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DISTINCTION BETWEEN KAOLINITE AND CHLORITE IN RECENT SEDIMENTS BY *X*-RAY DIFFRACTION

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ABSTRACT

In a study of Recent deep-sea sediments from the Atlantic, Antarctic and western Indian Oceans, kaolinite and chlorite have been routinely differentiated by resolving, respectively, their second and fourth order basal *x*-ray diffraction peaks at 3.5 Å. This distinction has been confirmed in these sediments by the relative intensities of all the low-order kaolinite and chlorite basal reflections, their d spacings, their reaction to hot HCl treatment and to potassium acetate and ammonium nitrate intersaltation treatments. The method is simple, involves only minor changes in *x*-ray diffraction conditions and requires no chemical or thermal treatment of the sample. However, resolution of the 3.5 Å peaks should be used in conjunction with the usual diffraction scan in order to detect other minerals or chlorites of different chemical compositions which may contribute other peaks in the 3.5 Å region and obscure or preclude kaolinite-chlorite distinction by this method.

INTRODUCTION

It is difficult to distinguish between kaolinite and chlorite by *x*-ray diffraction techniques when both are present in a clay mineral assemblage (Griffin and Goldberg, 1963; Griffin, 1962; Johns and Grim, 1958; Murray and Harrison, 1956). This is due to the similar d spacings of the kaolinite (001) and chlorite (002) at 7 Å, and the kaolinite (002) and chlorite (004) at 3.5 Å. Distinction based on differences in the *b* cell parameter as seen in the (060) reflection is usually not possible because of the similar *b* parameters of other layered silicates present. Workers have used various techniques to distinguish kaolinite from chlorite, most involving thermal and/or chemical treatment prior to or after making the usual preferred orientation slide. Preferential destruction of chlorite basal planes other than (001) by heating in the region of 450° C. has been used as a criterion. Uncertainties in this method arising from variations in chlorite composition and crystallinity have been discussed by Martin Vivaldi and Gallego (1961), Nelson (1960), Zen (1959) and Nelson and Roy (1954). The use of a variety of heating temperatures and heating times by various workers has further complicated thermal techniques. Chlorite is preferentially dissolved in dilute hydrochloric acid, and this has been used as a means of distinguishing it from kaolinite (Brindley, 1961; Vivaldi and Gallego, 1961). Wada (1961) and Andrew *et al.* (1960) have suggested that preferential intersaltation of the kaolinite layer lattice by several salts, which results in shifting of its basal diffraction maxima to larger d spacings, can be used to distinguish kaolinite from chlorite. Hashimoto

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and Jackson (1960) and Dixon and Jackson (1960) have used a differential solution-chemical analysis scheme to obtain quantitative distinction between kaolinite and chlorite as well as other clay minerals.

Some of these methods involve less uncertainty than others, but all require more or less elaborate preparatory and analytical techniques. In 1954 Bradley suggested *x*-ray resolution of the "double peaks" at 3.5 Å—the chlorite (004) and kaolinite (002)—coupled with displacement of the peaks after simple heating treatments as a means of distinguishing between the two minerals. He also suggested that the (003) of kaolinite would provide supplementary confirmation of its presence as the (006) of most chlorites has little or no intensity. Pinsak and Murray (1959) used displacement of the double peaks, in addition to behavior of the 7 Å peak after heating the sample to 450° C. Zen (1959) used the non-destruction of the 7 Å reflection on heating to 450° C. as indicative of kaolinite, and noted the occasional resolution of the double peaks at 3.5 Å. It is not clear whether resolution, when observed, was on heated or unheated samples or both. Taggart and Kaiser (1960) utilized the occasional resolution of the double peaks in unheated samples as evidence in the distinction between kaolinite and chlorite.

RESULTS

In a study of the clay mineralogy of Atlantic, western Indian and Antarctic Ocean deep-sea sediments distinction between kaolinite and chlorite has been routinely made on the basis of resolving the (002) kaolinite from the (004) chlorite on untreated slides, using higher resolution *x*-ray diffractometer conditions and slower scanning speed than usually used in clay mineral studies in sediments.[1] To date samples from the top or near-top of almost 500 deep-sea cores have been *x*-rayed. Both the $<2\mu$ and $2–20\mu$ size fractions have been run under fast scan conditions through the whole useful 2θ range and under slow scan conditions (0.05° detector slit) in the 3.5 Å region. Sixty of the core samples were also *x*-rayed under slow scan conditions (with 0.02° detector slit) in the 7, 3.5, and 2.38 Å regions. Forty of the samples were subjected to several of the chemical tests for distinguishing kaolinite and chlorite, though not all tests were performed on all forty samples. The results can be summarized as follows:

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[1] Work was done on a General Electric XRD-5 diffractometer under the following general conditions: Cu radiation, line source; 0.0005 inch Ni filter; 35 kvp; 23 ma; 1° beam slit; scintillation counter detection with pulse height selection at E = 6.5v, Window = 13.5v. The following conditions obtained during "lower resolution" scans, hereafter called "fast scan": $2°2\theta$/min scanning speed; 0.1° detector slit; 1.5 sec time constant; 60 inch/hr chart speed giving 2°/inch on chart. The following conditions obtained during "higher resolution" scans, hereafter called "slow scan" conditions: $0.2°2\theta$/min scanning speed; 0.05° and 0.02° detector slits with time constants of 7.5 and 3 seconds respectively; 12 inch/hr chart speed giving 1°/inch on the chart.

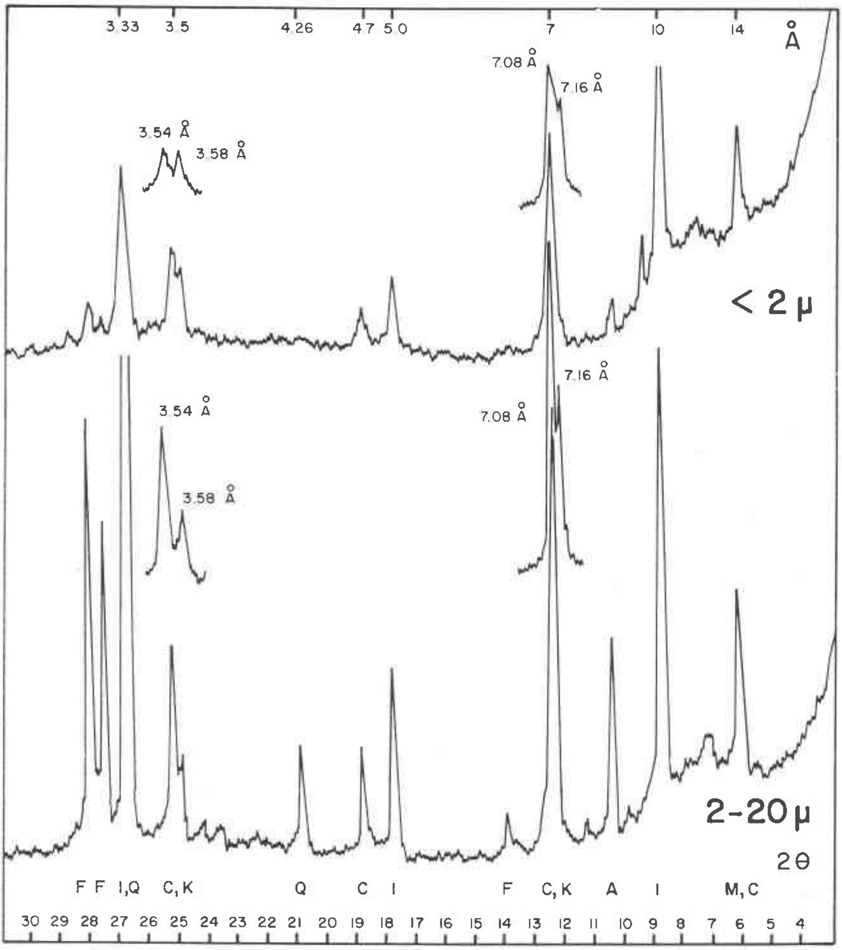

FIG. 1. *X*-ray diffractometer tracings of unglycolated, unheated, preferred orientation size fractions (carbonate-free) from deep-sea core A153–141/9 cm depth (33°26′N-53°48′W). "Slow scans" of 7 Å and 3.5 Å peaks (1°2θ/inch) are traced above corresponding peaks on the "fast scan" diffractograms (2°2θ/inch). The lower 3.58 Å/3.54 Å peak intensity ratio in the 2–20μ fraction compared with the $<2\mu$ fraction is typical of samples from deep-sea sediments. Degrees 2θ at bottom are CuKα radiation. Peaks are identified by the following symbols. C = chlorite, M = montmorillonite, I = illite, A = amphibole, K = kaolinite, F = feldspar, Q = quartz.

(1) The 7 Å peak on fast scan is resolved into two on slow scan whose average d spacings are 7.16 and 7.08 Å each with a variation of about ±0.02 Å (Fig. 1). The average 2θ separation of 0.14° 2θ is sufficient to resolve the peak tops where both are of approximately equal intensity. Where one is considerably more intense, the other becomes a shoulder on

the major peak. The double peaks at 3.5 Å, commonly resolved on fast scan, are much better resolved on slow scan, and improved counting statistics on slow scan make resolution of the peaks more reproducible. Except where one of the peaks is very much more intense and the other becomes a shoulder, the two peaks' average spacings are 3.576 and 3.537 Å (hereafter referred to as 3.58 and 3.54 Å). Variation in spacing of well resolved peaks is about ±0.01 Å.

(2) The ratio of peak heights of the 7.16 to 7.08 Å peaks (small separation precludes measuring peak areas) are approximately the same as the ratio of peak heights of the 3.58 to 3.54 Å peaks in any sample.

(3) In those samples with very strong 7.16 and 3.58 Å peaks, a small peak is often found at 2.384 Å, corresponding to the (003) of kaolinite. In these samples the approximate relative intensities of the 7, 3.58, and 2.384 Å peaks are 10:4:0.2 respectively (measured directly on the diffractogram).

(4) In those samples in which the 7.08 and 3.54 Å peaks are relatively very strong, a peak has not yet been found at 2.384 Å and there is always a peak at 4.72 Å. In these samples the relative intensities (approximately the same for peak heights and areas) corresponding to the first four basal reflections of chlorite are respectively, 7:10:2:5, again, measured directly on the diffractogram. The GE XRD-5 permits use of a 3″ long glass slide for oriented samples so that the entire beam impinges on sample material for angles greater than $4°2\theta$, which includes the chlorite (001), and even the glycol-expanded montmorillonite (001).

(5) The $<2\mu$ fraction of over thirty samples was heated at 80° C. in 2N HCl for one hour and the $2–20\mu$ fraction for four hours. Subsequent *x*-ray study showed that in every case the 7.08 and 3.54 Å peaks had been very much diminished and the 7.16 and 3.58 Å peaks left relatively untouched by the acid treatment.

(6) A slight modification of the kaolinite intersaltation technique of Andrew, *et al.* (1960) has been suggested by John Hathaway (1963, pers. comm.)[1] and applied to about fifteen deep-sea sediment samples. Increase

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[1] Andrews *et al.* (1960) grind the sample with potassium acetate, but even a slight amount of grinding is very detrimental to clay mineral crystallinity for recent sediments. Hathaway suggests mixing clay with potassium acetate in a Vortex mixer and uses a common machine screw in the tube to aid mixing. The writer has found a small piece of Tygon tubing effective. After the mixture sits at 70% R. H. overnight, instead of smearing onto a glass slide, it is smeared onto a porous ceramic slide while applying suction to the underside. The slide is *x*-rayed moist for expansion of kaolinite from 7 to 14 Å. The ammonium nitrate solution can then be sucked through the sample, forming the 11.6 Å kaolinite-salt complex which is *x*-rayed after drying the slide. Using suction on the ceramic slides eliminates most of the salts which so dilute the sample on a glass slide, and seems to aid in achieving preferred orientation of the sample.

of the 14 Å peak on potassium acetate intersaltation, and relative intensity of the 11.6 Å peak after the ammonium nitrate wash, was approximately proportional to the relative intensity of the 3.58 Å peak in the untreated sample. Slow scan of the 3.5 Å region of the acetate-expanded clays in only one case revealed a small amount of unexpanded material at 3.58 Å. Andrew *et al.* (1960) warn that the 6N ammonium nitrate may collapse some kaolinite from the acetate-expanded 14 Å all the way back to 7 Å and that 10N solution must be used in such cases. I have found that even after treatment with 10N ammonium nitrate, slow scans of the 7 and 3.5 Å regions show weak peaks at 7.16 and 3.58 Å not present in the scan of the acetate-expanded sample.

Discussion

Plotting the ratio 3.58 Å peak area/3.54 Å peak area for both size fractions over the entire study area shows a definitely latitudinal dependence, the ratio being highest in equatorial sediments, diminishing with distance from continents, and diminishing to the north and south of the equator. Results (1) to (6) strongly suggest that the 3.54 Å peak represents chlorite and the 3.58 Å peak represents, for the most part, kaolinite. A valid distinction between the two minerals seems possible over wide areas of deep-sea sediments by the relatively simple means of resolving the double peaks at 3.5 Å on untreated samples subject to the reservations discussed in detail below.

Successful application of this method obviously depends upon the absence of other minerals that have reflections interfering with the 3.5 Å double peaks. In most samples, but not all, the presence or absence of other contributors can be determined from the fast scan of the whole diffraction spectrum. Some of the minerals most likely to interfere are zeolites, possibly septechlorites and serpentines, vermiculite and chlorites of "unusual" compositions.

Zeolites, especially the phillipsite-harmotome series, are well known from Pacific Ocean sediments (Arrhenius, 1963; Griffin and Goldberg, 1963) but have been only rarely reported from the Atlantic Ocean (Dekeyser, 1958). This isomorphic series has important reflections which could coincide with both the 7 and 3.5 Å basals of chlorite and kaolinite. However their presence should be detectable by other reflections, especially in oriented samples. These zeolites have reflections parallel to cleavage faces in normally unoccupied 2θ regions. In two samples of sediment from the southwest Indian Ocean, one Paleocene in age, the other Cretaceous (Herman, 1963), I have found what is apparently clinoptilolite in appreciable quantity in the 2–20μ fraction of the non-carbonate material. The mineral in oriented slides has a strong reflection at 3.57 Å, corresponding to a (050) spacing parallel to the perfect (010) cleavage of clinoptilolite. If this mineral is present in quantity it completely precludes kaolinite-chlorite distinction by resolution of the double peaks, but its presence is readily detected in the fast scan by other reflections.

Of the several septechlorites, all of which have 7 and 3.5 Å reflections, chamosite is the one, if any, most likely to be found in the deep-sea sediments. Deer *et al.* (1962, v. 3, p. 166) report it often occurring with other clay minerals in lateritic clay deposits. While the basal spacings of chamosite vary with composition and oxidation state, the range of d(00l) given by Brindley (1961) is 7.04–7.11 Å which is sufficiently smaller in both the first and second order to distinguish it from kaolinite. The range does overlap that of the chlorites most common in the deep-sea samples, but the general lack of references to chamosite in the clay minerals literature of recent sediments suggests that it is not a common contributor to the 7 and 3.5 Å reflections in the deep-sea sediments.

Serpentine minerals have basal reflections around 7 and 3.5 Å, but Brindley (1961) indicates that for the most common serpentines, these basal spacings are sufficiently larger than those of either kaolinite or chlorite to be easily resolved under slow scan conditions. Aluminian serpentines have smaller basal spacings which might coincide with those of kaolinite or chlorite (Bailey and Tyler, 1960; Roy and Roy, 1954). These are rare however, the one known natural occurrence being listed by Bailey and Tyler (1960) among the rare or unusual clay-size minerals associated with the Lake Superior iron ores. The serpentine minerals in the serpentinites of the Mid-Atlantic Ridge are reported to be the more common varieties—chrysotile, antigorite (Shand, 1949)—and therefore could be recognized by their larger 7 and 3.5 Å spacings if significantly added to the sediment by submarine "weathering" and erosion.

Vermiculite has a basal spacing similar to chlorite and therefore might interfere with the kaolinite-chlorite distinction if present. However Barshad (1950) indicates a (002) basal spacing of 15.1 Å for calcium-saturated vermiculite which would make the (008) spacing about 3.7 Å. All samples in the deep-sea sediment study were saturated with calcium ion in preparation for *x*-ray study so, if one can assume that the spacing found by Barshad would apply here, any reflection by vermiculite at 3.7 Å would be easily resolved from the double peaks. Even if the (002) of vermiculite were coincident with the chlorite at 14.1 Å, dioctahedral vermiculite displays only very weak scattering at higher orders compared with that at (002) (Nelson, 1960). Thus its presence in sufficient quantity to affect the kaolinite and chlorite 3.5 Å peaks would be indicated by an abnormally intense 14 Å reflection.

Chlorite itself may range in chemical composition and basal spacing and thereby constitute a hazard to the double peaks distinction of kaolinite from chlorite. The average basal spacing of the "usual" chlorites in the deep-sea sediments is at the low end of known chlorite spacings and suggests high aluminum content (Albee, 1962) and high iron content (Martin, 1955). Brindley and Gillery (1956) reported a similar correlation of d(001) with aluminum and also noted the positive correlation of low basal spacing with high Fe^{2+} and Fe^{3+} content. They also note a tendency in iron-rich chlorites to give even-numbered basal reflections of greater intensity than those of the odd-numbered reflections. The basal intensities and spacings of the chlorites in the presence of a chlorite of different composition with a (004) basal reflection intermediate between 3.58 and 3.54 Å could interfere with resolution of the kaolinite (002) reflection. Several deep-sea samples from this study that may contain "unusual" chlorite are discussed below.

In most Atlantic samples with approximately equal 3.58 and 3.54 Å intensities, the double peaks are resolved to slightly better than half their peak height in the 2–20μ fraction, that is, the bottom of the "valley" between the peaks is slightly below the peaks' half-height. The $<2\mu$ fraction shows poorer resolution, ranging from half to three-quarters of the peak heights. Several samples along the Mid-Atlantic Ridge, particularly near the Azores, exhibit a filling in of this valley and in some samples even have a distinct third peak between the usual double peaks. It is possible that this represents the addition of locally weathered chlorite of lower iron and/or aluminum content from the volcanic rocks of the Ridge. Hathaway (1963, pers. comm.) has found resolvable 3.5 Å double peaks, neither of which is expanded after potassium-acetate intersaltation treatment in the clay fraction of continental shelf sediments in and near the Gulf of Maine. Deep-sea sediments for acetate intersaltation in this study were chosen near the shelf at several locations in the North American Basin to see if this phase was present, and in only one case was any reflection left at 3.58 Å after potassium acetate treatment. Peak area of the remainder was negligible compared to the untreated sample.

CONCLUSIONS

It is possible to distinguish between kaolinite and chlorite in some recent sediments over large areas of the ocean bottom by the relatively simple means of resolving the kaolinite (002) and chlorite (004) reflections by x-ray diffraction. The method should be used in conjunction with the usual diffraction "fast" scans, but requires no special preparation or treatment techniques. It involves only slightly more x-ray time than the usual for clay mineral analysis with only minor modification of diffractometer conditions. Other techniques for distinguishing kaolinite from chlorite such as acid leach, heat treatments and acetate intersaltation can be used in conjunction with the fast scan to check the x-ray technique for other minerals that might contribute to the double peaks.

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