Figure 1. Uranyl cations retained on the surface of muscovite No. 2 after washings with various solvents.

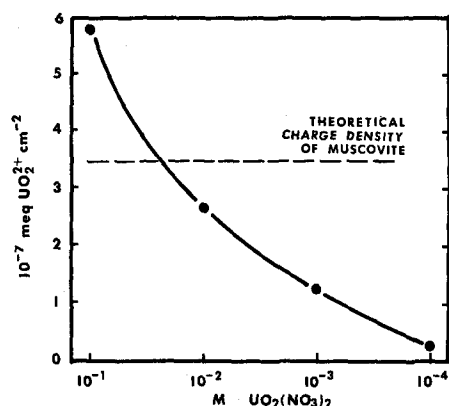


Figure 2. Uranyl cations retained on the surface of muscovite after washing with different uranyl concentrations in 0.01 M  $\text{HNO}_3$ .

concentration of uranyl cation in the washing solutions (Figure 2). Controls (cover glasses) similarly dried with filter paper showed negligibly low fission track counts from the dilute  $\text{UO}_2^{2+}$  solutions used for washing out the excess salts. The exchange sites of the muscovite planar surface were nearly saturated (the theoretical CEC of  $3.5 \times 10^{-7}$  mequiv./ $\text{cm}^2$  as calculated from the structural formula (Mokma *et al.*, 1970) with uranyl cations at concentrations near 0.01 to 0.02 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.01 M  $\text{HNO}_3$  (pH 2). When the micas were washed with Solution B, 0.01 M

$\text{UO}_2(\text{NO}_3)_2$  in 0.005 M  $\text{HNO}_3$  of pH 2.4, the  $\text{UO}_2^{2+}$  retained on the cleavage surface (mean  $3.58 \pm 0.23 \times 10^{-7}$  mequiv./ $\text{cm}^2$ ;  $\pm 1\sigma$ ) was nearly equivalent to the theoretical surface charge of several micas (Table 1).

The difference of uranium retention between 0.01 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.01 M  $\text{HNO}_3$  (pH 2), 0.005 M  $\text{HNO}_3$  (pH 2.4), and less acid solutions suggests that the hydrogen ions compete with uranyl cations on exchange sites of minerals (Table 2). At 0.02 M  $\text{UO}_2(\text{NO}_3)_2$  concentrations, the uranium retained on the muscovite surface increased with increasing pH (Table 2), even in the presence of competing  $\text{H}^+$  cations in the solution. The pH dependency of uranium retention above pH 2.4 may be attributed to adsorption of polymeric uranyl ions formed by hydrolysis (Sutton, 1949);  $\text{UO}_2^{2+}$  is the dominant ion at pH < 2.5,  $\text{U}_2\text{O}_7^{2+}$  at pH 2.5–3.0; and  $\text{U}_3\text{O}_8^{2+}$  at pH 3–6. The polymeric ions have the same charge as the uranyl ion but the number of uranium atoms per cation increases from 1 to 3. Uranium adsorption on montmorillonite increased with pH, reaching a maximum at pH 6, and then decreased above pH 6 (Tsvetan and Radka, 1973).

When muscovite was presaturated with Ca, Ba and Cs as saturating cations, the CEC values were from 8 to  $10 \times 10^{-7}$  mequiv./ $\text{cm}^2$  (Mokma *et al.*, 1970). The greater experimental CEC has been attributed

Table 1. Uranyl cations retained on the surface of micas and vermiculites after washing with two dilute uranyl solutions

Samples	Source	$\text{UO}_2^{2+}$ retained on surface after washing with	
		Solution A* ( $10^{-7}$ mequiv./ $\text{cm}^2$ )	Solution B† ( $10^{-7}$ mequiv./ $\text{cm}^2$ )
<b>Micas:</b>			
Muscovite	Mitchell, NY	5.01	3.66
Muscovite	Unknown (No. 2)	4.70	3.74
Lepidolite	Western Australia	4.87	3.27
Biotite	Bancroft, Ontario	5.34	3.87
Phlogopite	Herimer, NY	5.33	3.61
Lepidomelane	Faraday, Ontario	4.97	3.34
		Mean $\pm$ S.D. (1 $\sigma$ ) $3.58 \pm 0.23$	
<b>Vermiculites:</b>			
K-vermiculite	Transvaal, South Africa		12.48
K-vermiculite	Libby, MT		14.59

\* Solution A; 0.02 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.005 M  $\text{HNO}_3$ .

† Solution B; 0.01 M  $\text{UO}_2(\text{NO}_3)_2$  in 0.005 M  $\text{HNO}_3$ .

Table 2. Uranium retained on the surface of muscovite after washing with various uranyl solutions

Washing solutions	pH	Uranium retained on surface ( $10^{-7}$ mequiv. $\text{UO}_2^{2+}$ / $\text{cm}^2$ )
0.01 M $\text{UO}_2(\text{NO}_3)_2$ in 0.01 M $\text{HNO}_3$	2.0	2.8
0.01 M $\text{UO}_2(\text{NO}_3)_2$ in 0.005 M $\text{HNO}_3$	2.4	3.7
0.02 M $\text{UO}_2(\text{NO}_3)_2$ in 0.005 M $\text{HNO}_3$	2.3	4.7
0.02 M $\text{UO}_2(\text{NO}_3)_2$ in 0.001 M $\text{HNO}_3$	3.0*	5.8
0.02 M $\text{UO}_2(\text{NO}_3)_2$	3.5†	6.9

\* Acid formed solely by hydrolysis.

† pH adjusted with 0.005 N NaOH.

to penetration of cations into the interlayers via edges, steps and fission tracks. In the present study, however, a perfect surface was always selected to measure the external planar site charge density (Figure 3d). Areas which had defects such as (*hk0*) steps, broken edges and natural fission tracks (Figure 3a, b and c), were avoided for counting the induced fission tracks. The uranyl cations were retained in the interlayer wedge sites near broken edges (Figure 3c) even after intensive washings, suggesting that the cations in the interlayer exchange sites were more tightly held than those on the planar exchange surfaces. The formation of wedge sites of micaceous minerals has been illustrated (Jackson, 1963) and directly observed by high resolution electron microscopy (Lee *et al.*, 1975). The observation of cation exchange sites by the fission track method provides direct evidence that the higher experimental CEC (Mokma *et al.*, 1970) determined by the radiocation exchange method can be attributed to crystals defects of micas.

#### Results with vermiculites

The uranium retention by naturally weathered micaceous vermiculites which were presaturated with various fixing cations and heated at 110°C, was much greater than that of the micas (for example, with K saturation, Table 1). The Kenya vermiculite flakes held such a high density of uranyl cations that it was impossible to quantify the track density on the muscovite replica even after only 30 sec of activation. With Na<sup>+</sup> saturation, the UO<sub>2</sub><sup>2+</sup> uptake was too high for track density counting with all three vermiculites. The uranyl cations in the solution moved into interlayers, displacing the presaturating interlayer cations, Na, K, Rb or Cs (Figure 4). The uranium concentration gradually decreased away from the broken edges (Figure 4e and f). The track densities suggest that the UO<sub>2</sub><sup>2+</sup> cation displaced Na<sup>+</sup> more easily than the other presaturating cations; differentiation among the other presaturating cations was not possible (Figure 4b, c and d). The specific behavior of uranium in soils and sediments has been uncertain because of the complexity of uranium chemistry in solution. One report suggested that uranium was more mobile than radium (Yastrebov, 1973). Present experimental results suggest that uranium cations may be competitive with common cations on exchange sites of micaceous minerals in soils and sediments when the solution pH is below 6. At pH above 7, uranium becomes an anionic species such as U<sub>3</sub>O<sub>8</sub>(OH)<sub>3</sub><sup>-</sup> and U<sub>3</sub>O<sub>8</sub>(OH)<sub>4</sub><sup>2-</sup> (Sutton, 1949). The anionic species may not be retained on the negatively charged mineral surface.

#### CONCLUSIONS

1. The surface charge densities of mica can be measured by the fission particle track replica method by saturation of the surface exchange sites with UO<sub>2</sub><sup>2+</sup>

by three washings with 0.5 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution (pH 2.0). Hydrolysis of the uranyl cation was best prevented by removal of the excess salt by three washings with 0.01 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in 0.005 M HNO<sub>3</sub> solution (pH 2.4), and drying in contact with a filter paper.

2. The uranyl cations on the mica surface were continuously hydrolyzed by washings with distilled water, 100% ethanol, or 100% acetone; the near neutral washings may cause formation of mobile uncharged polymeric molecules such as U<sub>3</sub>O<sub>8</sub>(OH)<sub>2</sub>.

3. The retention of uranyl cation on mica surfaces increases with increasing pH from 2.3 to 3.5, an increase attributable to the formation of polymeric cations with higher U content per unit charge, such as U<sub>2</sub>O<sub>5</sub><sup>2+</sup> at pH 2.5–3.0 and U<sub>3</sub>O<sub>8</sub><sup>+</sup> at pH 3 or higher. Uranium retention on the negatively charged mica surfaces decreases drastically above pH 3.5 by formation of neutral or anionic polymeric species.

4. Increasing amounts of uranium are retained on interlayer wedge sites near (*hk0*), crystallographical steps and broken edge defects of micas.

5. Naturally weathered micaceous vermiculites, pretreated with various cations and heated at 110°C, retained more UO<sub>2</sub><sup>2+</sup> than micas; uranyl cations in the solution displaced even fixing interlayer cations such as K, Rb and Cs.

6. Uranium is fixed in defects of micaceous minerals (common in soils and sediments) in forms not replaced by neutral salts, thus simulating the U analogue, <sup>239</sup>Pu (*t*<sub>1/2</sub> = 24,000 yr), retention in 1.9 b.y. old sandstone through complete decay to neodymium isotopes (Cowan, 1976).

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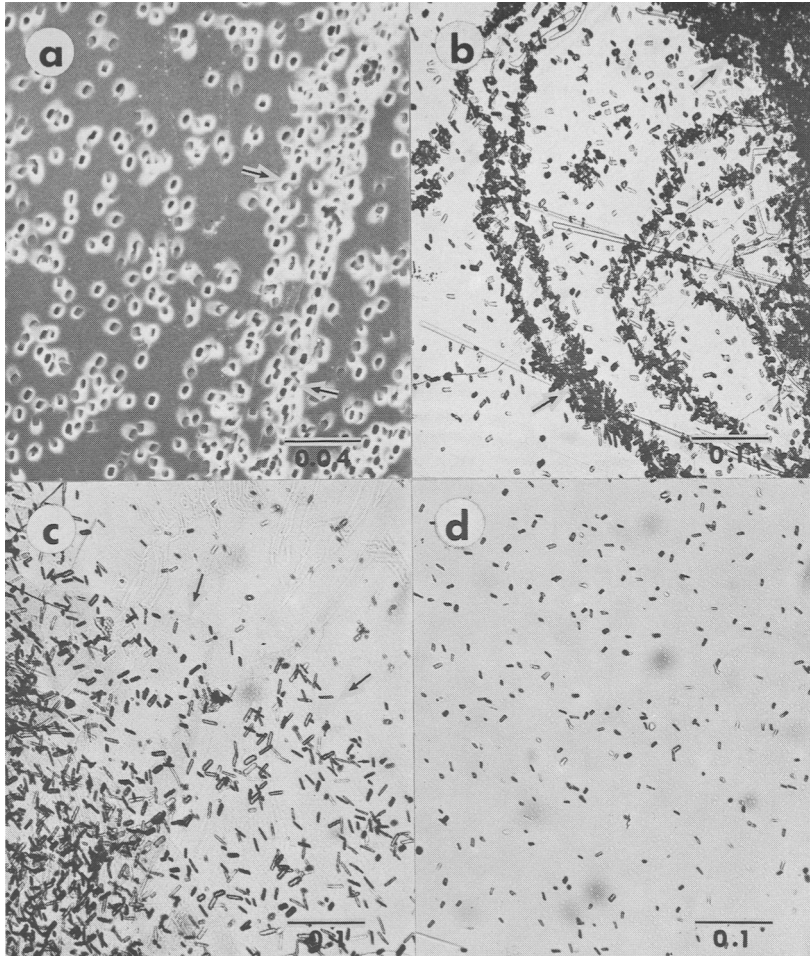


Figure 3. Fission particle tracks on mica cleavage surface: (a) higher track density on crystallographical steps (arrows) on a biotite examined by SEM; (b) higher track density on broken edges of a muscovite flake, with a light microscope; (c) uranyl cations moved into the interlayer of a muscovite showing higher track density (arrows indicate boundary between open and closed interlayer surfaces); and (d) muscovite surface without defects, used for surface charge density determination. Units  $\approx$  mm.

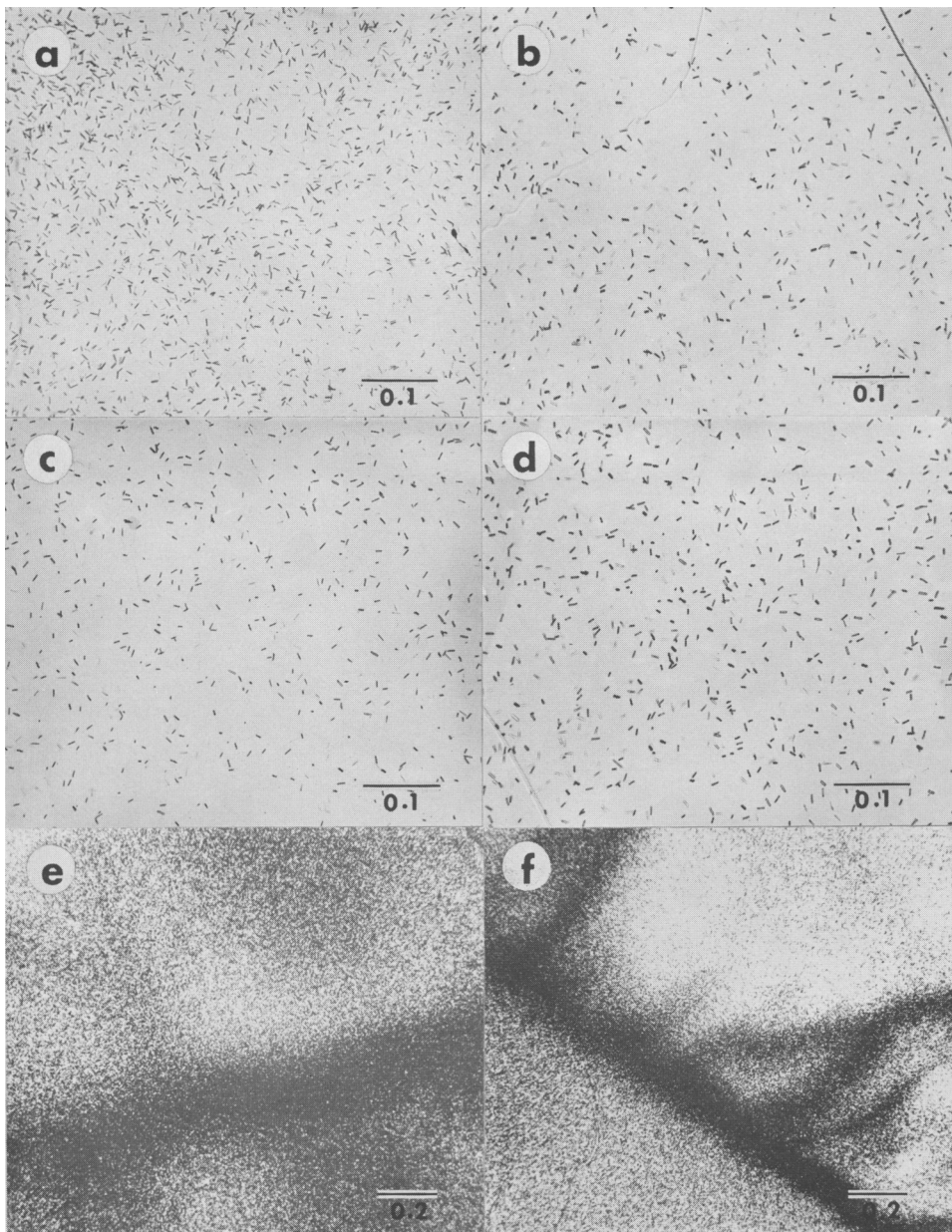


Figure 4. Fission particle tracks of  $\text{UO}_2^{2+}$  saturated Libby, MT, vermiculite replicated on a muscovite substrate. The vermiculite was presaturated (a) with Na; (b) with K; (c) with Rb; (d) with Cs; (e) with Na, darker area indicating broken edge step; and (f) with Cs, still showing penetration at broken edge step. Units = mm.

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