Clays and Clay Minerals, Vol. 33, No. 5, 463–467, 1985.

NOTES

ORDERED 1:1 INTERSTRATIFICATION OF ILLITE AND CHLORITE: A TRANSMISSION AND ANALYTICAL ELECTRON MICROSCOPY STUDY[1]

Key Words—Analytical electron microscopy, Chlorite, Illite, Interstratification, Lattice fringe image, Transmission electron microscopy.

Mixed layering of dioctahedral and trioctahedral phyllosilicates has rarely been observed. Page and Wenk (1979) and Knipe (1981), however, noted mixed-layered illite/chlorite in lattice fringe images as observed using transmission electron microscopy (TEM), and Craw *et al.* (1982) reported biotite/kaolin mixed layering on the basis of powder X-ray diffraction data. Bailey (1982) pointed out the possibility of 1:1 di- and trioctahedral mixed layering in tosudite (1:1 regularly interstratified chlorite/smectite). From transmission and analytical electron microscopy (TEM-AEM), Iijima and Zhu (1982) reported an intergrowth of muscovite and biotite. Recently Veblen (1983), using the same technique, presented evidence for submicroscopically intergrown layers of kaolinite and wonesite (trioctahedral Na mica) and interstratifications of the trioctahedral phyllosilicates chlorite, wonesite, biotite, and talc. Lee *et al.* (1984) reported that the mixed layering of illite/chlorite is random at an individual layer level and that it separates into discrete packets of illite and chlorite layers as burial metamorphism proceeds. Lee and Peacor (1983) also described transitions within individual layers, from dioctahedral to trioctahedral phyllosilicates, in regions of specimens where layers of illite (10 Å), chlorite (14 Å) and berthierine (7-Å, serpentine-type structure) were randomly interstratified. In the present paper an ordered 24-Å, 1:1 illite/chlorite mixed-layer material is reported from the Martinsburg Formation at Lehigh Gap, Pennsylvania.

EXPERIMENTAL

An outcrop of the Martinsburg Formation at Lehigh Gap, Pennsylvania, is composed of rocks representing a continuous transition from mudstone to slate within 130 m of exposure. Detailed descriptions of the outcrop were given by Holeywell and Tullis (1975), Lewis (1980), and Lee *et al.* (1984). The sample examined in the present study is from the intermediate range of the transition where well-defined slaty cleavage is not developed in hand specimens (see Holeywell and Tullis, 1975).

An ion-thinned specimen was prepared following procedures described by Blake *et al.* (1982) for a study using the JEOL JEM-100CX scanning-transmission electron microscope (STEM). The sample was oriented so that the phyllosilicate layers were perpendicular to the plane of observation, i.e., parallel to the electron beam. The microscope was fitted with a solid state detector for energy dispersive X-ray (EDX) analysis and was modified as described by Blake *et al.* (1980) and Allard and Blake (1982) for accurate and high-resolution analytical electron microscopy.

Bright-field lattice fringe images of 00*l* diffractions were obtained using a through-focus imaging technique. The image taken at the focus which gave the highest contrast then reflected true lattice periodicities without adopting high-resolution structure-imaging techniques. Therefore, conditions for high-resolution imaging did not have to be calibrated for lattice periodicities of 7 Å or larger (Allpress *et al.*, 1972; Anderson, 1978). Rapid damage of phyllosilicates (especially illite) by the electron beam greatly limited the time of observation. To compensate for this restriction, the magnification for studies of such minerals was kept significantly lower than the maximum capability of the instrument. EDX analyses were carried out by comparing the peak intensity ratio of each element to Si for the unknown and standards, as described by Cliff and Lorimer (1975). The standards used were adularia from Gotthard, Switzerland, for K and Al and Marjhalari olivine ($Mg_{1.8}Fe_{0.2}SiO_4$) for Mg and Fe. The analysis of a sample at thin edges does not require correction for atomic number, absorption, and fluorescence effects (within 10% error) according to Goldstein *et al.* (1977). The analysis of K in illite was difficult because K diffused away from the area of analysis, and the

[1] Contribution Number 404 from the Mineralogical Laboratory, Department of Geological Sciences, The University of Michigan.

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https://doi.org/10.1346/CCMN.1985.0330514 Published online by Cambridge University Press

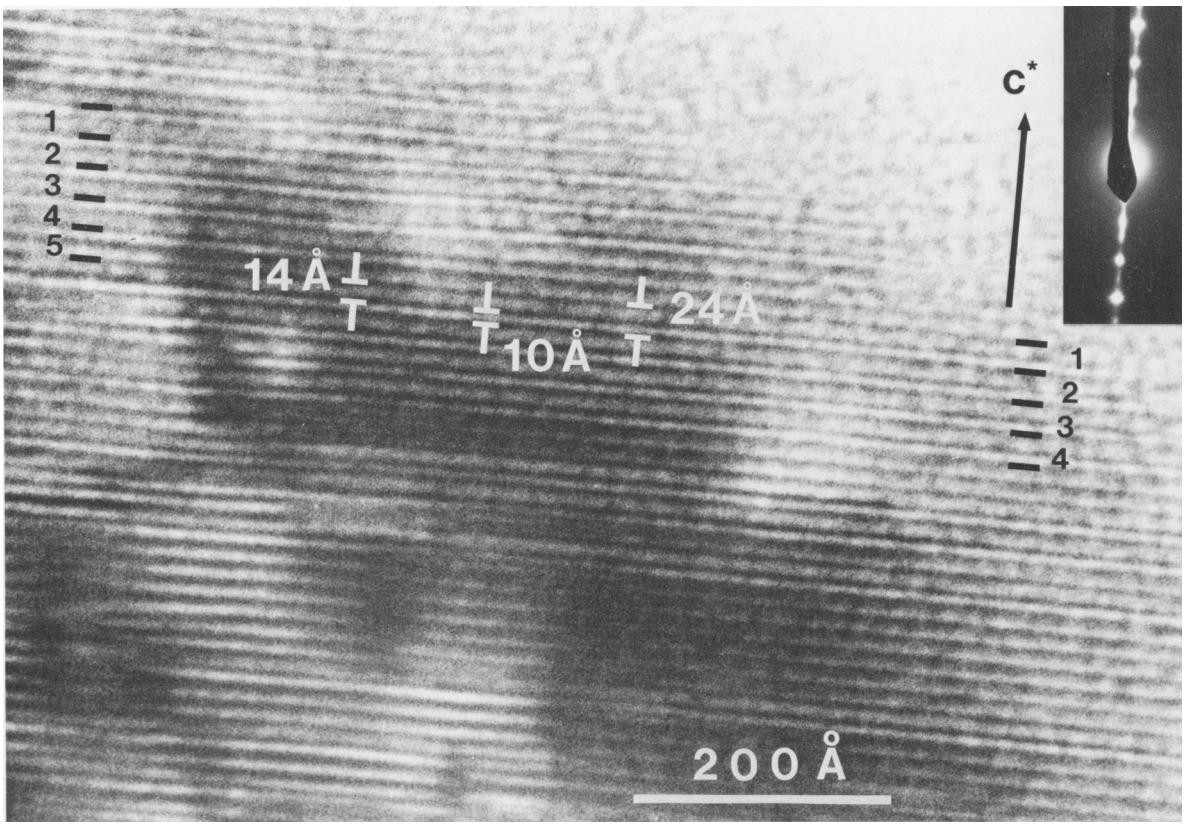


Figure 1. Lattice-fringe image of typical illite/chlorite interstratification. The interstratification is random in general, although short-range 1:1 ordering can be seen in some areas. The electron diffraction pattern in the inset shows streaking and diffuseness along c* superimposed on 10-Å illite and 14-Å chlorite patterns.

resulting amounts measured were lower than the actual concentrations. Craw (1981) demonstrated that EDX counts for K in electron microprobe analysis vary significantly due to K mobility under the electron beam. Diffusion of K is affected by many factors, including thickness of the specimen, electron beam intensity and size of the analyzing beam. Optimum conditions of the instrument for the analyses were therefore calibrated and used to obtain consistent results in K content between the standard and the specimen.

OBSERVATIONS AND DISCUSSION

Many phyllosilicate grains in the sample displayed random mixed layering of illite and chlorite as shown in Figure 1. Lattice fringes shown in Figure 1 represent structural layers of illite and chlorite with periodicities of 10 and 14 Å, respectively. In Figure 1, regions of 1:1 ordered illite/chlorite mixed layering can be seen with 24-Å periodicity, although the 1:1 mixed layering is limited only to small regions. Faults in 1:1 ordering of illite/chlorite are common; indeed, 14-Å layers can be seen next to other 14-Å layers. This disorder in 1:1 ordering is also reflected by streaking along c* in the inserted diffraction pattern. The diffraction pattern also contains the 00*l* sequences of regular 14-Å chlorite, the layers of which are in an area outside of that shown in the figure. Lastly, the grains that displayed local 1:1, ordered mixed layering were associated with regions that also contained randomly interstratified illite/chlorite. No exceptions were observed.

Figure 2 is a lattice fringe image of a region showing relatively extended units of ordered 1:1 illite/chlorite. As many as 9 consecutive units of 24-Å periodicity were observed. As a consequence, the corresponding selected-area diffraction pattern shows very little diffuseness parallel to c* and has well-defined, sharp reflections with 24-Å periodicity.

The chemical compositions of randomly and regularly interstratified regions of phyllosilicate grains must be a composite of the compositions of illite and chlorite (see Figure 2 of Lee and Peacor, 1983). The individual chemical compositions of illite and chlorite were estimated from the composite analysis in the following way. First, the composition of illite in the illite/chlorite interstratification was assumed to be the same as that of the homogeneous illite found in other grains of the

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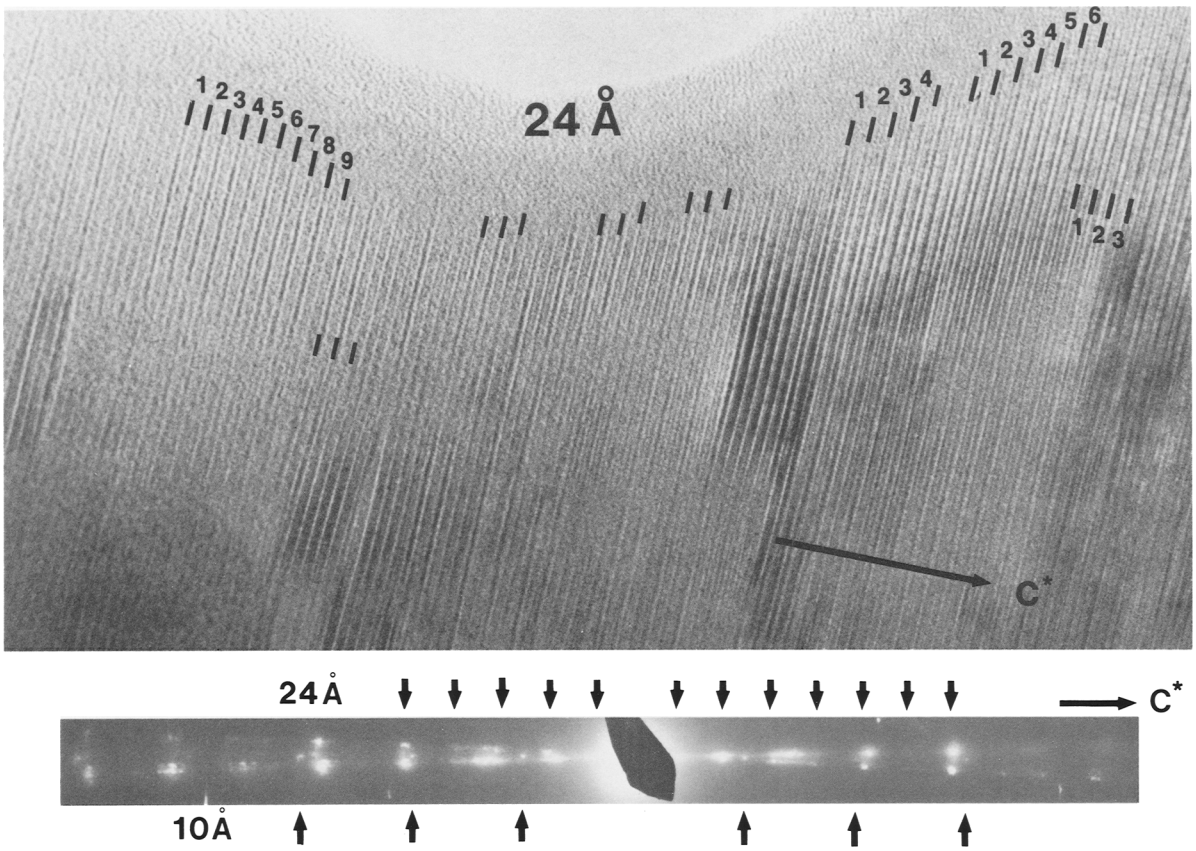


Figure 2. Lattice-fringe image and electron diffraction pattern of a crystal that shows interstratification of illite and chlorite. The crystal contains an area of the ordered 1:1 mixed-layered phase larger than that of any other grains observed. The electron diffraction pattern shows relatively sharp reflections of 24-Å periodicity. The 10-Å 00*l* reflections are from the illite layers outside the photograph.

same sample (Table 1). The proportion of the illite component in the mixed-layered region was then determined using the K content of the mixture (40% illite and 60% chlorite from the analysis in Table 1), assuming that all of the K was in the 10-Å illite component. This illite:chlorite proportion is consistent with the proportions of lattice fringes in the figure. The illite component was then subtracted from the total analysis, leaving the chlorite component as the remainder (see Table 1). The resulting chlorite composition is high in Fe and Mg (Fe > Mg) and low in Al and is similar to that of the average chlorite (Table 1) in the entire sample. These analyses therefore support the concept of interstratification of dioctahedral illite and trioctahedral chlorite. Detailed AEM data for homogeneous illite and chlorite from the same sample were given in Lee *et al.* (1984).

The possibility exists that the 10- and 14-Å components have similar, average, di- and trioctahedral components, as suggested by D. Veblen (Johns Hopkins University, Baltimore, Maryland, personal communication, 1984); i.e., all 2:1 layer units may be almost identical, with no division into separate illite-like 10-Å and chlorite-like 14-Å subunits. If so, charges in the interlayer regions must all be identical, with no potential for ordering of K vis-à-vis $Mg(OH)_2$. The ordering of K and $Mg(OH)_2$ into interlayer units must in turn be coupled directly with charge and composition differences within alternate 2:1 layers. Because the lattice fringe images and electron diffraction patterns indicate that two different phases with d values of 10 and 14 Å alternate in a regular manner, these subunits cannot be identical, and therefore compositions must be different. Nevertheless, we had no direct way of determining the composition of individual layers, and it is possible that alternate 2:1 layer units were at least related, if not identical in composition, even though the likelihood of this compositional similarity is small.

Random interstratification of illite and chlorite were observed only in those mudstones that were clearly part of a transitional diagenetic sequence toward slate (Lee *et al.*, 1984). The equivalents of these samples that had been transformed to slate displayed no local illite/chlorite mixed layering. Instead, regions within

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Table 1. Analytical electron microscope data[1] for illite, chlorite and mixed-layer illite/chlorite (I/C).

Element	Illite[2] (cations)	Chlorite[3] (cations)	Illite/chlorite (I/C) Mixed-layer[4] I/C	Illite[5] in I/C		Chlorite[3] in I/C (cations)
Si	6.2	4.8	1.00	0.40		5.1
Al^{IV}	1.8	3.2	0.86	0.34	IV	2.9
Al^{VI}	3.6	1.8			VI	1.6
Fe	0.2	6.3[6]	0.75	0.02		6.2
Mg	0.2	3.9	0.49	0.01		4.2
K	1.2	—	0.08	0.08		—

[1] Analysis conditions: 100 kV, 100 μA, manual condenser lens (No. 1) current of 170 mA, beam size of ~0.1 μm and 35° specimen tilt angle.

[2] Average of three analyses of a transitional sample normalized to 12 total tetrahedral and octahedral cations.

[3] Average of 61 analyses of 11 different grains. Normalized to 20 total cations.

[4] Values presented are molar ratios to Si converted from the measured intensity ratios. Average of 5 analyses of the same sample as in footnote 2.

[5] The proportion of illite in the mixed-layer illite/chlorite estimated from K contents of the analysis. The illite composition in footnote 2 was used. Values are molar ratios. The value for Si indicates that there is 40 mole percent illite in the mixed layer which is consistent with the proportions of lattice fringes in Figure 2.

[6] 1.4 ferric and 4.9 ferrous iron atoms, as calculated from charge-balancing considerations.

an individual grain were found to be composed of ordered chlorite which formed packets of layers several thousand Ångstrom units thick which in turn were adjacent to packets of homogeneous illite (or muscovite) layers. These relations demonstrate the transitional nature of the illite/chlorite mixed-layer structures in a very low grade metamorphic environment. Lee *et al.* (1984) hypothesized that the randomly interstratified material was a result of transition of an original Fe-Mg rich smectite such that the trioctahedral and dioctahedral components of this precursor phase were represented, to a first approximation only, by chlorite and illite, respectively.

The *b* crystallographic dimensions of the illite and chlorite were calculated from the compositions in Table 1 using the equation given by Radoslovich (1962). They show a difference of 0.3 Å between illite (b = 9.00 ± 0.03 Å) and chlorite (b = 9.30 ± 0.03 Å). This rather large difference implies that considerable strain must exist across the layer boundaries, which are at least semi-coherent as shown in Figures 1 and 2. Such misfit further implies that ordered mixed layering of this type should not be stable over large volumes. This admittedly qualitative reasoning implies that ordered 1:1 mixed-layer illite/chlorite units should be found only as metastable structures under conditions of low-temperature diagenesis. As temperature increases to greenschist facies conditions, such complex mixed-layering may be expected to be replaced by packets of layers of the separate phases, as is observed in other specimens.

ACKNOWLEDGMENTS

The manuscript was reviewed by Robert Wintsch of the Department of Geology, Indiana University, and Eric Essene of the Department of Geological Sciences, The University of Michigan. Wintsch is especially thanked for providing the samples. The authors thank David Veblen of Johns Hopkins University for his insightful comments on crystal structure and chemistry of mixed-layer phyllosilicates. This study was supported by NSF grant EAR-8107529 to Donald R. Peacor.

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(Received 26 January 1984; accepted 22 February 1985; Ms. 1329)

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