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HYDROXYL STRETCHING FREQUENCIES OF SYNTHETIC Ni-, Al-, AND Mg-HYDROXY INTERLAYERS IN EXPANDING CLAYS*

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Abstract—Interlayers were produced in montmorillonite, vermiculite and hectorite in aqueous suspensions by precipitation from metal chloride salt, by hydrolysis of metal amalgams, and by slow hydrolysis of metal acetate during refluxing. In several systems an external phase of bayerite, gibbsite, or brucite was also formed. A prominent high frequency OH stretching vibration is associated with the interlayer in montmorillonites with approximate frequencies of 3660 cm^{-1} with nickel interlayers, 3690 cm^{-1} with aluminium interlayers and 3710 cm^{-1} with magnesium interlayers. Pleochroism studies indicate transition moment of interlayer OH to be at a relatively high angle to the planar surface of the clay crystals. Aluminium interlayers show some evidence of an additional weak absorption in the lower frequency region of 3570–3600 cm^{-1}. In differential studies the lower frequency absorption is more evident and is shown to be unaffected by orientation. Techniques involving balancing of water deformation bands in differential spectra and D_2O exchange suggest that it is not a water band. D_2O flushing to remove water leaves the low frequency interlayer OH band more prominent in hectorite where the clay crystal OH is at 3680 cm^{-1}. Deuteration studies show that flushing with D_2O at room temperature removes water, and heating at 100°C in D_2O vapor exchanges interlayer OH but not the clay crystal OH. Study of the OD stretching of the systems with deuterated interlayers supports observations made in the OH stretching bands.

INTRODUCTION

HYDROXY interlayers synthetically produced in expanding clays should contribute to the hydroxyl portions of the infrared spectrum. Brydon and Kodama (1966) observed a high frequency shoulder at 3700 cm^{-1} and a low frequency band at 3480 cm^{-1} interpreted to be from the hydroxyl stretching of aluminium interlayers in montmorillonite. Weismiller (1966) and Weismiller *et al.* (1967) also suggested the presence of contributions from two distinct frequencies of interlayer hydroxyls in comparable aluminum interlayer systems but their low frequency band was near 3600 cm^{-1}.

Although X-ray and chemical studies have given considerable information on interlayers, the infrared spectra of the hydroxyls of the various interlayers offer the possibility of providing information on structural arrangement and of showing distinct differences between interlayers produced from different metal ions.

This study was designed to determine the character of the hydroxyl stretching frequency contributions of Ni-, Al-, and Mg-interlayers. It includes a comparison of interlayer preparation by various techniques and an effort to separate the bands of interlayer hydroxyls from the overlapping bands of water and clay structural hydroxyl.

MATERIALS AND METHODS

The clays used were a Wyoming montmorillonite, Wilkinite, with a c.e.c. of 90 me./100g, a Scottish vermiculite, Loch Scye, (Aitken, 1965) with a c.e.c. of about 190 me./100 g and hectorite from Hector, California. All were $<2\,\mu$ with the vermiculite being reduced in particle size by the procedure of Walker (1960).

Aluminum, magnesium and nickel interlayers were made in montmorillonite, and aluminum interlayers were made in vermiculite and hectorite. The montmorillonite exchange complex was presaturated with the metal ion of the proposed interlayer, while with vermiculite and hectorite the sodium forms were used. Interlayers were produced in the clay by precipitation of chloride salts (Slaughter and Milne, 1960), by hydrolysis of amalgams and by refluxing in acetate salt (Besson *et al.*, 1966).

Infrared spectra were obtained on self-supporting films of clays and in some cases from KBr discs. Except where expressly stated, the figures

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are spectra of self-supporting films. Both grating (2–8 μ) and prism (2–16 μ) spectra were run with a Grubb-Parsons S4, double-beam spectrophotometer. Differential spectra were from carefully matched KBr discs and matched self-supporting films.

Deuteration was done in a vacuum system by repeated flushing and evacuating of the sample with D_2O. Some systems required heating to 100°C in D_2O vapor to deuterate interlayer material. The deuterated samples were kept in a vacuum cell with $AgCl_2$ windows for heat treatments and infrared spectral runs.

Specimens for X-ray diffraction measurements were prepared by heating powdered samples to 300°C and sealing in capillary tubes. The specimen was mounted in a powder camera and an X-ray pattern recorded on film using a Raymax 60 X-ray diffraction unit equipped with a cobalt target.

RESULTS AND DISCUSSION

A prominent hydroxyl stretching band appears at a high frequency in all interlayer systems prepared in montmorillonite. The frequency varies from a low of 3660 cm^{-1} with nickel interlayers to a high of 3711 cm^{-1} with magnesium interlayers, and aluminum appears as a broad shoulder at an intermediate frequency of about 3695 cm^{-1} (Fig. 1).

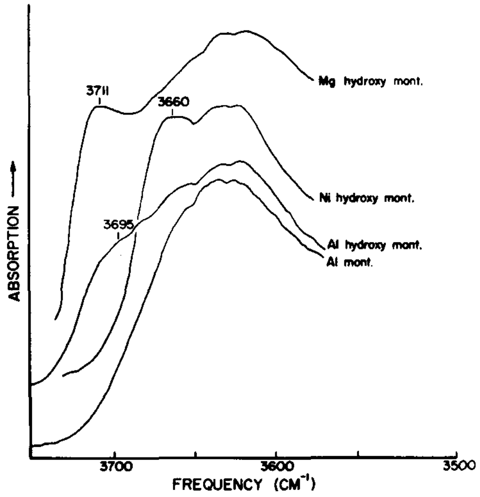

Fig. 1. Infrared spectra of the high frequency OH stretching bands of Mg-, Ni- and Al-hydroxy-interlayer in montmorillonite in comparison to Al-montmorillonite.

As a reference, the spectra of an aluminum montmorillonite without an interlayer is included. The interlayers in Fig. 1 were all prepared by the metal chloride-base titration method at 0·5 N concentrations with 12 me. of metal ion added per gram of clay. The magnesium system was prepared according to Slaughter and Milne (1960). The nickel systems were titrated with 2 OH per Ni. The aluminum system had 1·5 hydroxyls added per aluminum and had a suspension pH below 3·5 which increased to 4·7 on washing.

These high frequency hydroxyl bands are the most prominent evidence of the interlayers in montmorillonite systems. The bands appear to be from interlayers, and possibly similar hydroxy material adsorbed to external surfaces, rather than from hydroxyl forms of the respective metals crystallized in the external phase. The systems were well washed with water after preparation so that fine external phase material and solution salts which would tend to crystallize when the suspension was dried during film preparation should be absent. The common aluminum hydroxide crystals of gibbsite and bayerite do not give prominent bands near 3700 cm^{-1} as does the interlayer system. Characteristic gibbsite and bayerite hydroxyl stretching bands were absent. The aluminum system was only half neutralized, 1·5 hydroxyl per aluminum, which leaves the system too acid normally to precipitate free crystals. Also no X-ray evidence of either gibbsite or bayerite could be found.

Russell (1965) reports that the magnesium hydroxide mineral, brucite, gives a 3700 cm^{-1} band when mechanically mixed with clay. This was in addition to a small 3711 cm^{-1} band which he observed in NH_3 treated magnesium montmorillonite. He attributed the 3711 cm^{-1} band to an interlayer precipitate of magnesium hydroxide formed on ammoniation, and also found the 3711 cm^{-1} band in a prepared magnesium interlayer in montmorillonite. The high frequency bands in the magnesium systems of this study shows up at 3711 cm^{-1} with an additional band at 3700 cm^{-1} in some preparations which had an environment suitable for free brucite crystal formation and which in some cases showed brucite in X-ray pattern. The upper two spectra of Fig. 2 are of the interlayers prepared by Russell.

The nickel interlayer systems were checked only by X-ray for evidence of nickel salts but none appeared to be present. Nickel precipitate produced in the absence of the clay went into solution on repeated water washing comparable to the washing given the nickel interlayer systems.

Comparison of interlayer preparation methods

Magnesium interlayers were prepared by three procedures. The procedure of Slaughter and Milne (1960) was first used. Sodium hydroxide and 12 me. of magnesium as $MgCl_2$ were titrated simultaneously into agitated montmorillonite suspension and the resultant suspension washed. The clay-interlayer produced had a distinct 3711 cm^{-1} band (Fig. 2) which was interpreted as characteristic of interlayer magnesium hydroxide. With 16 me. magnesium per gram of clay it appears that more magnesium hydroxide was produced than could enter the interlayer. This was evident by the production of an external brucite phase in such a sample as shown by the 3704 cm^{-1} band in its spectra.

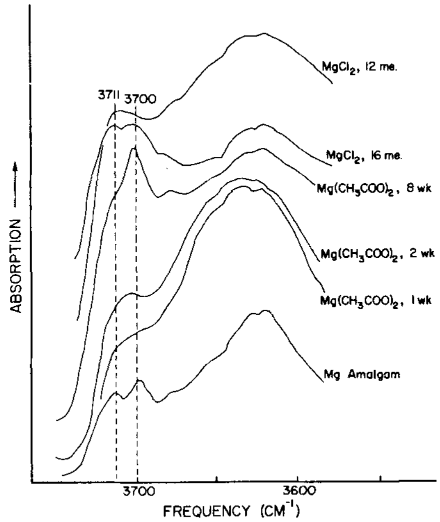

Fig. 2. Infrared spectra of Mg-hydroxy-interlayer montmorillonite prepared by $MgCl_2$ precipitation at 12 me. Mg/g and 16 me. Mg/g; by $Mg(CH_3COO)_2$ refluxing for 2 months with drying, 2 weeks and 1 week; and by Mg-amalgam hydrolysis.

Refluxing Mg-montmorillonite in 1 N magnesium acetate causes gradual hydrolysis of the acetate and production of a hydroxide interlayer. Besson *et al.* (1966) found that refluxing for 6 months gave quite stable magnesium interlayers in Camp Berteaux montmorillonite as evidenced by X-ray, T.G.A., and chemical analysis. Fig. 2 shows that the procedure developed a significant high frequency shoulder on the hydroxyl stretching region of its infrared spectra after one week of refluxing. Continued refluxing for two weeks and one month gave some increased development of the high frequency shoulder, but it remained broad across the interlayer, 3711 cm^{-1}, and brucite, 3704 cm^{-1} regions. X-ray diffraction showed the first evidence of interlayer in the one month sample. The above treatment produced material which gave X-ray diffraction evidence for a trioctahedral serpentine-like phase even before the interlayer appeared. Evidence for a trioctahedral phase was also obtained by Besson *et al.* (1966). After one month the sample was boiled dry and again taken up in water and refluxed for another month. This sample, labeled "$Mg(CH_3COO)_2$, 8 wk" in Fig. 2, showed strong infrared and X-ray evidence for both brucite and interlayer. Its pH was 10·2 compared with pH values of 7·85 for the one and two week samples and 8·3 for the one month sample.

Magnesium amalgam prepared by triturating magnesium metal ribbon in clean mercury reacted quickly with a stirred aqueous montmorillonite suspension and showed evidence of both the interlayer band and a brucite band in the i.r. spectra (Fig. 2). The suspension pH of the final product was 10·4. The excessively rapid hydrolysis of the magnesium and the large amount of mercury needed for amalgam preparation made this appear to be a less desirable method with magnesium than with aluminum. The excess mercury would not separate from the system and resulted in a dark grey suspension.

Aluminum interlayers from various methods of $AlCl_3$ precipitation have been reported by a number of workers including Slaughter and Milne (1960), Sawhney (1960), Shen and Rich (1962), and Barnhisel and Rich (1963). Preparations from $AlCl_3$ precipitation in agitated montmorillonite suspensions show (Fig. 3) the high frequency 3695 cm^{-1} shoulder characteristic of these interlayers. A rate of 12 me. of aluminum as $AlCl_3$ per gram of montomorillonite precipitate with NaOH at a level of 1·5 OH/1 Al gave excellent results.

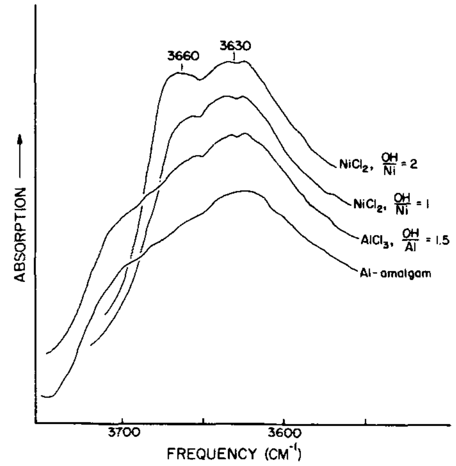

Fig. 3. Infrared spectra of interlayered montmorillonites prepared with 12 me. of metal ion by $NiCl_2$ precipitation with 2 OH per Ni and with 1 OH/Ni; by $AlCl_3$ precipitation with 1·5 OH/Al; and by Al-amalgam hydrolysis.

Neutralizing to 3 OH/1 Al gave nearly equal results but 4·5 OH/1 Al gave a high pH system with no interlayer. The pH after washing was 4·7, 7·5 and 10·4 respectively for the three suspensions. X-ray pattern of samples showed first order spacings of 14·4 Å for the 1·5 OH/Al and 15·2 Å for the 3 OH/Al system.

Aluminum amalgam, prepared by dipping clean aluminum wire into 1% $HgCl_2$-in-acetone for 10 sec, hydrolyzed slowly in a clay suspension. Overnight stirring gave complete reaction when 12 me. of aluminum was added per gram of clay and a good interlayer was produced (Fig. 3). X-ray patterns gave sharp first order spacings of 14·58 Å but with no higher orders evident. The amount of mercury in this amalgam was small and, although it darkened the suspensions initially, it separated and the clay suspension became its natural color with completion of the reaction. Long standing in aqueous suspension caused the interlayer to disappear slowly while external phase gibbsite developed. At 6 months both the i.r. spectra and the X-ray pattern showed only a small amount of interlayer remained while abundant gibbsite was present.

Nickel interlayers were prepared at concentrations of 12 me. nickel per gram of montmorillonite and gave a strong 3655 cm^{-1} frequency presumed to be from the interlayers. Half neutralization of $NiCl_2$, 1 OH/Ni, produced an interlayer which gave a weaker band than complete neutralization, 2 OH/Ni (Fig. 3). X-ray spacings in the system with 1 OH/Ni were 14·45 Å when air dry. When heated and sealed in a capillary 7·78 Å was the highest order evident. The system with 2 OH/Ni gave spacings of 7·53 Å air dry and 7·30 Å heated and sealed. These low spacings must be second order of an interlayer system with a repeat distance of 14–15 Å. The scattering power of the Ni interlayer must match that of the silicate layer leading to a very low intensity of the 001.

Thus a variety of preparation methods gave good Al, Mg, and Ni interlayers. The chloride salt precipitation worked well with all systems and the amalgam system worked especially well with aluminum. Several magnesium systems gave evidence of external phase hydroxyl crystal development. This was particularly evident when 16 me. of $MgCl_2$ were used per gram of clay, when the magnesium amalgam was used, and when the refluxing magnesium acetate system was allowed to go to dryness.

Attempts to produce an interlayer in vermiculite by adding 12 me. of Al as amalgam per gram of Al vermiculite produced only external phase bayerite. $AlCl_3$ titrated to half neutralization with NaOH into agitated Na-vermiculite did, however, produce some interlayer with no evidence of bayerite formation. Interlayer formation in vermiculite has previously been reported by Hsu and Bates (1964). Vermiculite may need more favorable conditions to form an interlayer, as observed by Barnhisel and Rich (1966) and as indicated by the fact that it developed in the Na-vermiculite but not in the Al-vermiculite. Some interlayer was also produced in Na-hectorite by titrating $AlCl_3$ to half neutralization.

External crystals

The external phase crystals produced are illustrated in Fig. 4. The fresh Al-amalgam system of Fig. 3 is a typical aluminum interlayer. Ageing 6 months in suspension gives the spectra of Fig. 4 with its prominent gibbsite-like spectra and very weak interlayer band. The amalgam hydrolysis in

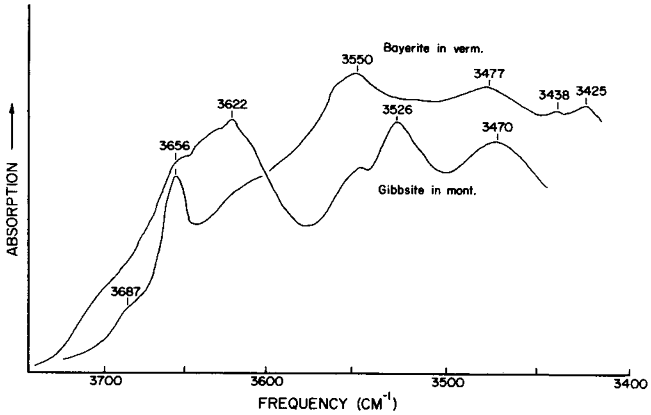

Fig. 4. Infrared spectra showing external-phase Al hydroxides of gibbsite in the aged montmorillonite interlayer system from Al-amalgam treatment and of bayerite in vermiculite treated with Al-amalgam.

Al-vermiculite developed no interlayer but directly produced the bayerite-like constituent shown in Fig. 4. The prominent 3700 cm^{-1} band produced by brucite in the Mg interlayer system was best shown by the amalgam spectrum and the $Mg(CH_3COO)_2$, 8 wk spectrum of Fig. 2.

Orientation effect

The high frequency interlayer bands show some evidence of an orientation effect when studied as self-supporting, oriented films (Fig. 5), which indicates a dipole change more parallel to the *c* axis of the clay crystal. These spectra show it most in the Mg and Ni systems. This orientation effect is even more pronounced when spectra of oriented films normal to the i.r. beam are compared to spectra from powdered samples in KBr discs. The random orientation in the KBr matrix accentuates the absorption by the high frequency hydroxyls of the interlayer beyond that observed in films at 45° angle. Additional data below (Figs. 6, 9) from differential spectra and from deuterated interlayers support the oriented nature of the hydroxyls producing the high frequency band and how the effect more prominently in the Al systems.

Differential observations

The Al interlayer was observed more closely by differential techniques comparable to the studies of Weismiller (1966). This causes an accentuation of spectra differences and a minimizing of likenesses. Al-montmorillonite was used as the reference and Al-OH-montmorillonite (interlayer) as the sample in all systems. Fig. 6 shows the spectra of several differential systems. The spectra from self-supporting films were balanced to show a slight excess of water absorption at the 1640 cm^{-1} deformation frequency for the reference Al-montmorillonite. This shows in the spectra as a negative adsorption band. The Al-OH-montmorillonite then gave a strong positive

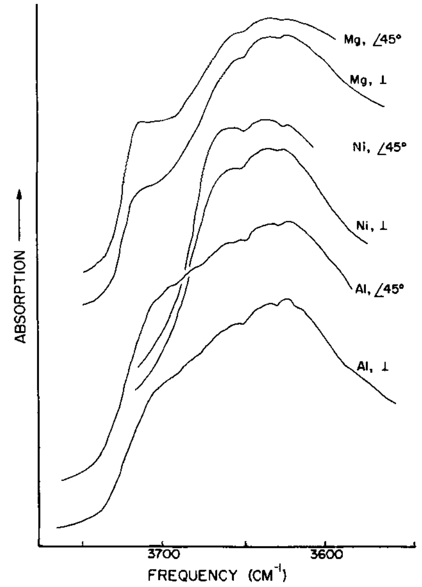

Fig. 5. Orientation effects on the intensity of hydroxyl stretching bands in montmorillonite with Mg-, Ni- and Al-hydroxy interlayers.

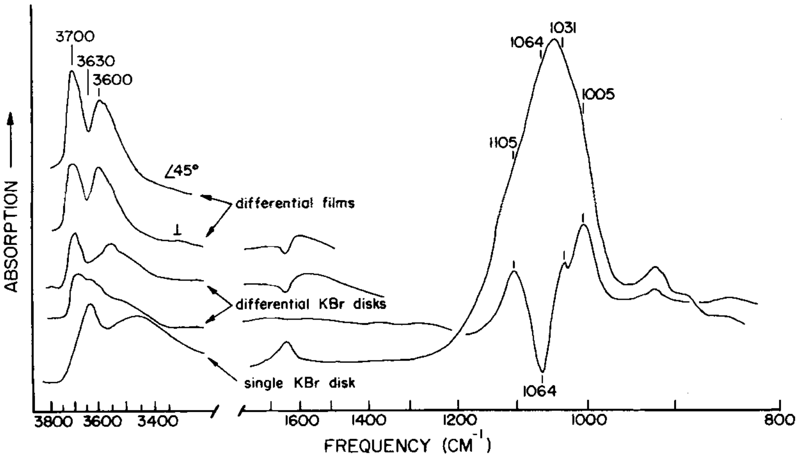

Fig. 6. Differential spectra of Al-hydroxy interlayer montmorillonite vs. Al montmorillonite as films at 45° and 90° to the beam, as KBr discs with greater and lesser amounts of compensating Al montmorillonite, and a nondifferential spectra of Al montmorillonite alone in a KBr disc.

adsorption at about 3700 cm^{-1} and 3600 cm^{-1}. Orienting the samples 45° from normal to the beam greatly accentuated the 3700 cm^{-1} band but did not affect the 3600 cm^{-1} band. No band was observed as low as 3480 cm^{-1} band found by Brydon and Kodama (1966).

Both the 3700 cm^{-1} and the 3600 cm^{-1} bands appear due to the interlayer. The negative water deformation band illustrates the excess water in the reference so the 3600 cm^{-1} band would not appear to be extra water in the interlayer system. The 3700 cm^{-1} and 3600 cm^{-1} could, however, be one broad band appearing as a doublet because of negative absorption at 3620 cm^{-1} from more montmorillonite crystal OH in the reference beam than in the sample. The two differential spectra from KBr discs in Fig. 6 illustrates that small imbalances in montmorillonite in the two beams contribute to the 3620 cm^{-1} region. Both are alike excepting that the lower spectra has less reference sample thickness. The 3620 cm^{-1} band of the sample has risen to mask much of the separation between the high and low frequency bands. The high frequency band would be expected to be more prominent relative to the low frequency band in spectra from KBr than in self-supporting films because of the random orientation in KBr discs maximizing the orientation effect.

Thus it is suggested that the absorption in the differential spectra at about 3700 cm^{-1} and 3600 cm^{-1} are both from interlayer hydroxyls and not from water bands. They also probably arise from two distinct types of hydroxyl groups because the high frequency band is affected by orientation while the low frequency one is not.

Some differences occur in the SiO region of the spectra in KBr discs. The 1105 cm^{-1} and 1010 cm^{-1} absorptions are accentuated and the 1066 cm^{-1} diminished in the interlayered system relative to the reference (Fig. 6). These differences may be related to differences in reaction of the KBr with the two systems, since it is uncertain whether the effects are present in the self-supporting films. Brydon and Kodama (1966) suggest that a 1080 cm^{-1} band in their interlayer system could be from a pesudoboehmite material adsorbed on external clay surfaces.

D_2O observations

The interlayers were not difficult to deuterate but it took more than flushing with D_2O at room temperature, about 25°C, to give a conversion of interlayer hydroxyl to deutero form. This is illustrated in the magnesium system (Fig. 7). Five flushings and standing in D_2O vapor over a period of 2 hr at 25°C removed water but did not affect the high frequency interlayer band in the 3711 cm^{-1} region. Heating at 100°C for 30 min in D_2O vapor nearly completely converted the interlayer to deutero form as indicated by the shoulder at about 2738 cm^{-1} (a D : H factor of 1·355) on the OD band at 2687 cm^{-1}. The 2687 cm^{-1} band gives evidence of being from the OD of the clay crystals.

In the Mg interlayer system containing an excess brucite phase the 3711 cm^{-1} shoulder of the interlayer was readily deuterated by the above treatment but the brucite band at 3700 cm^{-1} showed little or no evidence of deuteration.

Evacuation of the deuterated Mg interlayer systems at 100°C removed much of the D_2O with

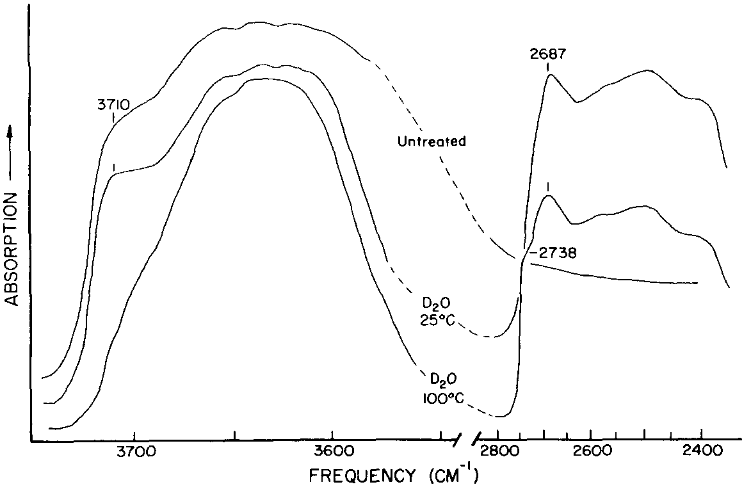

Fig. 7. Infrared spectra of Mg-interlayer-montmorillonite showing response to D_2O treatment of samples which were untreated, D_2O flushed five times over two hours, and in D_2O vapors at 100°C for 30 min.

a consequent improved resolution of the 2738 cm^{-1} band of interlayer OD (Fig. 8). At 200°C the 2738 cm^{-1} band also starts to diminish and at 300°C it is very small presumably because of the exchange of interlayer OD with structural OH of montmorillonite at these elevated temperatures. This is evident from an increased prominence of the 2687 cm^{-1} band. As this exchange occurred there was evidence of the 3711 cm^{-1} band starting to regenerate. As a comparison, deuterated Mg montmorillonite without the interlayer lost nearly all of its D_2O and OD upon evacuating at 100°C for 1 hr. The main remnant was a very small 2687 cm^{-1} hand apparently from exchange of a small amount of clay crystal OH.

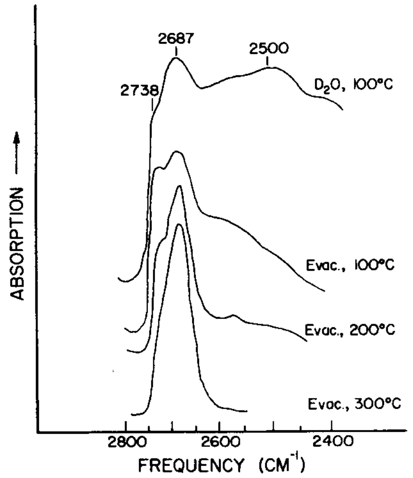

Fig. 8. Effects of heating and evacuating on the OD stretching spectra of deuterated Mg-hydroxy montmorillonite showing spectra of sample deuterated in D_2O vapor at 100°C for 30 min, evacuated at 100°C for 1 hr, evacuated at 200°C for 1 more hr, and evacuated at 300°C for 1 more hr.

Al and Ni systems also required heating at 100°C in D_2O vapor to deuterate the interlayer material. Subsequent evacuation of excess D_2O at 100°C left high frequency OD bands near 2720 cm^{-1} and 2695 cm^{-1} respectively for Al and Ni interlayer, compared to 2684 cm^{-1} when no interlayer was present. As the temperature of evacuation was raised to 200°C the maxima of the OD bands from the interlayer system dropped to about 2687 cm^{-1} which is more characteristic of crystal OH of the clay. The Al system again showed a tendency to regenerate its interlayer OH band. This indicates again that the interlayer OD readily exchange with the crystal OH in montmorillonite at this temperature.

If deuteration of the interlayer in D_2O vapor at 100°C converts both the interlayer OH to OD and H_2O to D_2O, then subsequent rehydration in atmospheric H_2O at room temperature should remove the D_2O and leave only the interlayer OD plus a small amount of clay crystal OD which may have exchanged during the 100°C deuteration. Figure 9 illustrates the resultant OD bands from such a treatment. Al-montmorillonite with no interlayer exhibits a doublet at 2704 and at about 2680 cm^{-1}. Upon heating the rehydrated sample to 100°C under vacuum for 1 hr the 2704 cm^{-1} band diminishes leaving a main band at 2688 cm^{-1} which probably results from deuteration of structural OH. The 2704 cm^{-1} band may arise from hydroxyls associated with the exchangeable aluminum as might be expected to result from hydrolysis in a well washed aluminum clay. The interlayered system again shows both higher, 2720 cm^{-1}, and lower, 2665 cm^{-1} frequency components giving a much broader band with obvious orientation response from the 2720 cm^{-1} band.

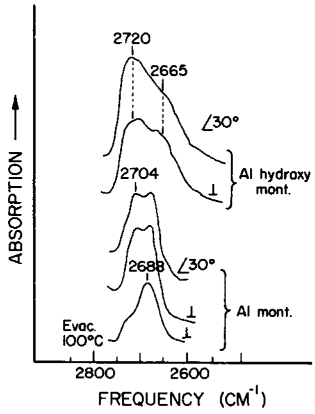

Fig. 9. OD stretching bands of both Al-hydroxy-interlayer montmorillonite and Al montmorillonite after D_2O treatment at 100°C and subsequent rehydration by atmospheric H_2O; normal and at 30 degrees to the incident beam. The lower spectra is the same Al montmorillonite heated at 100°C with evacuation for 1 hr after the rehydration.

CONCLUSIONS

The hydroxy-interlayers contribute to the OH stretching region of clays over a small enough frequency range to indicate considerable organization. This is supported by the orientation effect of the high frequency OH band.

The metal ion used to form the hydroxy interlayer determines the frequency of the OH contribution of the i.r. spectra as would be expected from studies of hydroxyls in clay minerals, micas, and metal hydroxides. The OH stretching frequency of the main band decreased going from Mg to Al to Ni interlayers.

Results are consistent with the suggestions by Hsu and Bates (1964) that the interlayer may be present as a six membered polymer ring. The low frequency band without orientation response could then be the outer OH of this ring and the high frequency band with orientation response could be the inner OH of the polymer as suggested by Weismiller *et al.* (1967). The DTA and DTGA data of Brydon and Kodama (1966) also showed evidence for two kinds of OH in the interlayer. The low frequency band found in the current study was near 3600 cm^{-1} with no evidence of the 3480 cm^{-1} band found in their work.

Added evidence from deuteration and differential studies supports the idea that the low frequency band is not a water band. The observation that it takes a temperature of about 100°C to deuterate interlayer and that it resists reversion to OH on exposure to H_2O vapors at room temperature may offer a technique for observing hydroxyl stretching bands of natural as well as synthetic pseudochlorites since 100°C is too low a temperature to deuterate structural hydroxyl groups of clay minerals to any significant degree.

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Résumé—On a produit des feuillets interstratifies dans le montmorillonite, le vermiculite et l'hectorite en suspensions acqueuses, par précipitation de sel de chlorure métallique, par hydrolyse d'amalgames de métal, et par hydrolyse lente d'acétate métallique pendant le refluage. Dans plusieurs systèmes, on a aussi remarqué une formation externe de bayerite, de gibbsite ou de brucite. Une vibration étendue à haute fréquence OH et d'importance prominente est associée à le feuillet interstratifie dans les montmorillonites avec des fréquences approximatives de 3660 cm^{-1} pour les couches intermédiaires en nickel, de 3690 cm^{-1} bour des feuillets interstratifies en aluminium et 3710 cm^{-1} pour les feuillets interstratifies en magnésium. Des études de pléochroïsme indiquent un moment de transition de le feuillet interstratifie OH qui doit être à un angle relativement élevé de la surface plane des cristaux d'argile. Des couches intermédiaires d'aluminium mettent en évidence la faible absorption supplémentaire dans la zone de plus basse fréquence de 3570 à 3600 cm^{-1}. Dans des études différentielles l'absorption en basse fréquence est plus évidente et elle n'est pas affectée par l'orientation. Des techniques intéressant le mouvement oscillant des bandes de déformation de l'eau dans des spectres différentiels et dans l'échange de D_2O suggèrent que ce n'est pas une bande d'eau. L'enlèvement de l'eau par D_2O laisse la bande de le feuillet interstratifie OH de basse fréquence plus en évidence que dans l'hectorite où le cristal d'argile OH est à 3680 cm^{-1}. Des études de deutération montrent que le balaiement avec D_2O à la température ambiante enlève l'eau et le chauffage à 100°C dans la vapeur de D_2O échange le feuillet interstratifie OH mais pas le cristal argileux OH. L'étude de l'élongation OD des systèmes avec des feuillets interstratifies deutérisées soutient les observations faites dans les bandes d'élongation OH.

Kurzreferat—In Montmorillonit, Vermiculit und Hectorit wurden in wässrigen Suspensionen Zwischenschichten erzeugt und zwar durch Niederschlag aus Metallchloridsalz, durch Hydrolyse des Metallamalgams und durch langsame Hydrolyse des Metallazetates während des Rücklaufes. In verschiedenen Fällen wurde auch eine äussere Phase von Bayerit, Gibbsit oder Brucit gebildet. Eine ausgesprochene Hochfrequenz OH Streckschwingung ist in Montmorilloniten mit der Zwischenschicht verknüpft, und zwar bei ungefähren Frequenzen von 3660 cm^{-1} mit Nickel Zwischenschichten, 3690 cm^{-1} mit Aluminium Zwischenschichten und 3710 cm^{-1} mit Magnesium Zwischenschichten. Pleochroismus-Studien deuten darauf hin, dass das Übergangsmoment des Zwischenschicht-OH an einem verhältnismässig hohem Winkel zu der ebenen Fläche der Tonkristalle ist. Aluminium-Zwischenschichten besitzen Anzeichen einer zusätzlichen schwachen Absorption im niedrigeren Frequenzbereich von 3570 bis 3660 cm^{-1}. In Differenzialstudien kommt die niedrigere Frequenzabsorption mehr zum Ausdruck und es zeigt sich, dass sie orientierungsunabhängig ist. Techniken, die eine Ausgleichung von Wasserdeformationsbändern in Differenzialspektren und D_2O Austausch mit einschliessen, deuten darauf hin, dass es kein Wasserband ist. Spülen mit D_2O, um das Wasser zu entfernen, bringt das Niedrigfrequenzschicht OH Band mehr zur Geltung im Hektorit, wo das Tonkristall-OH bei 3680 cm^{-1} liegt. Deuterationsstudien zeigen an, dass eine Spülung mit D_2O bei Zimmertemperatur Wasser entfernt, und dass Erwärmung auf 100°C in D_2O Dampf das Zwischenschicht-OH austauscht, aber nicht das Tonkristall-OH. Eine Untersuchung der OD-Streckung der Systeme mit deuterisierten Zwischenschichten bekräftigt die in den OH-Streckbändern gemachten Beobachtungen.

Резюме—Прослойки были изготовлены из монтмориллонита, вермикулита и гекторита в водных суспензиях осаждением из хлорида металла, гидролизом амальгам металлов и медленным гидролизом металлического ацетата в ходе дефлегмации. В ряде систем образуется также внешняя (диспергирующая) фаза байерита, гибсита или брусита. Крупное высокочастотное расширяющее колебание OH связано с промежуточным слоем в монтмориллонитах при частотах прибл. 3660 cm^{-1} с никелевыми прослойками, 3690 cm^{-1} с алюминиевыми прослойками и 3710 cm^{-1} с магниевыми прослойками. Исследования плеохроизма указывают, что переходной момент промежуточного слоя OH будет под относительно высоким углом к плоскостной поверхности кристаллов глины. Алюминиевые прослойки дают некоторые указания дополнительной слбой абсорбции в более низком диапазоне 3570–3600 cm^{-1}. В дифференциальных изучениях низшечастотная абсорбция более очевидна и не подвергается воздействию ориентации. Методы включающие уравновешивание полос водяной деформации в дифференциальных спектрах и в обмене D_2O подсказывают, что это не водяная полоса. Промывка D_2O для удаления воды оставляет низкочастотную полосу промежуточного слоя OH более выступающей в гекторите, где кристалл глины OH–3680 cm^{-1}. Исследования дейтерирования показывают, что промывка, пользуясь D_2O при комнатной температуре удаляет воду, а нагрев при 100 °C в парах D_2O обменивает прослоек OH, но не кристалл глины OH. Исследование расширения OD систем посредством дейтерированных промежуточных слоев подтверждает наблюдения, полученные в расширяющих полосах OH.