

SELECTIVITY EFFECT OF CESIUM ON CLAY SIZE WEATHERED MICA; TRANSMISSION ELECTRON MICROSCOPY STUDIES*

M. GAL† and C. I. RICH

Agronomy Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

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Abstract—The use of electron diffraction contrast to detect local concentrations of interlayer cations in mica-vermiculites was examined. Cs and Mg, because of their contrasting atomic scattering amplitudes for electrons, were chosen as exchange ions for Ca. Cs was absorbed to the near exclusion of Mg by the clays from the three soils and by weathered clay-size muscovite and phlogopite. The presence of Cs in addition to the other interlayer cations, K and Ca, caused bending and perhaps splitting of the mica-vermiculite layers. Extinction bend contours were common in Cs-treated specimens but not those Ca-treated. After freeze-drying of specimens of Cs-Ca Nason clay, differential destruction by the electron beam of the central core in clay-size vermiculite containing hydrated Ca ions may indicate the edge location of Cs.

INTRODUCTION

THE DETERMINATION of the location of specific ions in a heterogeneous population of exchange ions on clay minerals would assist in assessing models that have been proposed regarding ion selectivity and unmixing of cations on these minerals. The electron microprobe has been used to locate exchangeable Rb, Sr, Ba, K, and Mg in 100–300 μ weathered particles of muscovite and biotite (Le Roux *et al.*, 1971). Because the resolution of electron microprobe instruments is limited at present to about 1 μ , this instrument cannot detect segregated zones of cations in clay-size layer silicates.

Because most of the cation exchange in soils and sediments occurs in clay-size particles, direct evidence for cation location in particles of such size would be applicable to the solution of exchange problems. The exchange of K, NH_4 , Rb, and Cs relative to that of the alkaline earth cations is of importance to the understanding of exchange reactions involving the radioactive isotopes of Cs and Sr in fallout as well as K and NH_4 fixation and release in soils and sediments.

The possibility that diffraction contrast, which is observed in transmission electron microscopy, could detect concentrations of specific exchange

ions was the principal object of this study. According to kinematic theory, only changes in interplanar spacing, crystal orientation, and atomic scattering amplitude can produce contrast (Heidenreich, 1964, p. 264). If cations of one species are localized in the interlayer of a vermiculite particle, then the zone containing these cations would have particular atomic scattering amplitude and interplanar spacing and the diffraction contrast effect would be different from that of zones containing other interlayer cations. The third factor, crystal orientation, was not initially considered an important variable but our results indicate this is probably the most important variable.

Exchange ions with marked differences in scattering amplitude would be expected to cause the greatest difference in diffraction contrast, assuming interplanar spacing and crystal orientation remained constant. Consequently, in the present study we chose Cs and Mg. In the region of the strong (060) reflection and where $\sin \theta/\lambda$ (θ is the angle of diffraction and λ is the wavelength) is approximately 0.35 \AA^{-1} , the atomic scattering amplitude of K for electrons is 1.90 \AA , whereas that of Mg is 1.01 \AA and Cs is 3.168 \AA (Heidenreich, 1964, p. 395–8). In addition, the scattering of Mg compared to Cs would be one-half that indicated because of the valence factor. The purpose of using both Cs and Mg was that in case segregation of these ions occurred (e.g. Cs at the edge and Mg away from the crystal edge), marked contrast might be observed.

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†Present address: Department of Soil Science, Faculty of Agriculture, The Hebrew University of Jerusalem, Rehovot, Israel.

MATERIALS AND METHODS

Coarse clay-size ($2\text{--}0.2\ \mu$) material was separated from three soils known to contain significant concentrations of vermiculite, from a wet-ground muscovite (Amelia, Va.), and from a low-iron phlogopite (Ontario, Canada). Further information on the soil clays is reported by Murdock and Rich (1972), and on the muscovite by Reichenbach and Rich (1968). Clays from the Nason and Tatum soils contain dioctahedral mica and vermiculite, whereas the Ramona contains trioctahedral mica and vermiculite.

The specimen muscovite and phlogopite were treated so as to exchange a portion of the K as follows: 300 mg of the clay was added to 3 l. of 0.2 N CaCl_2 contained in a Nalgene bottle. The suspensions were heated in an autoclave at 120–122°C for two days. After decanting the supernatant solution, a fresh solution was added and the autoclave treatment was repeated. Three treatments were sufficient to remove most of the K from phlogopite whereas 15 treatments of the muscovite were required to remove less than half of the K.

The soil clays were Ca saturated at room temperature by 5 washes with 0.2 N CaCl_2 . Excess salts were removed by washing with water and centrifuging. Portions of the Ca-treated clays were prepared for electron microscopy studies. The remaining portions of the clays (except muscovite) were treated with a mixed Cs–Mg chloride solution (0.002 N with respect to each cation). Ten ml of the solution was added to approximately 100 mg of wet samples and after shaking for 10 minutes, the suspension was centrifuged and the supernatant solution was decanted. This treatment was repeated 11 times. The muscovite was subjected to three 48 hr autoclave treatments in the same Cs–Mg chloride solution described above.

The decanted and original solutions were analyzed for Cs, K, Mg, and Ca by atomic absorption analysis using a Perkin–Elmer, Model 303 instrument. The amount of exchange of each element was determined from the difference in concentration in the original solution and then after exchange. An elemental analysis was made also to determine K, Cs, and Ca in the clay samples.

The analytical results for muscovite and phlogopite are based on the weight of the 2:1 layer (free of interlayer cations and water). The results for the soil clays are based on air dry weights not corrected for cations.

Approximately 100 ppm suspensions of both the Ca and the Cs–Mg treated clays were shaken for 48 hr to disperse the samples. However, electron microscopic study revealed excessive aggregation of particles so the suspensions were stirred for

10 min at 16,000 rpm in a Sorvall Omni-Mixer. This treatment provided suitable dispersion. A drop of each suspension was placed on a 200 mesh Formvar and carbon coated grid and was permitted to dry under a watch glass. In some cases, the grid was cooled on a brass block previously cooled on dry ice and the drop was subsequently freeze-dried. The grids were examined under bright field conditions using a RCA EMU-3 electron microscope at 50 kV.

RESULTS AND DISCUSSION

Cs and Mg exchange

Ten successive washes of the Ca-saturated soil clays with the Cs–Mg solution resulted in clay containing a large proportion of Cs (Table 1). In agreement with the work of Coleman and Le Roux (1965) very little Mg was taken up in the presence of Cs. In subsequent work, treatment of the clays with a solution containing 0.002 N Cs and 0.02 N Mg actually decreased Mg uptake and after 12 washes the proportion of the CEC occupied by Cs ranged from 68% in the C horizon of the Nason soil to 160% in the A12 horizon of the Ramona soil. Cs uptake in excess of the indicated CEC can be explained on the basis that Cs can enter wedge sites that are inaccessible to the large hydrated Mg ion, which was used as the index ion for CEC.

The Cs–Mg treated phlogopite and muscovite did not take up Cs as completely as did the soil clays (Table 2). This may be due to the higher charge and more easily collapsible edges of the altered specimen micas. No detectable Mg was taken up by the specimen micas.

Although very little or no Mg was taken up by the clays, in all samples there are significant proportions of two or more cations that have contrasting atomic scattering amplitudes for electrons. Thus, it was expected that diffraction contrast caused by local concentrations of the same kind of cations in the altered micas might be observed.

Transmission electron microscopy

This technique has many pitfalls as well as potentialities. In Fig. 1, are seen several edges at steps present in a mica–vermiculite particle and the out-of-focus effect at each of these edges. The multiple steps would impede the observation of diffraction contrast due to cation concentration. The dark edges of each layer are caused by this photograph being out-of-focus and could be mistaken for concentrations of Cs.

Figure 2 shows some particles observed in the Cs–Mg treated clay from the Nason C horizon. This grid had been prepared by freezing the drop

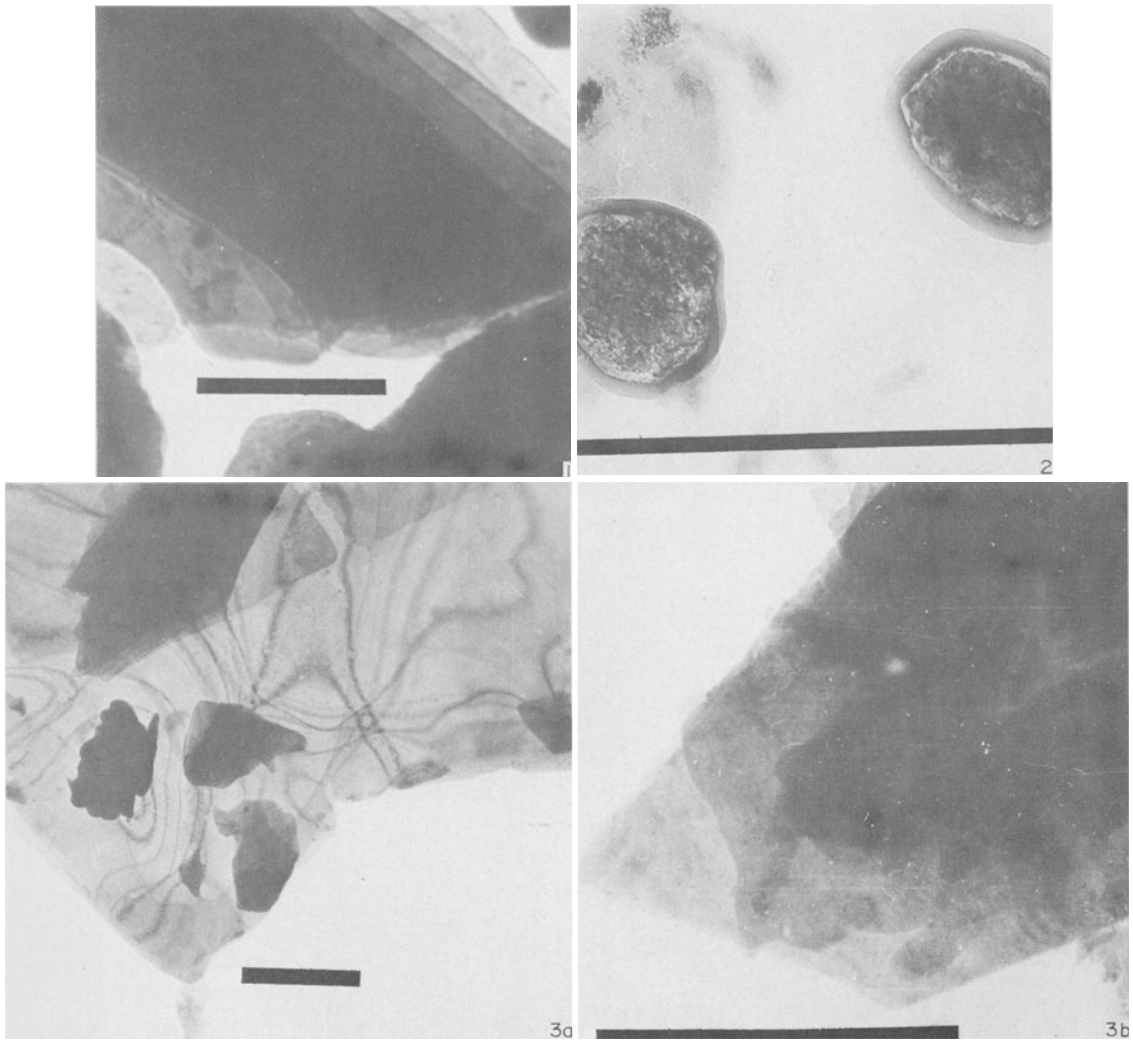


Fig. 1. Transmission electron micrograph of vermiculite-mica particle from Nason A horizon. Ca-saturated, then Cs-Mg treated. Dark edges due to out-of-focus effect at steps are noted. Bar indicates 1 μ .

Fig. 2. Transmission electron micrograph of freeze-dried Ca-saturated, then Cs-Mg treated mica-vermiculite particles from Nason C horizon. Rim may be represent extent of Cs exchange. Bar indicates 1 μ .

Fig. 3. Electron micrograph of weathered muscovite particles. (A) Interlayer cations—Cs, Ca, and K. (B) Interlayer cations—Ca and K. Complex extinction bend contours in A are seen. Bar indicates 1 μ .

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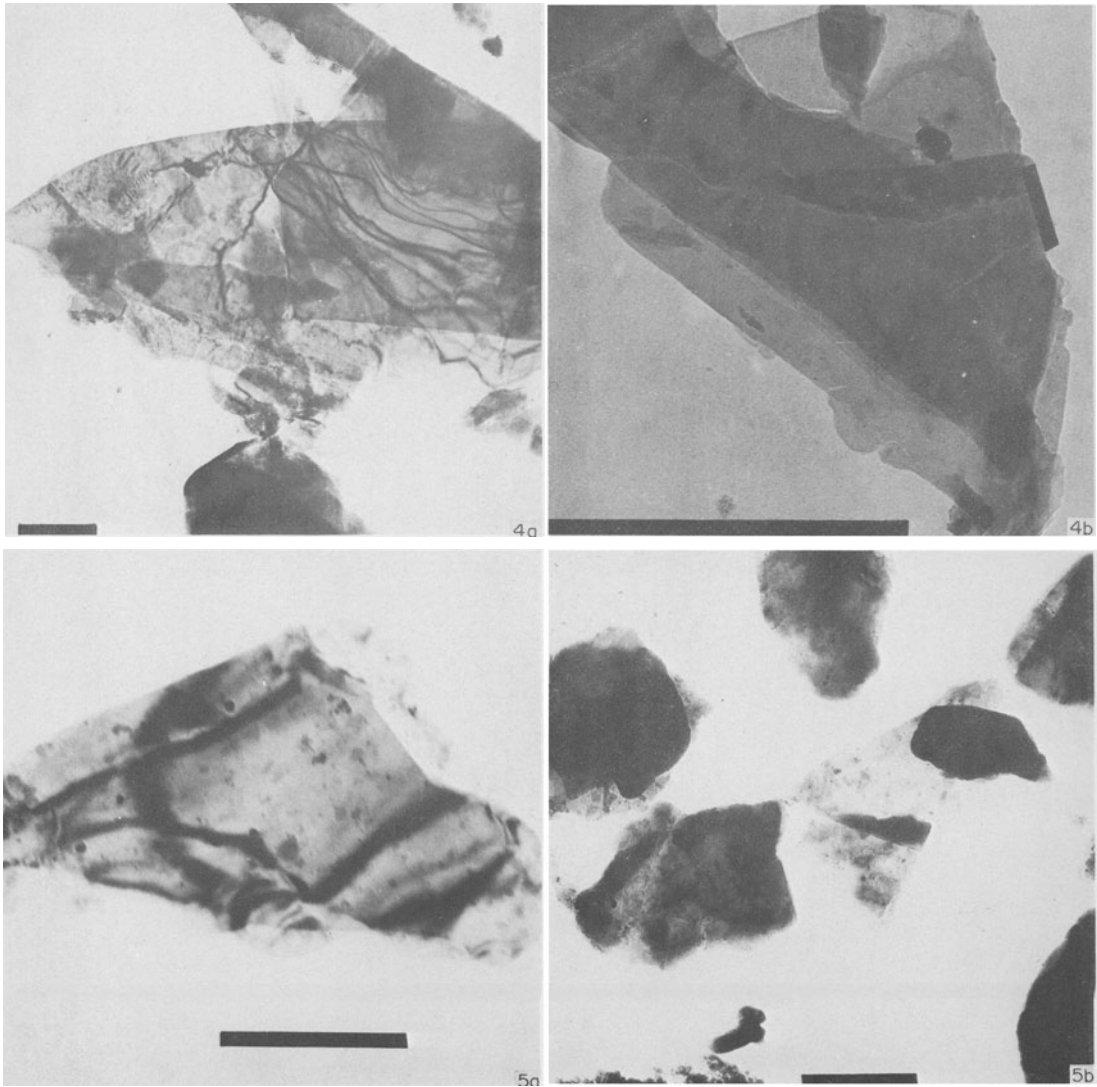


Fig. 4. Electron micrograph of weathered phlogopite particles. (A) Interlayer cations Cs, Ca, and K. (B) Interlayer cations Ca and K. Bar indicates 1 μ .

Fig. 5. Electron micrograph of vermiculite-mica particles from Nason A2 horizon. (A) Ca-saturated, then Cs-Mg treated. (B) Ca saturated. Bar indicates 1 μ .

Table 1. Cs and Mg uptake by initially Ca-saturated 2-0.2 μ fraction from three vermiculitic soils

Horizon	CEC* (me/100 g)	Cs			Mg	
		Difference method (me/100 g)	Total Cs method (me/100g)	% of CEC†	Difference method (me/100 g)	% of CEC†
Ramona						
A12	20.7	13.2	13.5	65	2.0	10
B23	25.3	16.7	16.4	65	2.1	8
C2	31.6	19.8	21.0	66	2.7	8
Nason						
A2	16.1	15.5	16.0	99	0.1	0
B2	25.5	20.4	20.5	80	1.8	7
C	32.0	25.0	24.1	75	1.7	5
Tatum						
A1	12.2	10.2	10.5	86	0.0	0
B2	12.4	7.2	8.8	71	0.0	0
C	14.1	11.7	11.6	82	0.0	0

*From Murdock and Rich (1972).

†Based on total Cs method.

Table 2. Effect of Cs-Mg treatment on Ca-"saturated" 2-0.2 μ fraction of phlogopite and muscovite

Mineral	K	Ca (me/100 g)	Cs	Total charge	Ca % of total charge	Cs
Ca-"saturated"						
Phlogopite	12.4	212.0	—	224.4	94.5	—
Muscovite	137.9	103.9	—	241.8	43.0	—
Ca-"saturated" then Cs-Mg treated						
Phlogopite	24.2	116.6	95.9	236.7	49.3	40.5
Muscovite	145.1	17.4	101.3	263.8	6.6	38.4

on a brass plate previously cooled on dry ice. The frozen drop was then dried by sublimation under a vacuum. The morphology of these particles may have resulted from dehydration of the Cs-bearing zones near edges of the vermiculite and the trapping of hydrated Ca in the central portion of the particle. At the very high vacuum in the electron microscope and the high temperature induced by the electron beam, the trapped water may have exploded and disrupted the Ca-bearing central portions. X-ray diffraction studies show that clay from this horizon is easily collapsed on K saturation and edge fixation with Cs is also likely.

Similar particles were seen in other freeze-dried specimens but not in the air dried specimens used in the remainder of this study. Freeze-drying was generally not as satisfactory as air-drying in preparing these specimens and the technique was used only in the early stages of the study.

Observation of several grids of Ca and Cs-Mg

treated clay specimens from all of the soil horizons examined, as well as the treated muscovite and phlogopite, indicate that the Ca treated samples were generally uniformly darker than the Cs-Mg treated specimens. Moreover, extinction bend contours were observed in the Ca and Cs-Mg treated samples but not in those subjected only to Ca-treatment (Figs. 3-5). Extinction bend contours are discussed in a second paper by the authors (Gal and Rich, 1972).

More uniform diffraction or thicker particles may account for the darker Ca-treated samples. Flat or uniformly thick particles would promote uniform diffraction, whereas bending would not. Furthermore, bending would create stresses that would promote splitting of the particles. Partial Cs saturation may distort the silicate layers by stretching the portion of the layers in which it is adsorbed, which results in warping of the whole particle. Leonard and Weed (1967) showed that

Cs increased the *b*-dimension of mica layers by 0.04 Å, which was greater than for any other interlayer cation tested.

In addition to warping, Cs may also induce splitting of the particles. Barrer and Reay (1958) found that the external surface area of montmorillonite increased from 20 M²/g for Na-montmorillonite to 90 M²/g for Cs-montmorillonite. They interpreted this in terms of average particle thickness—8 elemental layers for Cs-montmorillonite and 82 layers for Na-montmorillonite.

There was no clear evidence that concentrations of interlayer cations were detected by diffraction contrast in the air dried samples. One Cs-Mg treated, partially expanded muscovite particle showed a darker zone around the edge where one would expect Cs to be located (Fig. 3a). This darkened edge zone was not observed in other particles and the dark zone in this particular specimen may be caused by one or more additional 10–14 Å layers. It is unusual, however, for the edge zone to be thicker than the central portion of the particles.

A further complexity of the particles appears to be non-uniform bending of the layers in a single particle. The complex system of superimposed bend contours, indicated individual warping of packets making up one particle. These packets are often observed as steps in single particles and also have been observed as coherent domains of 10–20 unit layers in transmission electron microscopy of ultramicrotome transverse sections of micas (Brown and Rich, 1968). Weathering probably occurs first along planes separating packets. After this initial separation of packets, warping

of each packet, generally independent of the others, is possible. Thus, the complexity of diffraction itself, further confounded by complex warping of packets within particles, make observation by diffraction contrast of zones of interlayer cations extremely difficult. The observation of particles only a few layers thick and consisting of a single packet may be more fruitful.

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Résumé—En vue de détecter les concentrations locales en cations interfeuilletés dans les micas-vermiculites, on a mis à profit le contraste existant en diffraction des électrons. Cs et Mg ont été choisis comme ions échangeurs du Ca, à cause du contraste qu'il y a entre leurs emplitudes de diffusion atomique des électrons. Cs a été adsorbé jusqu'à exclusion presque complète de Mg par les argiles provenant de trois sols et par de la muscovite et de la phlogopite altérées de la taille de l'argile. La présence de Cs en plus des autres cations interfeuilletés K et Ca, entraîne une déformation et peut être une séparation des feuilletés du mica-vermiculite. Des contours d'extinction déformés s'observent couramment dans les échantillons traités par Cs, mais ne s'observent pas dans les échantillons traités par Ca. Après cryodessiccation des échantillons de l'argile de Nason sous forme Cs-Ca, la destruction différentielle par le faisceau d'électrons du noyau central de la vermiculite de la taille de l'argile contenant des ions Ca hydratés peut indiquer une localisation du Cs sur les bords.

Kurzreferat—Die Verwendung von Elektronenbeugungskontrast zur Auffindung örtlicher Konzentrationen von Zwischenschichtkationen in Glimmer-Vermiculiten wurde überprüft. Cs und Mg wurden im Hinblick auf ihre kontrastierenden Atomstreuweiten für Elektronen als Austauschaktionen für Ca gewählt. Die Tone der drei Böden sowie verwitterter Muscovit und Phlogopit von Tongröße absorbierten Cs mit beinahe vollständigem Ausschluss von Mg. Die Anwesenheit von Cs zusätzlich zu den anderen Zwischenschichtkationen, K und Ca, verursachte Biegung und möglicherweise Spaltung der Glimmer-Vermiculitschichten. Auslöschungsbiegungskonturen waren gewöhnlich bei Cs-behandelten Proben, jedoch nicht bei den Ca-behandelten, vorhanden. Nach Gefriertrocknung von Proben von Cs-Ca Nason kann Differentialzerstörung des mittleren Kernes in Vermiculit von Tongröße mit einem Gehalt von hydratisierten Ca-Ionen durch den Elektronenstrahl die Kantenebene von Cs anzeigen.

Резюме — Исследовалось применение контрастов дифракции электронов для обнаружения по месту концентраций прослоек катионов в слюдяных вермикулитах. Cs и Mg, вследствие их противоположных амплитуд атомного рассеяния электронов, были выбраны в качестве ионов обмена для Ca. Cs абсорбировался почти до полного исключения Mg глинами из трех видов почвы и выветренными мусковитом и флогопитом с частицами размеров глины. Присутствие Cs вдобавок к другим катионам прослоек, K и Ca, причиняли изгиб и, вероятно, расщепление слоев слюдяных вермикулитов. Исчезающие контуры изгиба встречались часто в обработанных Cs образцах, но не в обработанных Ca. После сушки образцов глины с Cs–Ca Назона при температуре ниже 0° дифференциальное разрушение электронным лучом содержащей гидрированные ионы Ca центральной части вермикулита размеров глины, может служить указанием положения края Cs.