

X-RAY DIFFRACTION CRITERIA FOR THE CHARACTERIZATION OF CHLORITIC MATERIAL IN SEDIMENTS¹

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ABSTRACT

Recent surveys of clay mineral assemblages in argillaceous sediments have indicated that chloritic minerals are of more frequent occurrence and of greater significance than was formerly recognized.

The wide latitude of compositional variations within the chlorite crystallization scheme introduces enough complexity into the x-ray diffraction identification and characterization of these minerals that a detailed description of a few typical clay mineral associations seems justified.

For the simplest cases, in which resolution of diffraction features from entirely chloritic grains can actually be demonstrated, analyses may be highly reliable. Further, for many unresolved instances, simple heat treatments effect reliable identifications.

For more complicated assemblages, in which coherently scattering domains are mixtures within themselves, individually planned heating or swelling reactions may become necessary.

Typical natural examples are illustrated, for which apparently proper distinctions have been made for characterizing associations on mono- and mixed-clay mineral grains.

The schematic analysis of the structure of the chlorite minerals was one of the first made for the layer silicate type (Pauling, 1930), and the structure has since been amply confirmed and refined in considerable detail for several specific examples (McMurchy, 1934; Brindley and Ali, 1950). Two of the earliest analyses of bi-mineral associations of layer silicates within a given macroscopic crystal were also made up of minerals of chloritic nature (Gruner, 1934; Hendricks and Jefferson, 1938). Other investigators, notably Barshad (1950) and several French authors (Cailliere and Henin, 1949; Bloch, 1950) have demonstrated laboratory "diageneses," some within rather sizeable crystal grains.

The frequency with which materials based on, or related to, the chlorite crystallization are encountered in sediments is only currently being fully realized (see titles in this volume). The concept that much clay mineral material is subject to extensive transport by weathering agencies, retaining large articulated skeletons, coordinated just as in their solid state, which

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simply lose and gain a few soluble ions in changing environments, has attracted the attention and interest of students of sediments in many fields.

It is planned in this short review to enumerate a few of the associations which are encountered frequently and to illustrate their x-ray diffraction effects.

The current widespread use of recording x-ray "spectrometers" or "diffractometers" is an especially fortunate circumstance. The flaky, fine-grained texture of the clays lends them to easy preparation of settled slides of a high degree of preferred orientation, such that all critical scattering effects fall on the pole of the aggregate, which is precisely that pole which the recording instruments scan. Records are thus in a semi-direct relation to the layer representations in reciprocal space.

Figure 1 is a schematic diagram of the separate 00/ reciprocal lattice nodes of the several layer lattice types most commonly encountered in the clay minerals. For any ideal mineral its successive nodes are precise

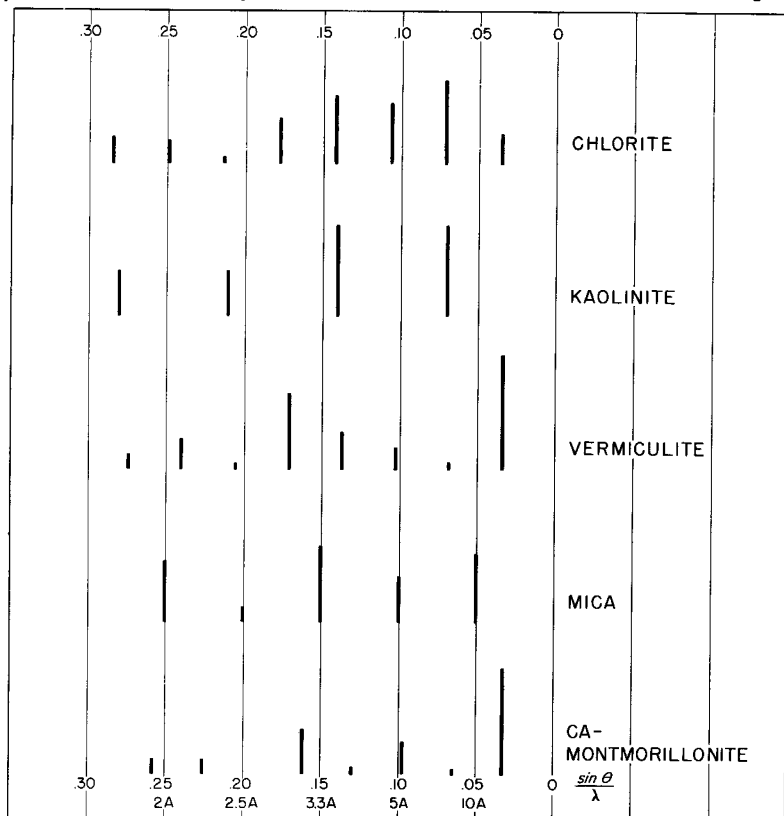


FIGURE 1.— Schematic representation of the relative positions of 00/ reciprocal lattice nodes for several characteristic layer silicates encountered in clays.

integral multiples, and this is characteristically true for kaolinite and muscovite, and commonly true for chlorites. Illites range from substantially integral sequences to obviously modified arrays. It is fortunate that, for many of the ancient sediments, representatives of these three groups conform sufficiently to their respective types that the ordinary procedures of powder analysis are applicable. Reference to Figure 1 does indicate, however, that resolution of kaolinite and chlorite peaks, for example, is a close question at best, and may be lost at specific chlorite compositions.

Recent studies of contemporary sediments concur that much of the mass of sediment discharged by rivers into the oceans is transported in a degraded, ion-deficient condition which one may vaguely describe as montmorillonite-like or possibly illite-like. In a marine environment regaining of suitable ions rebuilds domains into better and better-ordered assemblages, with improved crystalline character.

The chloritic materials afford an opportunity for analysis on a rather complex basis. Figure 2 is a schematic representation of the layer structure

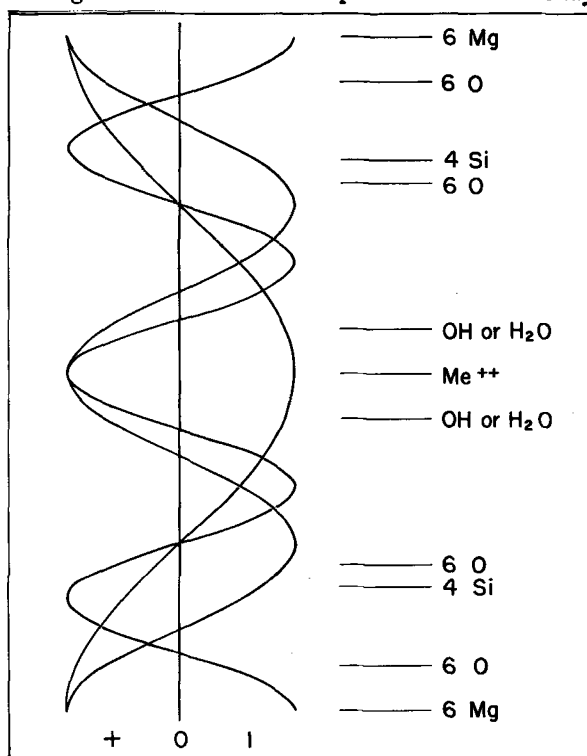


FIGURE 2.—Phase relationships in 14A minerals. First- and second-order net amplitudes are + with respect to origin at layer center, and third-order amplitude is—. Deficiencies of interlayer scattering matter strengthen first order and weaken second and third. Excesses have opposite effects.

suitable for discussion of the relations between chemical composition and x-ray diffraction character. The middle portion is familiarly called the brucite layer. The analysis by Brindley and Ali (1950) of the modification of well-crystallized chlorites by heating confirms in a general way the intensity trends which are realized as the brucite portion is modified. Removal of scattering matter, whether by physical or chemical means, intensifies specific orders and diminishes the intensities of others. The sparsely populated interlayer state (population by exchange ions and water) is the air-dried stage of Ca-montmorillonites and of vermiculites. The precipitation of brucite in this space is easily accomplished in the laboratory, and it is only natural to assume that the Mg^{2+} (and Fe^{2+}) content and high pH of sea water cause the same precipitation.

Neither laboratory nor natural precipitations necessarily completely saturate the interlayer space, however, and since the more loosely bound states have a slightly greater average layer thickness, the precise spacings of reciprocal lattice nodes are decreased, the diffraction character becoming that of a mixed layer assemblage. As will be shown later, there is fair evidence that interlayer matter actually does tend to become regular within any one given layer, rather than partially filling all layers to equal extent. Recent chamosite analyses (Brindley and Youell, 1953) suggest that the state of oxidation of iron-bearing chlorites would also be reflected in small displacements of reciprocal lattice nodes.

Since the establishment by Hendricks and Teller (1942) of the principles of scattering of x-rays by mixed layer assemblages, interlayerings have become increasingly frequently recognized. The pertinent observation is that random mixtures of two (or more) species afford scattering maxima whose positions are intermediate between their respective reciprocal lattice nodes, and whose intensities increase with relative nearness of the nodes. For all practical purposes, positions of maxima may be taken as varying linearly between respective lattice nodes. Maxima in the actual Hendricks and Teller mixing function deviate only slightly from the positions for which average phase angles are whole numbers. For a first maximum this position represents the average thickness of the several layers of a domain. When such maxima are broad and fall upon steep flanks of an observed intensity curve, positions do migrate up such flanks, but the broad maxima are necessarily the weaker, and errors introduced by ignoring the effects are probably less than uncertainties in the reduction of data.

In reduction of data from spectrometer records registered under Brentano focusing conditions, it is observed that reduction as for Debye-Scherrer lines reproduces reality better than reduction as for an extended face. An illustration is not easily drawn for the chlorites, but is included later in connection with associations of extraneous layers with illites.

Scattering maxima for mixed associations of two kinds of layers, each near 14A thick and differing by only a few percent, do not depart from

positions of integral order sequences until relatively high orders, not necessarily observable in diagrams complicated by presence of other minerals. Hydrous layers do collapse on heating more readily than brucite layers, and even a small number of collapsed layers distributed among uncollapsed layers can be detected. It is equally true that hydrous layers may be distinguished by expansion (with glycol, for example) but heating techniques are easier to demonstrate.

The consequence of the above relations is that mechanical mixtures of kaolinite with chlorites are identifiable either on the one hand by natural resolution or on the other by heat treatment chosen to induce resolution. The point may seem trivial now, but considerable doubt must be entertained whether such distinctions have always been properly made in the older literature.

Illustrations in Plate 1 show a sediment in which the character of the chlorite member is such that kaolinite peaks would clearly have been resolved if kaolinite had been present, a sediment in which both are present and resolved, and a sediment in which both are present but not resolved.

Heat treatments of the second case illustrate the responses which are critical, and the proximity of kaolinite and chlorite nodes constitutes an internal standard which relieves the need for meticulous positioning of slides, which may be difficult because of warping during heat treatments. In this case it is readily apparent that the chloritic component has lost intensity relative to kaolinite following firing to only 400°C. The next succeeding heat has deteriorated both components. The salient consequences are that the 7A feature of the chlorite is displaced to a smaller angle, and the 3.5A feature to a larger angle, each relative to the kaolinite. Calibrations also establish that 14A features are displaced to larger angles.

The interpretation is that within coherently scattering chlorite domains some particular layers have collapsed to thicknesses of only 9 or 10 Å, presumably because their brucite layers were deficient in the original state. Reference to Figure 1 recalls that, relative to chlorite, nearest nodes for a 9 or 10 Å layer fall between the first and second chlorite reflections, and to the left of the 4th. Displacements in the 5A region are apparently too small to be noticeable. This can actually be taken to indicate that collapsed layers are in fact near 9.4Å or 9.5Å rather than either somewhat thinner or thicker, for a second node of a 9.4 or 9.5Å layer is nearly coincident with the chlorite third-order node.

For an unresolved case, as in Plate 1(g), meaning is thus given, for example, the low-angle bulge developed on the 7A feature by heating to 400°C. One can conclude that the integral sequence of the original is a superposition of kaolinite nodes on chloride nodes, and not simply a chlorite set of anomalous intensities. The interpretation is also supported by the presence of a distinct 37.5° reflection. Typical chlorite compositions give little or no intensity at the 6th order position, but kaolinite has a distinct third order of intensity about $\frac{1}{8}$ that of its second.

This 37.5° generalization is not an unequivocal "truth," but has great supplementary value. In approximate terms the scattering amplitude for the sixth order for chlorite is a little less than the difference between the scattering power of all the oxygen and the scattering power of all the octahedrally coordinated cations, and is near zero for many common compositions. The related amplitude for kaolinite (which lacks central symmetry) is the vector sum of the above term and a scattering power term for all the silicon, disposed to it at about 90° . It is always as great as the scattering power of all the silicon both for kaolin minerals and for possible Mg or Fe analogues.

Detailed examinations of the relative intensities of basal reflections of sedimentary chlorites, as well as of better crystallized examples, frequently indicate that no solution for chemical composition exists. In such instances the explanations of anomalies are to be sought in geometrical considerations, as in the analyses by Dr. Brindley in this same program.

The trace reproduced in Plate 1(a) is an example. Although the general trend of intensities is superficially typical for a chlorite it is apparently true that odd orders are somewhat less intense relative to the even than would be predicted by any specific chlorite crystal model. (Note that the 7th order is augmented by an illite reflection.) A simple one-dimensional synthesis of the difference between the observed sequence and that anticipated from a model indicates that some scattering matter at the silicon level of the model is actually on the opposite side of the nearest adjacent oxygen level. Such moderate departures from type are not considered to invalidate description of their phases as chloritic materials.

The foregoing discussion has applied to components in which chlorite is dominant within individual scattering domains. Mixed layer assemblages of chloritic layers with micas are also recognizable. Among the better crystallized types, the clear examples of hydrobiotite have probably been well enough reviewed to require no attention here (Walker, 1951; Bradley, 1950).

The association of extraneous layers with mica in illites is also well known, but can be amplified by discussion of a few illustrations.

The modifications of mica diffraction maxima imposed by the presence of a few thicker layers, either chloritic or expandable, are on the low-angle side of the first mica node and on the high-angle side of the third.

In the absence of a rigorous analysis of the intensities of diffracted radiation under the operating conditions of focusing spectrometers, one is forced to rely on rather qualitative observation. At low angles all traces seem to indicate anomalously high intensities inversely proportional to the diffracting angle. Angle and sine being essentially equal, it is convenient to apply the standard Debye-Scherrer intensity correction factor to these traces from aggregates which actually resemble more an extended crystal face.

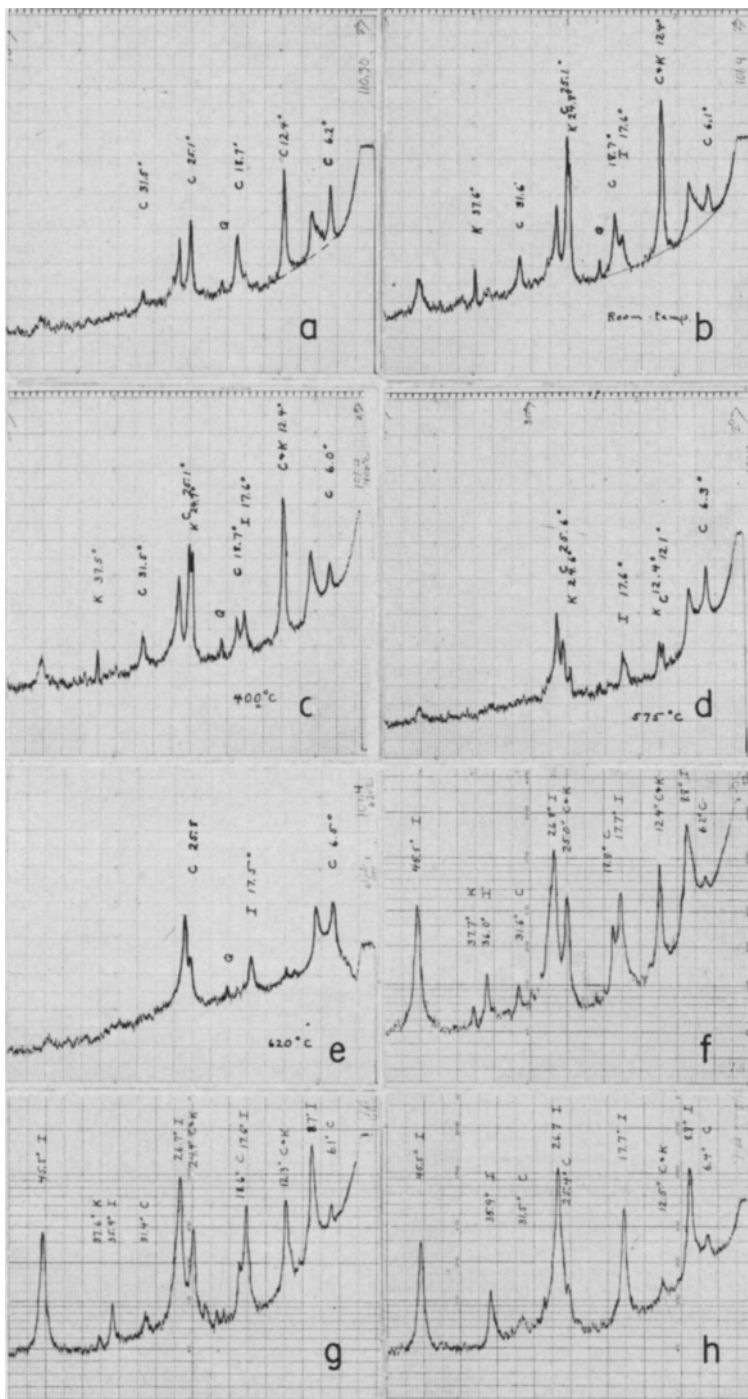


PLATE 1.—Spectrometer records of several oriented clay mineral slides containing a chloritic mineral member.

- a. Chlorite (with modified illite and quartz).
- b. Chlorite and kaolinite maxima resolved at about 25° (also with modified illite and quartz).
- c. Slide (b) after heating to 400° C. Some decline in third- and fourth-order chlorite intensities (illite modification reduced).
- d. Slide (b) after heating to 575° C. Both intensities and positions of chlorite maxima are altered. Kaolinite maxima are sharply reduced.
- e. Slide (b) after heating to 620° C. Only the modified chlorite sequence (and illite and quartz effects) remains.
- f. Chlorite and kaolinite maxima not resolved (illite also prominent and some quartz present).
- g. Slide (f) after heating to 400° C. Displacement of the chlorite reflection at 12.5° is indicated by a shoulder on the low-angle side of the unmodified kaolinite feature.
- h. Slide (f) after heating to 550° C. Modified chlorite sequence, trivial kaolinite remnants, and the prominent illite sequence.

All thin lines on traces have been blackened freehand for reproduction. Each record extends from $2\theta = 0^\circ$ to $2\theta = 50^\circ$.

A record of a typical illite, made up of thin packets of 10A layers, is reproduced in Figure 3. Diffuseness of maxima is such that quite different reduction factors are applicable on the high- and low-angle flanks. Actual shape of the first maximum is sketched by a dashed line on the low-angle side reduced point by point according to a relation

$$I \text{ corrected} = I \text{ observed} \times \frac{\text{Debye-Scherrer factor at } \theta_{001} + \delta}{\text{Debye-Scherrer factor at } \theta_{001} - \delta}$$

where θ_{001} is the Bragg angle for the first maximum. It is seen that the real feature is about as symmetrical as are the succeeding orders for which corrections would be trivial.

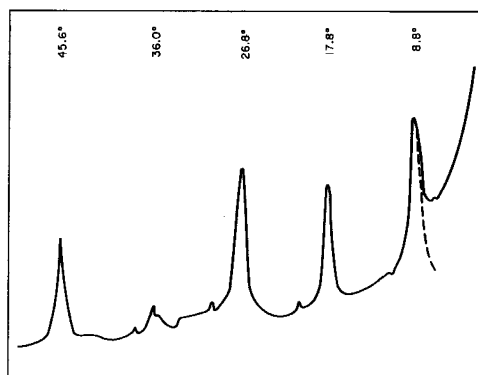


FIGURE 3.—Tracing from a spectrometer record for an unmodified illite specimen. The dashed line indicates the real shape of the first maximum after correction for relative diffraction efficiencies over the angular spread of the broad maximum.

Diagrams of illites modified by small proportions of oversize layers within packets exhibit real asymmetry, with significant diffraction on the low-angle side of the first maximum and on the high-angle side of the third. Oversize layers are commonly about 14A, and if these swell in liquids or collapse readily at moderate heats, they may be called montmorillonitic; if not, chloritic.

The Hendricks-Teller formulation applies to "infinite" arrays in random sequence, and such conditions substantially prevail in many hydrobiotites and metabentonites. In shales it seems more commonly true that scattering domains vary in the richness of the proportion of extraneous layers, yielding effects for continuously varying proportions, which either may or may not have local maxima relating to abundant ratios.

To attempt to integrate quantitatively such vague gradational features would probably be an abuse of data, but it is reasonably reliable to estimate qualitatively that diffraction effects of modifying layers either are or are not important in a given angular position, and to observe whether they are or are not displaced by swelling or heating techniques.

Illustrations chosen for Plate 2 represent assemblages for which the appraisals noted seem justified. The principles illustrated have been applied successfully to extensive surveys of Illinois Paleozoic clays and shales.

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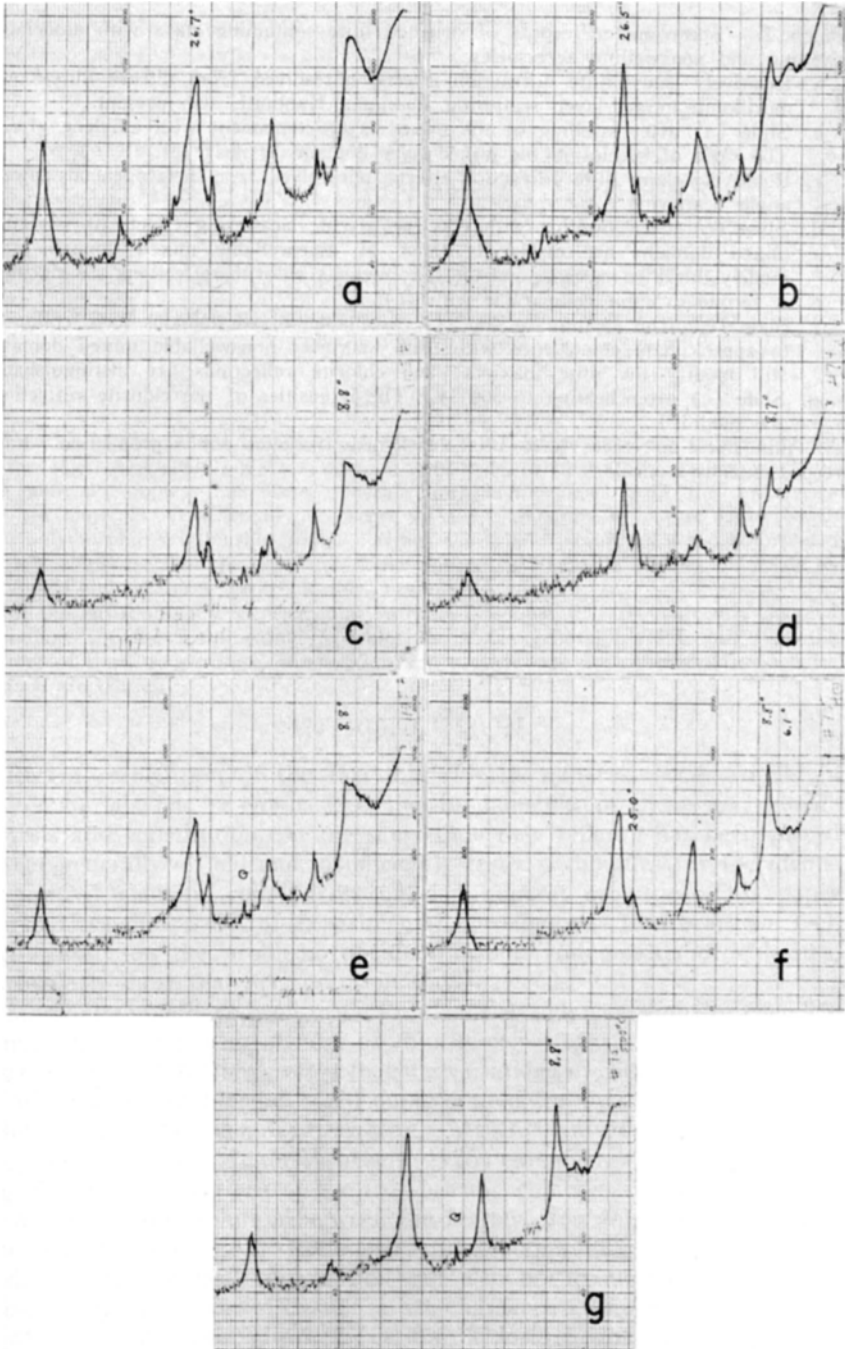


PLATE 2.—Spectrometer records of oriented illite containing clays with associated swelling and nonswelling accessories.

- a. Relatively sharp illite diffraction effects, unresolved from diffuse illite-montmorillonite mixed-layer scattering maxima. Kaolinite also present.
- b. Slide (a) after swelling of the mixed layer component with ethylene glycol. The ratio of species in the mixed-layer domains is near 1:1.
- c. Relatively sharp illite diffraction effects, unresolved from heterogeneous lower-angle scattering.
- d. Slide (c) after swelling with ethylene glycol. Scattering effects of swellable mixed domains are displaced; those of nonswellable mixed domains still modify the illite maxima, and the low intensity chlorite reflections are clarified.
- e. A second example comparable with (c).
- f. Slide (e) after heating to 400° C. Swellable mixed domains have collapsed to approximate coincidence with illite maxima; nonswellable mixed domains still modify the illite maxima; and chlorite reflections are distinguishable.
- g. Slide (e) after heating to 500° C. The intensities of the chlorite reflections are modified.

All thin lines on traces have been blackened freehand for reproduction. Each record extends from $2\theta = 0^\circ$ to $2\theta = 50^\circ$.