CHLORITE EXAMINATION BY ULTRAMICROTOMY AND
HIGH RESOLUTION ELECTRON MICROSCOPY

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For Clays and Clay Minerals

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HIGH RESOLUTION ELECTRON MICROSCOPY

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Received _____ 1972

Abstract--Mafic chlorite from Benton, AR was comminuted by high speed rotary blending of a suspension. The particle size fraction less than 2 micrometers in diameter was separated by sedimentation in H₂O. Droplets of suspension of the <2 μ m fraction were dried on a layer of Epoxy resin and then additional Epoxy was added and heat-cured to form a resin sandwich. Cross-sections 600 to 900 Å thickness were made of this sandwich on a Reichert automated ultramicrotome. The sections were collected on standard electron microscope specimen screens, reenforced by vacuum evaporated C, and examined by transmission electron microscopy (TEM) with a Phillips EM 200 electron microscope with a "microgun" source to minimize heating of the specimen and to improve contrast and high resolution (HREM). Images of the (001) chlorite

crystallographic planes spaced at 13.9 Å intervals were visible on many of the particle sections. Imaging of the planes depended upon their being nearly parallel to the electron beam (within $0^{\circ} 10'$) and, therefore, many particles having other orientations did not show the 13.9 Å lattice HREM image. Micrographs made before an appreciable irradiation by the electron beam revealed images of the 7.22 Å structural planes of chlorite, representing the distance between the (002) planes of atomic nuclei in interlayer hydroxyl layers and hydroxyl layers. Loss of the images at 7.22 Å intervals and reenforcement of those at 13.9 Å intervals was caused by the electron beam heating of the chlorite. This is analogous to the well-known partial loss of interlayer hydroxyl on heating at 550 to 760°C with loss of the 7.2 Å x-ray diffraction peak of chlorite and reenforcement of a 13.9 Å spacing.

INTRODUCTION

The interlayer surfaces of phyllosilicates are the sites for intercalation of not only hydrated exchangeable cations but also of hydroxy-metal layers such as those of Fe, Al, and Mg, for which chlorite (Pauling, 1930) is a model mineral. These interlayer configurations are important in cation exchange of radioactive and other ions (Rich, 1968; Syers et al., 1972) and other clay transformations (Jackson, 1963, 1965). Direct photography of ultramicrotomed sections of the crystals examined by high resolution electron microscopy (HREM) have revealed the configuration of the layers and interlayers of the phyllosilicates, chrysotile (Yada, 1967) and muscovite (Brown and Rich, 1968). The pyridine intercalated complex of TS_2 has similarly been photographed (Fernandez-Moran et al., 1971).

Margins of montmorillonite particles showed scrolled portions in which the layer intervals were observed edge-on as parallel fringes at 10 Å (Barclay and Thompson, 1969) and 18 to 40 Å with organic complexes (Suito et al., 1969). Imogolite fiber cross sections were observed as thin tubes about 19 Å in diameter in ultramicrotomed sections (Wada et al., 1971). In electron microscope studies of replicas of ferruginous interlayer coatings of micaceous vermiculite (Roth et al., 1967), chlorite was included as a control, for which photographs of crystal layers and hydroxyl interlayers were ultramicrotomed and directly photographed (Brown and Jackson, 1970) by high resolution electron microscopy (UM-HREM) in the present study.

METHODS

A mafic chlorite from Benton, AR (courtesy of S. L. Chapman) was ground in suspension in distilled water with a high speed rotary blender. A suspension of the particle size fraction less than $2\text{ }\mu\text{m}$ in equivalent spherical diameter was separated by centrifugation. The sample gave a sharp $14.4\text{\AA}$ basal x-ray diffraction peak and higher integral order peaks for chlorite.

Droplets of the chlorite suspension in water were dried on a cured Epoxy (Araldite 6005 from Cargille Sons, 194 Second Ave., Little Falls, NJ) layer to obtain parallel orientation of the clay particles. Additional Epoxy solution was then added and heat cured at 48°C overnight (about 12 hours) to form an Epoxy sandwich (Brown and Rich, 1968). A small block was sawed from the Epoxy, suitably shaped by filing, then sectioned by means of a Reichert OmU2 ultra-microtome (Wm. J. Hacker and Co., Inc., P. O. Box 646, West Caldwell, NJ) with a diamond knife. The section was made perpendicularly across the sediment plane so as to cut through the flat faces of the platy particles. The particle platelets and (001) crystal planes in the section thus were approximately normal to the section surface. The thin sections were 600 to $900\text{\AA}$ thickness, as judged from the Sorvall (Norwalk, Conn., 06852) color chart for reflected light. The thin sections were collected from the water-filled

boat by touching them with the flat surface of a standard electron microscope grid previously coated with 0.1% bovin albumin (Armour Pharmaceutical Co., Kankakee, IL) and dried. The specimen was dried in an air stream and then strengthened with a very thin layer of C (about 100Å thick) by vacuum evaporation, and examined by transmission electron microscopy (TEM) with a Philips EM200 electron microscope with a "microgun" source to minimize heating of the specimen and to improve contrast and resolution. An accelerating voltage of 100 kv was employed, giving an effective electron beam wavelength of 0.037Å. A 50-μm back focal plane objective aperture was employed, with which the angular aperture of the microscope is sufficient to pass Bragg reflections from crystal spacings as close as 4Å. Eastman-P426 35-mm film was employed for the electron micrographs.

RESULTS AND DISCUSSION

Intermediate magnification

Insert
Fig. 1

The sectioned chlorite platelets distributed in the Epoxy resin are visible (Fig. 1a) at intermediate magnification. During sectioning, the Epoxy tears in places (Fig. 1a) and the clay platelets sometimes fall out. The carbon film helps to prevent this. The C film is essential to ground out the electrostatic charge that tends to build up on the particles in the electron beam. This keeps the Epoxy film mount intact during the examination in the electron microscope. Without the C layer, the Epoxy film quickly ruptures during the electron microscopic examination. Larger than 2 μm phyllosilicate particles tend to be torn from the section by the diamond knife instead of being cut. Particles much smaller than 1 μm tend to cake and not accept Epoxy resin between the individual particles and thus do not remain securely anchored in the cured resin so as to be sectioned.

High magnification

Calibration of the electron microscope magnification, based on a replica of an optical diffraction grating, shows the fringe-to-fringe spacing of the HREM images to represent a 13.9 $\text{\AA}$ spacing (Fig. 1b, c) in many of the outlines of the sectioned particles. This spacing is equal to the (001) X-ray diffraction spacing of chlorite and corresponds to the interval of the 2:1 phyllosilicate crystallographic layers of chlorite.

When rapid photomicrography of the specimen was carried out so as to minimize the exposure of the crystal in the intense electron beam of the electron microscope required for imaging at high magnification, more closely spaced structural images were observed at a 7.22 Å interval (Fig. 2a, b). The 7.22 Å image spacing corresponds to the (002) X-ray diffraction spacing of the chlorite, at approximately one-half the interval of the (001) images (as will be discussed below).

Insert
Fig. 2

A crystallographic plane of atoms diffracts (scatters) electrons in much the same way that X-rays are diffracted; however, the electrons are diffracted by interactions with the electric fields within the atom in a basic Rutherford scattering process, whereas the X-rays are scattered by the electron clouds surrounding the atomic nuclei. Electron diffraction is much more effective with fewer crystal planes than is X-ray diffraction. For both types of radiation, the Bragg equation, $n\lambda = 2d \sin \theta$, applies. Since the electron wavelengths used are much shorter than the X-ray wavelengths ordinarily used for crystal diffraction study, the values for $\sin \theta$ are very much smaller. For the 14 Å (001) and 7 Å (002) reflecting planes of chlorite, the θ angle is on the order of 4' 30" and 8' 57", respectively, i.e. a small fraction of a degree. To form an image of a given crystallographic plane sequence, the incident electron beam must have this Bragg angle with respect to the planes of atomic nuclei in the crystal and the objective aperture must be large

enough to accept the zero order and at least one diffracted beam. Since electron optical imaging by diffraction from the crystal planes depends on having the Bragg angle with respect to the electron beam, many particles (e.g., Fig. 1c, arrow), having other tilt angles, do not show the (001) and/or (002) structural lines within the usual mass contrast TEM image. In accordance with the Abbé theory of microscope resolution for periodic structures, it is necessary to combine optically the zero order and at least the first order diffraction beam (Thomas, 1962, p. 52). Because of spherical aberration in the objective lens of the electron microscope, only those diffracted beams which are sufficiently near the objective axis can be successfully used for imaging; otherwise the conditions in the image plane with respect to phase will be such that contrast will be lost.

These observations illustrate the two basic types of TEM image contrast in the electron microscope, i.e. amplitude (mass thickness) contrast and phase contrast. Amplitude contrast is produced by the back-focal-plane objective aperture and includes both mass-thickness and diffraction contrast. This mechanism applies to distances in the object much larger than interatomic spacings. Phase contrast is produced by recombination of direct and scattered rays at the image plane and is the important mechanism for producing images of crystallographic planes (Fig. 1b, c). For essentially amorphous mineral material (as with most biological

materials) in which the short range order of individual organizational units is smaller than the resolution of the microscope, the contrast in the image is dependent solely on mass thickness differences recorded in ordinary transmission electron microscopy, for example low-mass Epoxy versus clay particles (Fig. 1a) or particles at non-diffracting tilt angles (Fig. 1c, arrow). For longer range crystalline order, as in the chlorite sections examined (Fig. 1b, c; 2a, b, c, d), where the crystal structural spacings are larger than the resolution of the electron microscope, the image contrast arises from phase contrast. Phase contrast images of 100 Å spacings in Yu Yen Stone (antigorite) crystals (Brindley et al., 1958) illustrate the HREM technique for superlattice spacings.

Phase changes (pc) cause light and dark zones in the chlorite images (pc, Fig. 2b) and left of center in Fig. 2d. These were also noted in micas (Brown and Rich, 1968, pc in their Fig. 1).

Dark spotty (mottled) areas in the chlorite sections (Fig. 1 and 2) are extinction contours caused by diffraction contrast in which many of the diffracted beams are intercepted by the objective aperture and their contribution to the final image is decreased. These effects also appeared as mottling in micaceous vermiculite (Raman and Jackson, 1964).

Crystal damage in the electron beam

The fringes depicting the 7.22 Å spacing (Fig. 2b, d) of chlorite were absent in most of the electron micrographs and were detected only when the photographs were made very rapidly in a given specimen area, by the through-focus technique. This relationship was attributed to crystal damage (dehydroxylation of the hydroxyl interlayers of the chlorite) by the intense electron beam irradiation necessary for imaging at high magnification, rather than to a change in the angle of repose of the crystal section. After a short exposure to heat in the electron beam, the electron diffraction leading to the electron optical image formation revealed only the fringes corresponding to the 2:1 layers spaced at 13.9 Å (Fig. 1b, c). In an analogous way, loss of the 7.3 Å fringes from chrysotile and change "to the amorphous state" occurred (Yada, 1967, p. 705) as a result of crystal damage by the electron beam irradiation. Crystal damage, concentrated in one part of the crystal (owing to compositional differences or chance) could contribute to difference in resolution of the 7.22 Å spacing images in different parts of the crystal. The disruption by heating of chlorite mineral in the electron microscope beam is analogous to the effect of furnace heating, which causes the well-known loss of 7.2 Å X-ray diffraction peak of chlorite and reenforcement of a 14.1 Å X-ray diffraction peak at 600°C and a 13.9 Å peak at 760°C (Brindley, 1961, p. 253; Alexiades and Jackson, 1967).

The 7.22 Å periodicity was resolved electron optically in part of some crystals while only the 13.9 Å periodicity showed in other parts of a given crystal (Fig. 2c, d). Since the Bragg angles involved are approximately the same as the angular aperture of the microscope, the size of the angle between the electron beam and the diffracting plane is critical. Since the diffraction angle for 7.22 Å planes is approximately twice that for 13.9 Å planes, a slightly different orientation of a portion of the chlorite crystal might reveal 13.9 Å spacings without showing the 7.22 Å spacings. The disappearance of the 7.22 Å spacings at a certain point along the crystal (Fig. 2c, d) could be caused by slight warping of the crystal which resulted in two different populations of crystal planes, one oriented at a Bragg angle to give 7.22 Å and the other to give 13.9 Å spacings. The electron optics are more difficult to resolve the structure images for the 7.22 Å spacing over the whole sectioned area because the permissible angular deviation from Bragg conditions is more critical (Yada, 1967, p. 707) than those for the 13.9 Å fringes. If this effect contributed to resolution of fewer 7.22 Å spacings images in the electron micrographs than 13.9 Å spacing images, the (001) spacing should have remained at the 14.4 Å spacing of unheated chlorite.

The electron microscope beam scattering, which is produced by the atomic nuclei lying within the crystallo-

graphic planes, depends heavily upon the atomic number of the chemical elements in the plane. Scattering by heavy atoms through dynamical diffraction (Heidenreich, 1964, p. 302), can cause a phase change in the wave front of the electron beam which would create corresponding interference (phase contrast) effects in the image plane. The heavier atoms, particularly Fe in 6-fold coordination in the mafic chlorite, are particularly effective in scattering the first order diffracted beam of electrons which is then focused with the primary beam to form the electron optical image (Thomas, 1962). A higher Fe concentration in either layers or interlayers, by dynamical diffraction, could make the 13.9 Å image intensity greater than the 7.22 Å image intensity. The 7.22 Å images from part of the same crystal which shows only the 13.9 Å images in other parts (Fig. 2c, d) might, therefore, be attributed in part to appropriate phase shifts resulting from a mosaic of varying elemental composition sequences of octahedral cation sheets in interlayers and layers. Interestingly, the 100 Å fringes of antigorite in one case are interspersed with faint fringes at 50 Å (Brindley et al., 1958, their Fig. 1, b).

Thickness and crystal perfection of the chlorite particles

A large proportion of the chlorite particles ($<2 \mu\text{m}$ fraction) are on the order of 150 to 200 Å thick (Fig. 1 and 2). Since the X-ray diffraction peaks at 14.4 and 7.2 Å for this sample were very intense (data not shown herein), the images (Fig. 1 and 2) show that as few as 10 to 20 (001) crystallographic units are ample for development of sharp X-ray diffraction maxima.

No crystal distortion is observable on the outside boundary of the chlorite crystal images (Fig. 1 and 2), indicating that no short range structural damage at the edges was created by surface tension effects or by the mechanical comminution process. No mass contrast image extended beyond the diffraction contrast image. The question as to whether outermost "disturbed" layers and/or edges would be created by comminution in a high speed rotary blender is thus settled negatively for this chlorite.

CONCLUSIONS

1. High resolution electron microscopy of ultramicrotomed sections made normal to the basal planes of the chlorite, revealed phase contrast electron optical image fringes of the 7.22 Å (002) atomic plane spacings of chlorite before heating and 13.9 Å spacings after heating.
2. Many more crystal specimens were seen with 13.9 Å spacings than with 7.22 Å spacings. Most crystals showed intensities of 13.9 Å fringes which were greater than intensities of the 7.22 Å fringes. A few crystals showed long sequences of equal-intensity fringes at 7.22 Å when the electron micrographs were made rapidly with the through-focus technique. The 7.22 Å phase contrast image was subject to loss during a few minutes of exposure in the intense electron beam of the microscope operated at 100 kv, leaving reenforced images, corresponding to planes spaced at 13.9 Å as for chlorite furnace heated at 760°C.
3. Single particles, <2 µm in equivalent spherical diameter and plate-shaped, were frequently of 10 to 20 unit cells (each of 14 Å) thickness. This size fraction gave very sharp X-ray diffraction peaks in separate studies.
4. No evidence of a "disturbed" layer, or coatings of short range order only, occurred in the outermost layer or at the ends of the chlorite particles, which had been comminuted by high-speed rotary blending of a suspension.

Acknowledgments--This cooperative research was supported in part by the College of Agricultural and Life Sciences, University of Wisconsin, under project 1336, in part by the Analytical Instrumentation Laboratories, Engineering Experiment Station, Georgia Institute of Technology, and in part by the Division of Biology and Medicine, Environmental Sciences Branch, United States Atomic Energy Commission Contract AT(11-1)-1515-Jackson (paper C00-1515-25) and the National Science Foundation grant GP1108-Jackson. Gratitude is expressed to Mr. S. Y. Lee for assistance with the printing and mounting of the electron micrographs.

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List of Figures

Fig. 1. Transmission electron micrograph of chlorite ($\leq 2 \mu\text{m}$) set in Epoxy plastic and thin-sectioned by a diamond-knife ultramicrotome (a) at intermediate magnification, showing some torn areas in the Epoxy; (b) at high magnification, showing $13.9 \text{ \AA}$ crystallographic spacings by phase contrast imaging; (c) same, with an area (arrow) not in proper position to show a phase contrast image.

Fig. 2. Transmission electron micrograph of chlorite sections taken rapidly with through-focus technique to minimize specimen heatings (a) showing $7.22 \text{ \AA}$ spacing; (b) same, with phase change fringes (PC); (c and d) same with areas of 7.22 and $13.9 \text{ \AA}$ spacings in different parts of the same crystal.

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