

FORMATION AND STABILITY OF HYDROXY-Mg INTERLAYERS IN PHYLLOSILICATES*

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Abstract—A study was conducted to (1) determine the conditions of hydroxy-Mg interlayer formation with respect to type of clay mineral, acidity, and time; (2) evaluate the stability of this interlayer to dissolution treatments; and (3) ascertain the effects of such treatments upon the determination of clay minerals in soils and sediments. Hydroxy-Mg interlayers were formed in montmorillonite and vermiculite by adding $MgCl_2$ and NaOH in amounts to give a wide range of pH. The resulting chloritic intergrades were examined after 10 days, 6 months, and 1 yr.

Alkaline conditions favored the formation of hydroxy magnesium interlayers in phyllosilicates. Hydroxy-Mg interlayered montmorillonite which resulted from 10 days equilibration at pH 10.4 did not expand upon solvation with ethylene glycol and exhibited practically no collapse after K-saturation and heating at 550°C. A small amount of interlayer was formed between pH 6.8 and 9.8 (10 days). In contrast, vermiculite exhibited no evidence of interlayer formation at pH values up to 9.7 (10 days). Chloritic intergrades formed at pH 10.7 did not collapse after K-saturation and heating at 300°C but did so at 550°C. Hydroxy-Mg interlayers were not formed in either mineral by using a drying method. This method apparently failed to provide the required alkaline conditions for interlayer formation.

The amount of magnesium interlayers present in the phyllosilicate systems decreased with time. The interlayers formed in vermiculite decreased more sharply than those in montmorillonite.

Sequential dissolution treatments included boiling 2 per cent Na_2CO_3 , buffered sodium citrate-dithionite, a second citrate-dithionite treatment, and boiling NaOH. Hydroxy-Mg interlayers in montmorillonite exhibited a higher stability to sequential treatments than the interlayers formed in vermiculite. A stable 14 Å line was observed in interlayered montmorillonite after the dithionite-citrate and NaOH treatments.

The interlayers in montmorillonite showed a relatively high stability to HCl dissolution treatments. In contrast, most of the magnesium interlayer in vermiculite was removed by two HCl washings.

The reagents used in this study are sometimes used to remove coatings and cementing agents from soil surfaces prior to particle size and clay analysis. The present data show that these treatments also remove some hydroxy-Mg interlayers and produce changes in properties of clays. A proper interpretation of data for clay mineral identification and characterization must recognize these changes due to treatment.

HYDROXY-Mg interlayers in phyllosilicates would be expected to occur in soils (Brydon, *et al.*, 1961) and marine sediments (Rich, 1968), but they have received little attention compared to aluminum interlayers. Singleton (1965) reported the presence of hydroxy-Mg in addition to hydroxy-Al and -Fe in the interlayer space of clays from the Lookout series in Oregon. The formation of secondary chlorite in the dark magnesium clay soils of Hawaii and in Grumusols (Ladybrook Series) of Queensland, Australia, was related to the hydroxy-Mg interlayering in montmorillonite (Jackson, 1959).

The presence of interlayered dioctahedral vermiculite, believed to contain at least some Mg-interlayer, and its relationships to the genesis of heat-stable chlorite were reported in Rappahannock estuary (Nelson, 1960), Neuse River of North Carolina (Brown and Ingram, 1954), and Chesapeake Bay area (Powers, 1954).

Synthetic hydroxy-Mg interlayers were prepared in montmorillonite by Caillère and Hémin (1949), Youell (1960), Slaughter and Milne (1960), and Carstea (1965, 1967). Caillère and Hémin (1949) converted a montmorillonite into a chlorite-like structure by adding ammonium hydroxide to a $MgCl_2$ -montmorillonite suspension. The new montmorillonite-hydroxide complex exhibited d_{001} spacings of 17.6 Å with the initial humidity of formation, 15.2 Å when dried in air, and 14.1 Å when dried at 105°C. Unlike chlorite, the resulting 14 Å clay mineral was unstable to 5 per cent hydrochloric acid or to heating at 350°C. Youell (1960) was able

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to introduce up to five layers of brucite between montmorillonite sheets by using $MgCl_2$ and hydroxyls supplied electrolytically. Slaughter and Milne (1960) prepared $Mg(OH)_2$ -montmorillonite by a slow and simultaneous addition of NaOH and $MgCl_2$ to a dilute clay suspension. Aging and dehydration were required to develop a chlorite-like structure with one brucite sheet between each montmorillonite layer. Synthesis of Mg-interlayers in vermiculite has not been previously reported.

The objectives of the present study were to (1) determine the conditions of hydroxy-Mg interlayers with respect to type of clay mineral, acidity, and time; (2) evaluate the stability of such interlayers to a series of sequential dissolution treatments; and (3) evaluate the implications on methodology and criteria for clay mineral identification.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The less than 2μ size fraction of montmorillonite 11 (Ward's Natural Science Establishment, Inc.) from Santa Rita, New Mexico, and the $50-2\mu$ fraction of African vermiculite from Perlite Company, Portland, Oregon, were used in the study. The $50-2\mu$ fraction of Prochlorite 6 (Ward's Natural Science Establishment, Inc.) from Chester, Vermont, was used for comparison. The bulk samples of the above materials were boiled with Na_2CO_3 prior to size separation (Jackson, 1956). The mica component present in the silt sized vermiculite was converted to vermiculite by treatment with NaCl (Rich, 1960; Carstea, 1965). These treatments were necessary in order to obtain essentially mono-mineralic systems as starting material. The properties of the "cleaned" samples prior to interlayer formation were typical for these types of minerals (Table 1(a)).

Homoionic systems were prepared by five washings with appropriate 1 N chloride solution. The soluble salts were removed by two washings with distilled water followed by washings with 99% methanol.

Interlayer formation

The hydroxy-Mg interlayers were prepared according to a method described by Slaughter and Milne (1960) and Carstea (1965, 1968). This is hereafter referred to as the titration method. A constant amount of $MgCl_2$ (16 me/g) and variable amounts of NaOH were simultaneously added to the dilute clay suspensions with continuous and vigorous stirring in order to obtain a wide range of pH values. In the first set of experiments, the samples were shaken twice daily for 10 days. The pH values were measured after one minute and after 10 days with a Beckman model G pH meter. X-

ray diffraction patterns were obtained at the end of the 10-day period. In order to test the effect of time, a second series of experiments was conducted in which the samples were equilibrated up to 1 yr with occasional shaking. Cation exchange capacities, pH values, and interlayer spacings were measured periodically.

The effect of drying upon interlayer formation was tested by drying 0.25 g portions of Mg- or Ca-saturated montmorillonite or vermiculite at $80^\circ C$ in the presence of $MgCl_2$ for periods ranging from 4 hr to 10 days. The amounts of added $MgCl_2$ varied from 1 me Mg^{2+}/g to 16 me Mg^{2+}/g .

Interlayer stability to dissolution

Sequential treatment. Clay-size montmorillonite and silt-size vermiculite which had been aged for 6 months under different conditions of acidity were withdrawn and subjected to a series of progressive dissolution treatments designed to test the stability of hydroxy-Mg interlayers. Standard clay minerals, without interlayers, were similarly treated in order to assess the extent to which the clay matrices were affected by the selected treatments. The treatments chosen to represent a range of increasing severity of dissolution were: boiling 2% sodium carbonate (Jackson, 1956), buffered sodium citrate-dithionite (Aguilera and Jackson, 1953), and boiling in 0.5 N NaOH (Hashimoto and Jackson, 1958). X-ray diffraction patterns and exchange capacities were obtained after each treatment in the sequence.

HCl treatment. Portions of about 0.5 g samples of the interlayered clays which had been equilibrated for 6 months were treated with 40 ml of cold 0.1 N HCl. The stoppered plastic cups were shaken for 20 min, centrifuged, and the excess acid was poured off. Following two washings with distilled water, subsamples were Ca- and K-saturated for X-ray diffraction analysis and exchange capacity measurements. The HCl treatment was repeated and subsamples were again analyzed as above. Standard clay minerals, without synthetic interlayers, were similarly treated and were used for comparison.

Analyses

Oriented Ca- and K-saturated specimens (Thiesen and Harward, 1962) were first air-dried and then dried at $65^\circ C$ for 2 hr. X-ray diffraction patterns were obtained using $CuK\alpha$ radiation. Ca-saturated specimens were solvated by condensation of ethylene glycol vapor (Kunze, 1955) and again analyzed. K-saturated were heated for 2 hr in a muffle furnace at $300^\circ C$ and $550^\circ C$ before additional diffraction analyses.

Cation exchange capacity was measured by Rich's method (1961) with the modification that

Table 1. Properties of standard clays: (a) as initially used in experimental work (prior to interlayer formation); (b) same as (a) but with sequential dissolution treatments; (c) same as (a) but with two HCl treatments

Materials	1st Order basal spacing (Å)				CEC (me/100 g)
	X-ray pretreatments				
	Ca Solv.	K 65°C	K 300°C	K 550°C	
(a) Prior to interlayer formation					
Montmorillonite ($< 2\mu$)	17.3	11.9	10.1	9.9	108
Vermiculite (50–2 μ)	15.2	10.3	10.2	10.1	152
Chlorite (50–2 μ)	14.2	14.2	14.2	14.2	2
(b) After sequential dissolution treatments					
Montmorillonite ($< 2\mu$)	16.9	12.1	10.2	9.8	116
Vermiculite (50–2 μ)	15.2	10.1	10.0	9.9	172
Chlorite (50–2 μ)	14.0	14.0	14.0	14.0	8
(c) After HCl treatment					
Montmorillonite ($< 2\mu$)	17.2	12.3	11.8	9.8	88
Vermiculite (50–2 μ)	15.2	10.5	10.4	10.0	133
Chlorite (50–2 μ)	<u>14.0*</u> 15.6	14.0	14.0	14.0	15

*Where two peaks were observed, the more prominent one is given first and underlined.

sodium was substituted for magnesium as the replacing cation (Carstea, 1967). Aliquots of NaCl extractions were titrated with cyclohexanediamine tetraacetic acid (CyDTA) using calcium as an indicator (Carlson and Johnson, 1961).

FACTORS CONTROLLING INTERLAYER FORMATION

The formation of hydroxy-Mg interlayers in phyllosilicates is pH dependent (Tables 2 and 3). Unlike aluminum and iron interlayers (Carstea, 1965, 1967), the formation of magnesium interlayers was favored by alkaline conditions. The initial formation and subsequent changes of interlayers over time were accompanied by decreases in pH values (Tables 2, 3 and Fig. 1). These decreases were larger for montmorillonite than vermiculite systems. Significant pH decreases were noted between 6 months and 1 yr of equilibration

(Fig. 1). In the past, decreases in pH have been taken as indicators of hydroxy-Al formation (Ragland and Coleman, 1960) or hydroxy-Fe interlayer formation (Carstea, 1965, 1967). The results of this study show that decreases in pH do not always correlate with the amount of hydroxy-Mg interlayer in phyllosilicates; continued decrease in pH with time was accompanied by decomposition of the magnesium interlayers.

The hydroxy-Mg interlayers were formed only by the titration method. There was no interlayer formation by drying in the presence of neutral salt (data not shown). This was probably due to insufficient alkalinity since pH values above 8 were required even when NaOH was added (Tables 2 and 3). Generally, larger amounts of interlayers were formed in montmorillonite than in vermiculite.

Magnesium-interlayered montmorillonite equilibrated at pH 10.4 (10 days) closely resembled

Table 2. Influence of pH upon hydroxy-Mg interlayer formation in montmorillonite-titration method

OH/Mg solution ratio	pH		1st Order basal spacing (Å)				Degree of interlayer formation*	
			X-ray pretreatments					
	1 min	10 days	Ca	Ca solv.	K 65°C	K 300°C		K 550°C
Check†			15.2	17.3	11.9	10.3	9.9	0
0.00	6.2	6.0	15.2	17.2	12.1	11.3b‡	10.0	0
0.10	7.0	6.8	15.2	17.2	12.1	11.3b	10.0	1
0.20	7.8	7.6	15.2	17.2	12.8	11.8b	10.3	1
0.42	9.1	8.8	15.2	17.2	13.2	12.1	11.0b	2-3
0.62	10.1	9.8	15.2	16.4	15.1	14.2	12.9b	4
1.25	11.1	10.4	15.2	15.5	15.2	14.5	14.5b	5
2.13	12.0	11.7	15.0	16.3	15.0	13.6b	12.6b	3-4

*Arbitrary scale with 0 being none and 5 being most marked.

†Check – standard mineral prior to hydroxy-interlayer formation.

‡b – stands for broad.

Table 3. Influence of pH upon hydroxy-Mg interlayer formation in vermiculite – titration method

OH/Mg solution ratio	pH		1st Order basal spacing (Å)			Degree of interlayer formation*
			X-ray pretreatments			
	1 min	10 days	K 65°C	K 300°C	K 550°C	
Check†			10.3	10.3	10.2	0
0.00	7.1	6.8	10.3	10.3	10.2	0
0.02	8.6	8.3	10.4	10.3	10.2	0
0.06	9.1	8.9	10.6	10.4	10.3	0
0.23	10.0	9.7	14.2	14.2	10.4	3
1.18	11.1	10.7	14.7	14.2	10.5b	4

*Arbitrary scale with 0 being none and 5 being most marked.

†Check – standard mineral prior to hydroxy-interlayer formation.

‡b – stands for broad.

natural chlorite. It did not expand upon solvation with ethylene glycol and exhibited practically no collapse after heating at 300°C and 550°C. Between pH 6.8 and 9.8 (10 days), the material expanded fully or almost fully, but it exhibited increasing heat stability as the pH of equilibration increased.

Unlike montmorillonite, vermiculite showed no signs of interlayering up to pH 9.7 (10 days). At this pH value, the magnesium interlayers produced moderate resistance to collapse at 300°C. The intergrade material resulting at pH 10.7 (10 days) showed chlorite-like properties following K-satura-

tion and heating at 65°C and 300°C. However, this material collapsed following heating at 550°C.

The data clearly show that under the proper conditions, Mg-hydroxy interlayers can be formed in both montmorillonite and vermiculite systems. Unfortunately, they do not provide an insight into the mechanism and most explanations are speculative.

Slaughter and Milne (1960) hypothesized that magnesium hydroxide precipitated first in the suspension and subsequently was adsorbed in the interlayer space of montmorillonite through hydro-

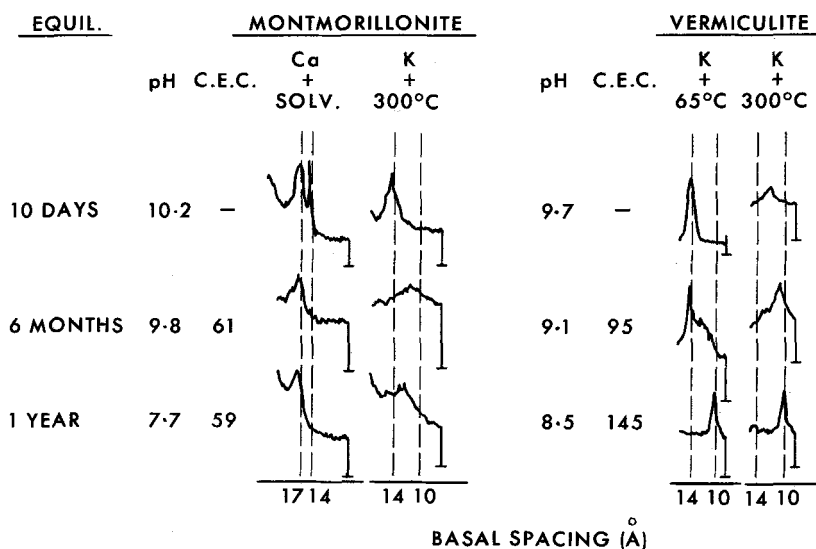


Fig. 1. X-ray diffraction patterns of Mg-interlayered montmorillonite and vermiculite after different periods of time. (CEC = cation exchange capacity, me/100 g).

gen bonding. In contrast, Caillière and Hénin (1949) advanced the idea of direct precipitation and adsorption of brucite-like material in the interlayer position of montmorillonite. The chloritic intergrades* obtained in this study from both montmorillonite and vermiculite exhibited various degrees of completeness as a function of pH. The hydroxy-Mg interlayers in montmorillonite were formed in slightly alkaline conditions. This would suggest that $MgOH^+$ as an intermediate step toward hydroxide formation can be important in the formation of interlayers. The formation of such basic ions would provide for an interlayer with a positive charge in balance with the negative charge of the silicate surface. The resulting ionic bonds are stronger than the hydrogen bonds of an uncharged interlayer. Chaussidon (1963) stated that divalent cations could behave as monovalent ions at pH in the vicinity of 10. Turner and Brydon (1962) reported that magnesium forms insoluble double hydroxides with either aluminum or ferric ions at lower pH than the one necessary to form simple magnesium hydroxide. A co-precipitation of double hydroxides at lower pH is, therefore, likely to occur in nature.

Time

After a 10-day period of equilibration, the X-ray diffraction patterns revealed the existence of ex-

pandable and non-expandable phases in magnesium-interlayered montmorillonite (Fig. 1). Following 6 months of equilibration, the material regained its full expansion upon solvation and exhibited only a partial collapse at 300°C. No significant changes in basal spacings or cation exchange capacity were noted between 6 months and 1 yr. By analogy to aluminum interlayers (Barnhisel and Rich, 1963), it is speculated that hydroxy-Mg moved outside the interlayer surfaces and deposited as hydroxide. In material prepared at pH 11.6 (10 days), the montmorillonite structure was destroyed following 6 months equilibration (not shown).

The hydroxy-Mg interlayers in vermiculite were even less stable with time than those in montmorillonite. Following 1 yr equilibration, the material showed the properties of typical vermiculite.

Type of clay mineral

The greater degree of hydroxy-interlayer formation observed here for montmorillonite than for vermiculite is consistent with structural considerations. This is primarily attributed to the differences in the amount and location of charge for these minerals (Carstea, 1968). Montmorillonite has a lower CEC than vermiculite (Table 1). Further, montmorillonite has a substitution of magnesium for aluminum in the octahedral layer whereas vermiculite has a substitution of aluminum for silicon in the tetrahedral layer. It is expected that vermiculite would have a smaller interlayer space than montmorillonite at the time of hydroxy inter-

*The term "chloritic intergrade" refers to a system with properties intermediate between chlorite and vermiculite or smectite.

layer preparation because the charge density of vermiculite is higher.

Particle size is also important since, at comparable charge densities, the time required for cations or polymers to reach the middle of the interlayer space increases with increasing particle size. Similarly, at comparable particle size, the degree of interlayering with hydroxy-Al and -Fe was higher for montmorillonite than vermiculite because of the differences in charge densities (Carstea, 1968). In the present study, clay-montmorillonite and silt-vermiculite were used. The long term experiments with hydroxy-Mg interlayer formation makes possible the comparison between the two minerals regarding the degree of interlayering. A close inspection of these results revealed a consistency with previous experimental findings and with theoretical considerations.

EFFECTS OF CHEMICAL TREATMENTS ON THE STABILITY OF INTERLAYERS

Sequential treatments

In order to facilitate the interpretation of data, the assumption was made that removal of hydroxy interlayers was independent of amount of interlayer present and dissolution was dependent only on the type of clay mineral. This assumption was necessary

since different amounts of interlayers were probably present in the various samples prior to sequential treatments.

It is also desirable to define two terms as used in this section. Standard clays refer to samples which were not treated and not equilibrated for interlayer formation. Checks refer to samples which were treated and equilibrated for hydroxy interlayer formation but prior to treatment for dissolution.

X-ray diffraction data revealed practically no differences between untreated standard samples and standard samples subjected to sequential treatments (Table 1, (b)). There was a slight increase in cation exchange capacity (CEC) for all standard minerals following the dissolution treatments, indicating some natural interlayers or diluents may have been removed.

The stability of hydroxy-Mg interlayer in montmorillonite was greater than that of vermiculite (Fig. 2). Except for the boiling NaOH treatment, the sequential treatments produced only minor changes in basal spacings and CEC of interlayered montmorillonite. A 14 Å peak, indicative of a chloritic component, was recorded in addition to strong 10 Å lines after NaOH treatment. The 14 Å lines occurred in samples that previously contained randomly interstratified systems as indicated by the

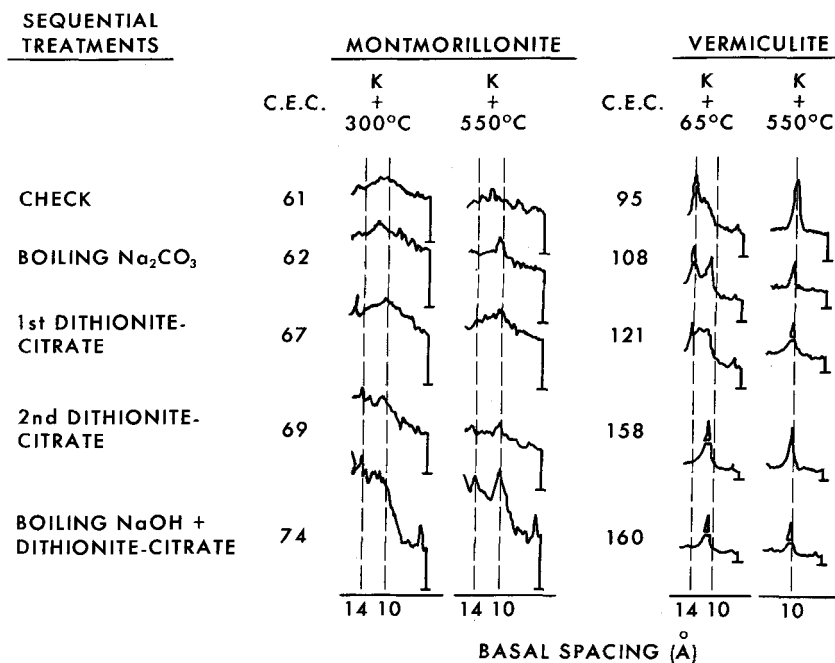


Fig. 2. X-ray diffraction patterns of Mg-interlayered montmorillonite and vermiculite after sequential dissolution treatments. Checks refer to samples which were treated and equilibrated for hydroxy interlayers formation but which were not treated for dissolution (CEC = cation exchange capacity, me/100 g).

intermediate position of the X-ray diffraction peaks. The sequential treatments progressively removed the amorphous coatings and the labile interlayers and resulted in increases in the intensity of the diffraction peaks.

The second dithionite-citrate treatment was effective in removing the hydroxy-Mg interlayer from vermiculite (Fig. 2). Following this treatment, the material exhibited a high degree of collapse and high CEC. The boiling NaOH treatment produced no visible changes in basal spacings and CEC.

The data show that hydroxy-Mg interlayers are removed by chemical treatments which are commonly used alone or in combination for dispersion and particle size separation prior to diffraction analysis. We have therefore adopted the practice of using two subsamples for routine identification and characterization of clays in soil samples. One is subjected to a mild treatment, namely carbonate and organic matter removal, and the clay fraction is separated by using dilute Na_2CO_3 (Jackson, 1956, pp. 32-36 and 123-146). This sample most closely reflects the nature of the clays as they

existed in situ. The other subsample is subjected to additional treatments to remove hydrous oxides, allophanic and other amorphous constituents. Analysis of this sample provides information on the stability of hydroxy interlayers present and the nature of the phyllosilicate matrix.

HCl treatment

The effects of HCl treatment upon standard clay minerals are presented in Table 1, (c). Montmorillonite and vermiculite showed significant decreases in CEC, while the CEC of chlorite increased sharply. The X-ray diffraction patterns revealed practically no changes of basal spacings for vermiculite, moderate resistance to collapse at 300°C for montmorillonite, and the occurrence of an expandable phase in chlorite. The expandable phase, as indicated by the appearance of a 15.6 Å peak, resulted from a partial degradation of the brucite interlayer following the HCl treatments.

Hydroxy-Mg interlayers in montmorillonite were more stable than those in vermiculite (Tables 4 and 5). Following two HCl washings, some inter-

Table 4. Influence of 0.1 N HCl treatment upon hydroxy-Mg interlayer in montmorillonite (pH = 9.8 after 6 months)

Sequential treatments	CEC (me/100 g)	1st Order basal spacing (Å)		Degree of interlayer removal
		X-ray pretreatments		
		K 300°C	K 550°C	
Check*	61	12.5 v.b.†	12.5 v.b.	
First HCl	77	12.5 b‡	10.2	Slight
Second HCl	84	12.6	10.2	Slight

*Check – interlayered material after 6 months equilibration and prior to HCl treatment.

†v.b. – very broad.

‡b. – broad.

Table 5. Influence of 0.1 N HCl treatment upon hydroxy-Mg interlayer in vermiculite (pH = 9.1 after 6 months)

Sequential treatments	CEC (me/100 g)	1st Order basal spacing (Å)		Degree of interlayer removal
		X-ray pretreatments		
		K 300°C	K 550°C	
Check*	95	14.2†	10.6	
		<u>11.8</u>	<u>13.0</u>	
First HCl	133	11.2	10.6	Strong
Second HCl	148	10.3	10.2	Strong

*Check – interlayered material after 6 months equilibration and prior to HCl treatment.

†Where two peaks were observed, the more prominent one is given first and underlined.

layers still remained in montmorillonite as indicated by resistance to collapse at 300°C and by CEC. In contrast, practically all interlayer was removed from vermiculite by the HCl treatment as indicated by collapse of vermiculite upon K-saturation.

SUMMARY

Larger amounts of hydroxy-Mg interlayer were formed initially in montmorillonite than in vermiculite. The interlayers in montmorillonite also exhibited higher stability to dissolution than the interlayers in vermiculite.

The formation of interlayer was strongly dependent upon pH, time and type of clay mineral. The interlayer in vermiculite was formed only in alkaline conditions (pH > 10.0). Although some interlayers were formed in montmorillonite at a pH as low as 6.8, the full development of Mg-interlayer occurred at pH of 10.4. The resulting interlayered montmorillonite closely resembled chlorite.

The amount of interlayers in both minerals decreased with time of equilibration but the decrease was more pronounced in vermiculite than in montmorillonite.

Except for the boiling NaOH treatment, all the sequential treatments produced only minor changes in basal spacings and CEC of the interlayered montmorillonite. A 14 Å peak upon K-saturation and heating, indicative of chloritic components, was recorded in addition to strong 10 Å lines following the NaOH treatment. In contrast, the second dithionite-citrate treatment removed practically all the synthetic interlayers from vermiculite.

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Résumé—Une étude a été effectuée pour (1) déterminer les conditions de la formation des couches intermédiaires d'hydroxyle de magnésium par rapport au type d'argile, de l'acidité, et du temps; (2) évaluer la stabilité de cette couche intermédiaire envers les traitements de dissolution et (3) constater l'effet de ces traitements sur la détermination des minéraux argileux dans les sols et les dépôts. Les couches intermédiaires d'hydroxyle de magnésium sont formées dans la montmorillonite et la vermiculite par l'addition de MgCl₂ et de NaOH en quantités suffisantes pour donner une grande

gamme de pH. Les qualités intermédiaires chloritiques qui en résultent ont été examinées après dix jours, six mois et un an.

Les conditions alcalines ont favorisé la formation des couches intermédiaires d'hydroxyle de magnésium dans les phyllosilicates. La montmorillonite exhibant des couches intermédiaires d'hydroxyle-Mg à partir de dix jours d'équilibrage à un pH de 10,4 ne s'est pas dilatée en solvatisation avec de l'éthylène glycol et ne présentait aucune rupture après saturation de K et chauffage à 550°C. Une petite quantité de couche intermédiaire s'est formée entre un pH de 6,8 et 9,8 (dix jours). Par contraste, la vermiculite ne présentait aucune évidence de la formation de couches intermédiaires aux valeurs de pH inférieures à 9,7 (dix jours). Des grades intermédiaires chloritiques formés à un pH de 10,7 n'ont montré aucune rupture après saturation de K et chauffage à 300°C, mais se sont brisés à 550°C. Aucune couche intermédiaire d'hydroxyle-Mg ne se formait dans les minéraux quand on employait une méthode de séchage. Cette méthode ne semble pas avoir fourni les conditions alcalines nécessaires pour la formation de couches intermédiaires.

La quantité de couches intermédiaires de magnésium présentes dans les systèmes de phyllosilicates diminuait avec le temps. Les couches intermédiaires formées dans la vermiculite diminuaient plus vite que celles formées dans la montmorillonite.

Les traitements de dissolution en série comprenaient une solution bouillante de Na_2CO_3 à 2%, du citrate-dithionite de sodium tampon, un second traitement au citrate-dithionite, et du NaOH bouillant. Les couches intermédiaires de l'hydroxyle Mg dans la montmorillonite ont montré une plus grande stabilité aux traitements en série que les couches intermédiaires formées dans la vermiculite. Une ligne stable à 14° a été observée dans la montmorillonite à couches intermédiaires après les traitements au citrate-dithionite et à NaOH.

Les couches intermédiaires de montmorillonite ont montré une stabilité assez élevée aux traitements de dissolution HCl. Au contraire la plupart des couches intermédiaires de magnésium dans la vermiculite a été extrait par deux lavages à HCl.

Les réactifs employés dans cette étude sont utilisés parfois pour ôter les enduits et les agents liants des surfaces du sol avant d'analyser la grosseur des particules et l'argile. Les données présentes indiquent que ces traitements ôtent également quelques couches intermédiaires d'hydroxyle-Mg et produisent des changements dans les propriétés des argiles. Une interprétation exacte des données d'identification et de caractérisation des minéraux argileux doit reconnaître ces changements dûs aux traitements.

Kurzreferat—Es wurde eine Untersuchung durchgeführt um (1) die Bedingungen für die Bildung von Hydroxy-Mg Zwischenschichten in Bezug auf die Art des Tonmaterials, die Azidität und die Zeit zu bestimmen; (2) die Beständigkeit dieser Zwischenschicht gegen Lösungsbehandlungen einzuschätzen, und (3) die Wirkungen solcher Behandlungen auf die Bestimmung von Tonmineralen in Böden und Ablagerungen festzustellen. Durch Zugabe von MgCl_2 und NaOH in den zum Erhalt eines weiten pH Bereiches erforderlichen Mengen wurden in Montmorillonit und Vermiculit Hydroxy-Mg Zwischenschichten gebildet. Die erhaltenen chloritischen Zwischenstufen wurden nach zehn Tagen, sechs Monaten und einem Jahr untersucht.

Alkalische Bedingungen begünstigten die Bildung von Hydroxymagnesium Zwischenschichten in Phyllosilikaten. Die sich nach einer zehntägigen Ausgleichung bei pH 10,4 ergebenden Montmorillonite mit Hydroxy-Mg Zwischenschichten erfuhren keine Ausdehnung bei der Solvation mit Äthylenglykol und wiesen praktisch keinen Zusammenbruch nach Sättigung mit K und Erwärmung auf 550°C auf. Zwischen pH 6,8 und 9,8 (zehn Tage) bildete sich eine geringe Menge einer Zwischenschicht. Im Gegensatz dazu konnten im Vermiculit bei pH Werten von bis zu 9,7 (zehn Tage) keine Bildung einer Zwischenschicht nachgewiesen werden. Chloritische Zwischenstufen, die sich bei pH 10,7 bildeten brachen nach K-Sättigung und Erwärmung auf 300°C nicht zusammen, taten dies jedoch bei 550°C. In keinem der Minerale bildeten sich Hydroxy-Mg Zwischenschichten wenn eine Trocknungsmethode verwendet wurde. Bei dieser Methode werden scheinbar die für eine Zwischenschichtbildung erforderlichen alkalischen Bedingungen nicht geschaffen.

Die Menge der in Phyllosilikatsystemen vorhandenen Magnesiumzwischenschichten verminderte sich mit der Zeit. Die Zwischenschichten im Vermiculit verminderten sich rapider als die im Montmorillonit.

Aufeinanderfolgende Lösungsbehandlungen umfassten: kochende 2% Na_2CO_3 , gepuffertes Natriumzitat-Dithionit, eine zweite Zitat-Dithionit Behandlung, sowie kochende NaOH. Die Hydroxy-Mg Zwischenschichten im Montmorillonit wiesen höhere Beständigkeit gegen aufeinanderfolgende Behandlungen auf als die in Vermiculit gebildeten Zwischenschichten. Im zwischengeschichteten Montmorillonit konnte nach den Dithionit-Zitrat und NaOH Behandlungen eine beständige 14 Å Linie beobachtet werden.

Die Zwischenschichten in Montmorillonit zeigten eine verhältnismässig hohe Beständigkeit gegen HCl Lösungsbehandlungen. Im Gegensatz dazu wurde im Vermiculit der Grossteil der Magnesiumzwischenschicht durch zwei HCl Wäschen entfernt.

Die in dieser Untersuchung verwendeten Reagenzien werden manchmal zur Entfernung von Beschichtungen und Klebmitteln von Bodenoberflächen vor der Teilchengröße- und Tonanalyse angewendet. Die vorliegenden Daten zeigen, dass diese Behandlungen auch einige der Hydroxy-Mg Zwischenschichten entfernen und Veränderungen in den Eigenschaften der Tone hervorrufen. In einer richtigen Auswertung der Daten für eine Identifizierung und Charakterisierung müssen diese durch die Behandlung hervorgerufenen Veränderungen in Betracht gezogen werden.

Резюме—Проведены исследования по: (1) определению условий образования гидроксимагниевых межслоевых промежуток в зависимости от типа глинистых минералов, кислотности и времени обработки; (2) оценке устойчивости межслоевых промежуток по отношению к различным растворителям; (3) выяснению значения обработок растворителями для определения глинистых минералов в почвах и осадках. Гидроксимагниевые межслоевые промежуток образовывались в монтмориллонитах и вермикулитах при добавлении $MgCl_2$ или $NaOH$ в количествах, обеспечивающих широкие пределы изменения pH. Полученные промежуточные хлоритовые формы исследовались после старения в течение 10 дней, 6 месяцев и одного года.

Установлено, что щелочная реакция благоприятствует образованию гидроксимагниевых межслоевых промежуток в филлосиликатах. Монтмориллонит с гидроксимагниевыми межслоевыми промежутками, который образовался при 10-дневной равновесной обработке реактивами при pH 10,4, не разбухает при насыщении этиленгликолем и практически не разрушается после насыщения калием и нагревания до $550^{\circ}C$. В небольших количествах межслоевые промежуток образуются в диапазоне pH от 6,8 до 9,8 (10 дней). В противоположность этому, в вермикулитах межслоевые промежуток не образуются при значениях pH до 9,7 (10 дней). Хлоритовые промежуточные формы, образующиеся при pH 10,7, не разрушаются при насыщении K и нагревании до $300^{\circ}C$, однако, начинают разрушаться при $550^{\circ}C$. При использовании методики высушивания гидроксимагниевые межслоевые промежуток не образуются ни в одном из минералов. Эта методика, очевидно, не создает щелочной реакции, необходимой для образования межслоевых промежуток.

Количество магниевых межслоевых промежуток в филлосиликатных системах уменьшается с течением времени; количество межслоевых промежуток в вермикулите уменьшается более резко, чем в монтмориллоните.

Последовательные операции растворения включали обработку кипящим 2% раствором Na_2CO_3 , буферным натриевым цитрат-дитионитом, вторичную обработку цитрат-дитионитом и кипящим раствором $NaOH$. Гидроксимагниевые межслоевые промежуток в монтмориллоните обнаруживают большую устойчивость по отношению к последовательной обработке, чем межслоевые промежуток в вермикулите. Монтмориллонит с межслоевыми промежутками после обработки дитионит-цитратом и $NaOH$ давал устойчивое отражение 14 \AA .

Межслоевые промежуток в монтмориллоните обнаруживают относительно высокую устойчивость к действию HCl . В противоположность этому большая часть магниевых межслоевых промежуток в вермикулите удалялась двумя обработками HCl .

Реагенты, использованные авторами, иногда применяются для удаления пленок и цементирующих веществ почв перед определением размера их частиц и анализом глинистой фракции. Данные авторов свидетельствуют о том, что подобные обработки удаляют также и некоторую часть гидроксимагниевых межслоевых промежуток и приводят к изменению свойств глин. Интерпретация данных для идентификации и характеристики глинистых минералов должна учитывать характер этих изменений.