

## EXTINCTION BEND CONTOURS IN ELECTRON MICROSCOPY OF CLAY-SIZE MICA-VERMICULITES\*

M. GAL† and C. I. RICH

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

(Received 16 December 1971)

**Abstract**—Extinction bend contours, observed in Cs-treated mica-vermiculites by transmission electron microscopy, give information on the morphology and crystal orientation and continuity in individual particles of clay size. Interlayer Cs apparently stretches that part of the silicate sheet in closest proximity and when exchange by Cs is incomplete, warping of the particle occurs. Warping favors the appearance of bend contours in transmission electron microscopic images of the particles. These contours terminate at crystal boundaries within a particle. A specimen tilting stage is useful in bringing the contours into view and in “exploring” individual particles.

### INTRODUCTION

EXTINCTION bend contours observed in transmission electron microscopy of thin, bent crystals give information on dislocations and stacking faults (Hirsch *et al.*, 1965). This phenomenon is used extensively in the study of metals but less so in the case of minerals.

When a single crystal is bent, conditions for strong diffraction by a single suite of planes are satisfied only locally. If the angle of diffraction is sufficient, the diffracted beam is stopped in the electron microscope by the objective aperture in the back focal plane. Thus, the zones of strong diffraction occur as dark bands in the bright field image. When a thin crystal is bent uniformly over a small distance, a pair of extinction contours for a set of planes,  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ , are observed (Hirsch *et al.*, p. 417). The identification of the Bragg planes giving the diffraction can be obtained by selected area diffraction in which the Bragg planes responsible occur as the darkest spots. In the case of layer silicates the orientation of the (001) planes are normally parallel with the grid. According to the work of Mering and Oberlin (1967) diffraction from  $hk$  planes 06, 33, 02, 11, 20, and 13 would be expected to be the most intense. A selected area diffraction pattern of a vermiculite particle by Farmer *et al.* (1971) show (020), (040), and (060) spotty reflections.

Extinction bend contours give information on the form of the warping and crystal boundaries within a particle. The termination of bend contours within a particle indicates a crystal boundary.

Phyllosilicates, because of their platy nature, should require little sample preparation. Most of the reported work involving extinction contours has been with large specimens that were cleaved to sufficient thinness. Nakahira and Uda (1966) studied thin flakes of muscovite and phlogopite obtained by successively attaching adhesive tape and cleaving thicker specimens. Transmission electron microscopy of natural and dehydroxylated specimens revealed complex diffraction effects caused by dislocation and moiré patterns. These complex patterns were ascribed to crystal growth, sample preparation, and dehydroxylation.

Extinction bend contours in natural phyllosilicates of clay size have not been as frequently reported as moiré patterns and other features of disorder. Nakahira and Uda (1967) reported that dislocations and faults in small particles of chlorite and kaolinite were very complicated and unstable.

Moiré patterns are frequently observed in electron micrographs of micas. These patterns change with the electron beam intensity as one layer or set of layers shifts with respect to layers above or below. Dyal (1953) observed moiré patterns in clay-size mica particles from soil and related them to movement of the mica laminae with respect to each other. Juang and Uehara (1968) also observed moiré patterns in micas from certain Hawaiian soils.

Dark bands in pyrophyllite and muscovite, similar to those observed in this study, have been

\*Support for this work by a grant (GA-18053) from the National Science Foundation is gratefully acknowledged.

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

reported by Beutelspacher and van der Marel (1967). The dark bands in muscovite were ascribed to interference effects caused by bending, which was attributed to weathering.

Suito and Nakahira (1971) published electron micrographs of thinned flakes of muscovite with well developed extinction bend contours. Moiré and other patterns indicative of a dislocation network were also observed in sericite.

Kishk and Barshad (1969) published electron micrographs for vermiculites from 11 soils. Although surface features were noted, extinction bend contours were not reported.

The infrequency of extinction bend contours in natural clays of less than  $2\ \mu\text{m}$  dia. may be due to their tendency to lie flat on the electron microscope grid. Specimens broken from large crystals in the laboratory may have more bending and distortions than natural clay size specimens.

Bending of certain natural clay minerals, however, can be induced. Gal and Rich (1972) found that when clay-size mica-vermiculite particles containing a large proportion of interlayer Cs were observed by bright field transmission electron microscopy, dark bands were seen. These were tentatively identified as extinction bend contours. When the samples contained Ca and K as the interlayer cations, no bend contours were observed. The objective of this paper was to examine the contours in more detail and to verify their presence through the use of the tilting stage.

#### METHODS AND MATERIALS

The materials and methods are described in more detail by Gal and Rich (1972). However, the interlayer cation contents of the samples are given in Table 1. Soil clays were first Ca saturated

in a centrifuge procedure. A portion of the interlayer K in the specimen micas was replaced by Ca in an autoclave procedure (Reichenbach and Rich, 1968). The Ca-treated samples were then washed with a mixed Cs-Mg chloride (0.002N each) solution 10 times. Approximately 100 ppm suspensions of both the Ca and the Cs-Mg-treated samples were shaken for 48 hr, followed by 10 min stirring in a Sorvall Omni-Mixer at 16,000 rev/min. A drop of each suspension was deposited on a 200 mesh Formvar- and carbon-coated electron microscope grid. After air drying, the grids were examined in a RCA-EMU3 electron microscope at 50 kV. A specimen-tilting stage was used to examine specimens at different angles with respect to the electron beam.

#### RESULTS AND DISCUSSION

Table 1 gives a summary of the interlayer composition of the bulk samples from which images of separate particles are shown in this paper.

In Fig. 1, a Cs-Mg treated phlogopite particle shows very strong extinction bend contours as well as subsidiary contours. The two strong centrally located bands are probably caused by strongly diffracting planes such as (020) and (0 $\bar{2}$ 0), whereas the two subsidiary pairs between may be secondary diffraction effects. The closer the two bands of a pair, the sharper the bend. Since the contours extend to the particle edges, we believe this is a single crystal.

The Cs-Mg treated muscovite particle in Fig. 2 shows a much more complex system of contours. These contours are not affected by over- or underlying particles. The complex system of contours seems in part due to independent warping of packets of layers.

Table 1. Interlayer composition of the clay specimens used for transmission electron microscopy

Specimen ( $2-0.2\ \mu\text{m}$ )	K	Ca (meq/100g)	Cs	Sum
		Specimen micas		
Muscovite (Amelia, Virginia)	145.1	17.4	101.3	263.8
Phlogopite (Ontario, Canada)	24.2	116.6	95.9	236.7
		Soil clays		
Ramona B23 (California)	—	8.6	16.7	25.3
Nason B2 (Virginia)	—	5.0	20.5	25.5

\*The interlayer composition of the muscovite and phlogopite samples is based on the 2:1 layer weight (free of all interlayer cations and water).

In the case of the soil clays only total Ca and Cs were measured in the treated sample. The K contents of the untreated specimens were 53.7 and 49.8 meq/100g for the Ramona and Nason clays, respectively (Murdock and Rich, 1972).

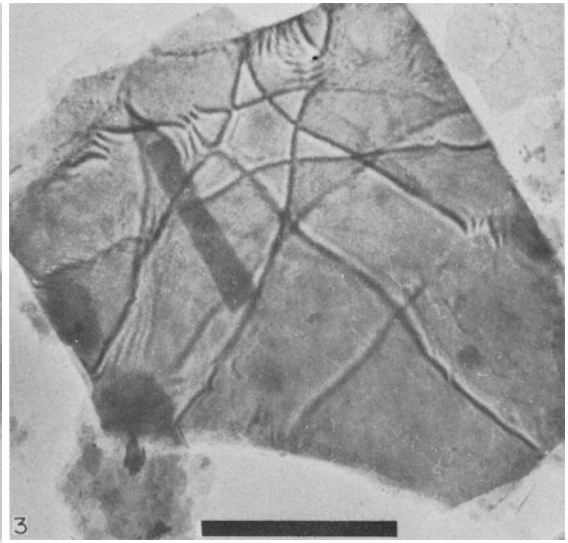
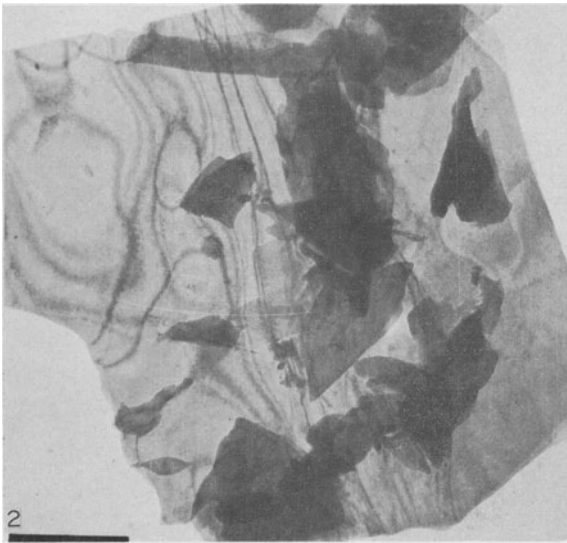


Fig. 1. Primary and subsidiary extinction bend contours seen in transmission electron micrograph of a weathered phlogopite particle. The bar indicates 1  $\mu\text{m}$ .

Fig. 2. Complex extinction bend contours seen in a weathered muscovite particle. Bar indicates 1  $\mu\text{m}$ .

Fig. 3. Hexagonal symmetry revealed by extinction bend contours of a weathered vermiculite-mica particle from the B23 horizon from Ramona soil. The bar indicates 1  $\mu\text{m}$ .

[Facing page 208]

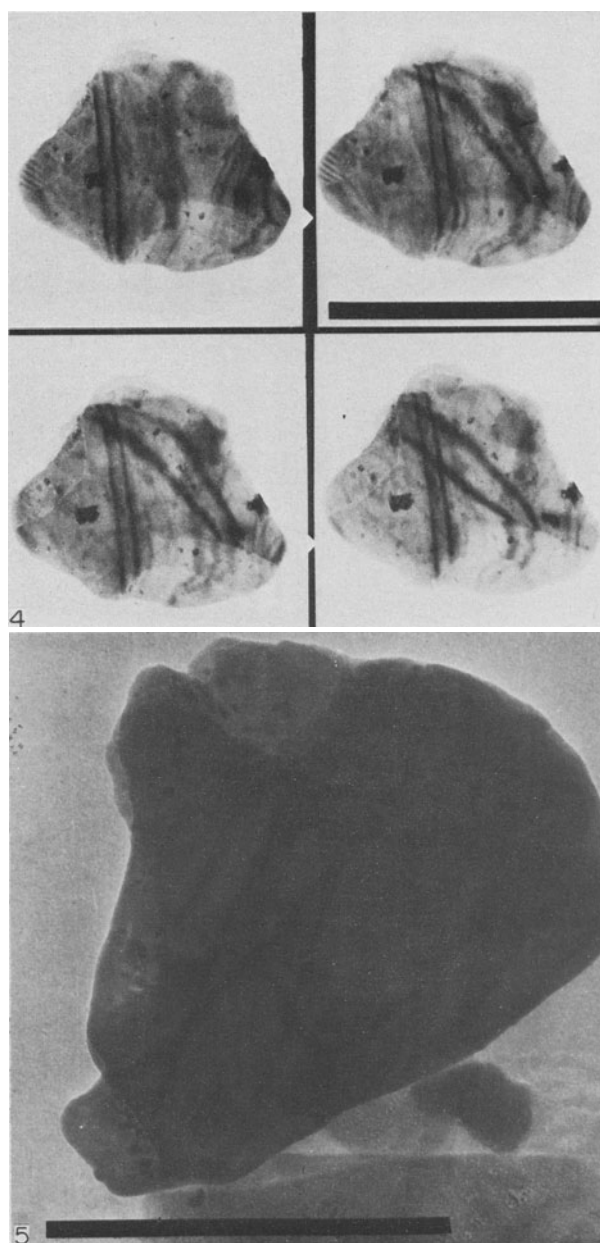


Fig. 4. Series of electron micrographs of vermiculite-mica particle from the Nason B horizon. Clay was Ca-saturated and then Cs-Mg treated. The particle was tilted (upper right corner of the particle moved up) successively as follows 5°, 10°, 20°, and 30° for the upper left, upper right, lower left and lower right, respectively. The bar indicates 1  $\mu\text{m}$ .

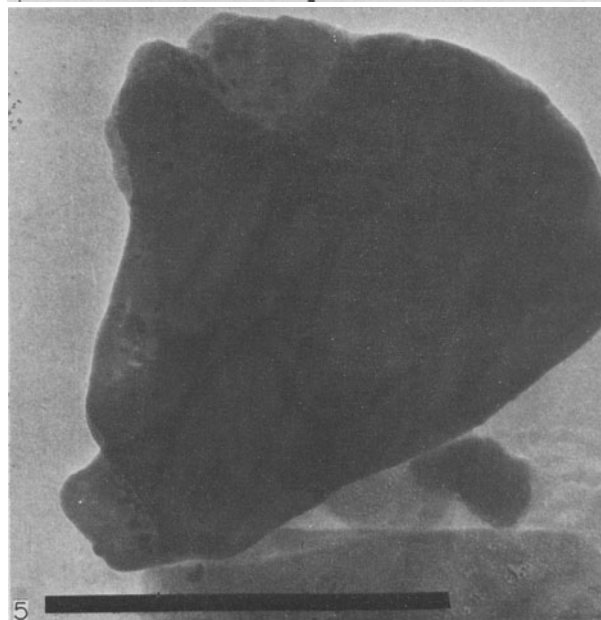


Fig. 5. Transmission electron micrograph of Nason B2 mica-vermiculite particle showing extinction bend contours in central portion and disorder at edges. The bar indicates 0.5  $\mu\text{m}$ .

Figure 3 shows three pairs of extinction bend contours in the image of a mica-vermiculite particle from a Ramona soil. The distorted hexagonal symmetry is due to three pairs of extinction bend contours from three sets of crystal planes from a flake with a saucer-shaped surface. From the work of Nakahira and Uda (1966) and of Mering and Oberlin (1967) on selected area diffraction patterns we believe that the three sets of contours observed in Fig. 3 are: (020), (0 $\bar{2}$ 0); (110), ( $\bar{1}$ 10); and ( $\bar{1}$ 10) and ( $\bar{1}$ 10). As a consequence of the pseudo-hexagonal symmetry, the choice of the  $a^*$ - and  $b^*$ -axis projections can be ambiguous and for the same reason (020) and (110) reflections occur at the same  $\theta$  angle (Zvyagin, 1967). The discontinuities in contours seen in Fig. 3 are probably related to the interaction of dislocations with the extinction bend contours or to changes in thickness of the diffracting packet. Vermiculite zones at edges merging into mica zones should change the positions of the contours.

To verify that the dark bands are extinction bend contours rather than local features of the particles, several specimens were examined using the tilting stage. An example is given in Fig. 4. As the particle was tilted, a new set of planes came into proper position for diffraction, so extinction contours moved or came into view. Some type of discontinuity is evident in the upper and lower right portions of the particle. A moiré pattern is also evident in the extreme left portion of the particle in the upper two pictures. The position of the bands was reversible on return of the tilt to the initial position.

The extinction bend contours in the Cs-treated Nason B2 mica-vermiculite were moved to the positions indicated in Fig. 5 by lowering the upper left corner of the stage by 5 degrees. The orientation of the crystal axes is indicated and the termination of the contours show zones of different orientation or disorder. The dark edge at the top may indicate the extent of Cs penetration at the particle edge.

All Cs-treated mica-vermiculite particles do not exhibit extinction contours on a flat grid. Some are too thick and it is evident that others either are not bent or are not tilted at the proper angle for diffraction contours to be observed.

Although the formation of extinction bend contours is a complex phenomenon, their occurrence may be useful in gaining information regarding the morphology and crystal orientation of some individual particles of clay minerals.

In our present study, moiré patterns were observed frequently in both the Cs and Ca treated samples. Moiré patterns differed from the dark bands we observed in that the moiré patterns were

much more variable with electron intensity changes and gave patches of finer bands compared to the more constant and simpler extinction bend contours. Cs, as an exchange ion in vermiculite, apparently increases the incidence of bending (Gal and Rich, 1972), and the observation of extinction bend contours in specimens containing Cs is more frequent. Conversely, it might be reasoned that Ca, as an exchange ion, promotes flatness of the particles and thus extinction bend contours are not seen.

The extinction bend contours of the clay particles from these soils appear to be less complex than those of muscovite and phlogopite particles broken from layer crystals. In natural weathering, separation of packets or layers would be expected to occur first at planes of disorder. If smaller particles possess better crystallinity than large particles, perhaps this explains the more rapid and complete depletion of K from large particles compared to small particles that has been observed by several workers (Reichenbach and Rich, 1968).

Extinction bend contours have been used to describe disorder within metals and minerals. Their use in the study of natural mica-vermiculites may be enhanced by Cs treatment and use of the tilting stage.

#### REFERENCES

- Beutelspacher, H. and Marel, H. W. van der (1967) *Atlas of Electron Microscopy of Clay Minerals and Their Admixtures*, Elsevier, Amsterdam.
- Dyal, R. S. (1953) Mica leptyls and wavellite content of clay fraction from Gainesville loamy fine sand of Florida: *Soil Sci. Soc. Am. Proc.* **17**, 55-58.
- Farmer, V. C., Russell, J. D., McHardy, W. J., Newman, A. C. D., Ahlrichs, J. L. and Rimsaite, J. Y. H. (1971) Evidence for loss of protons and octahedral iron from oxidized biotites and vermiculites: *Mineral Mag.* **38**, 21-37.
- Gal, M. and Rich, C.I. (1972) Selectivity effect of Cs on clay size weathered mica; transmission electron microscopy studies: *Clays and Clay Minerals* **20**, (In press).
- Hirsch, P. B., Howie, A., Nicholson, R. B., Pashley, D. W. and Whelan, M. J. (1956) *Electron Microscopy of Thin Crystals*, Butterworths, Washington.
- Kishk, F. M. and Barshad, I. (1969) Morphology of vermiculite clay particles as affected by their genesis: *Am. Mineralogist* **54**, 849-857.
- Juang, T. C. and Uehara, G. (1968) Mica genesis in Hawaiian soils: *Soil Sci. Soc. Am. Proc.* **32**, 31-35.
- Mering, J. and Oberlin, A. (1967) Electron optical studies of smectites: *Clays and Clay Minerals* **15**, 3-25.
- Murdock, L. W. and Rich, C. I. (1972) Ion selectivity of three soil profiles as influenced by mineralogical characteristics: *Soil Sci. Soc. Am. Proc.* **33**, 167-171.
- Nakahira, N. and Uda, M. (1966) Electron microscopic

- observations of dehydroxylated micas: *Am. Mineralogist* 51, 454–463.
- Nakahira, M. and Uda, M. (1967) Defect structures of clay minerals: *Zeits. Krist.* 124, 420–427.
- Reichenbach, H. G. von and Rich, C. I. (1968) Potassium release from muscovite as influenced by particle size: *Clays and Clay Minerals* 17, 23–29.
- Suito, E. and Nakahira, M. (1971) Micas and related minerals: In *The Electronoptical Investigation of Clays* (Edited by J. A. Gard), pp. 231–254, Mineralogical Society, London.
- Zvyagin, B. B. (1967) *Electron Diffraction Analysis of Clay Mineral Structures*, Plenum Press, New York.

**Résumé**— Les contours d’extinction déformés observés en microscopie électronique par transmission dans les micas-vermiculites traités au Cs donnent une information sur la morphologie et l’orientation des cristaux, et sur la continuité des particules individuelles de la taille de l’argile. Apparemment, le Cs interfeuillet distend la partie de la couche silicatée qui est dans son voisinage immédiat et lorsque l’échange par Cs est incomplet, on observe un gauchissement de la particule. Ce gauchissement favorise l’apparition de contours déformés dans les images des particules obtenues en microscopie électronique par transmission. Ces contours s’établissent aux zones limites des cristaux à l’intérieur d’une particule. Un dispositif d’orientation de l’échantillon se révèle utile pour bien observer ces contours et pour “explorer” les particules individuelles.

**Kurzreferat**— Die durch das Elektronen-Durchstrahlungsmikroskop beobachteten Extinktions-Biegungskonturen in Cs-behandelten Glimmer-Vermiculiten geben Auskunft über die Morphologie und Kristallorientierung und -kontinuität in Einzelteilchen von Tongröße. Es scheint, dass zwischenschichtiges Cs den am nächsten liegenden Teil der Silikattafel am meisten streckt, und wenn der Austausch durch Cs unvollständig ist, so tritt Werfung des Teilchens auf. Die Werfung begünstigt das Erscheinen von Biegungskonturen in Bildern des Teilchens im Elektronen-Durchstrahlungsmikroskop. Diese Konturen enden an den Kristallgrenzen innerhalb eines Teilchens. Ein kippbarer Präparathalter ist dazu geeignet die Konturen ins Blickfeld zu bringen und Einzelteilchen zu “erforschen”.

**Резюме** — Обнаруженная при помощи электронного микроскопа экстинкция контуров изгиба в слюдяных вермикулитах, обработанных Cs, дает сведения о морфологии и ориентации кристаллов и о неразрывности индивидуальных частиц глины. Межслоевой Cs, очевидно, растягивает самую близкую к нему часть силикатной пластинки, и если обмен с Cs неполный, то происходит искривление частицы. Искривление способствует появлению контура изгиба на изображениях частиц под электронным микроскопом. Эти контуры заканчиваются на границах кристалла в пределах частицы. Для введения контуров в поле зрения при изучении отдельных частиц, рекомендуется наклонить образец.