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Hg-complex intergrades in smectite

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COMPLEX intergrades of Al, Mg and Fe in smectites and vermiculites have been well documented both as found in the natural environment (MacEwan, 1950; Dixon and Jackson, 1962; Jackson, 1963 and Singleton, 1966) and as produced synthetically in the laboratory (Sawhney, 1968; Carstea, 1968 and Slaughter and Milne, 1960). However, little or no evidence to my knowledge has been found to indicate the formation of Hg-complex intergrades in the natural environment.

Since the early 1900's, mercury has been added to the soil in the form of air and water pollutants and also as a fungicide on agricultural seed grains (Montague, 1971). Studies by Melton *et al.* (1971) and by the U.S.D.A., as reported by Montague (1971), indicate that Hg remains in the soil for some time. However, the form of the mercury in the soil is not known. The purpose of this note is to present data on the formation of Hg-complex intergrades in smectite.

EXPERIMENTAL METHODS AND MATERIALS

Materials

Montmorillonite from Upton, Wyoming was obtained from Ward's Natural Science Establishment. Vermiculite from Scotscalder, Scotland was obtained from the Macaulay Institute for Soil Research, Aberdeen, Scotland.

The less than 2 μm size fraction of both minerals, obtained by centrifugation, was Ca-saturated by washing three times in a 2N $CaCl_2$ solution, then washed until chloride free as indicated by the silver nitrate test.

Method

Attempts were made to form synthetic Hg-complex interlayers by a two step process: (1) addition of $HgCl_2$ to a 2 weight per cent stock suspension of montmorillonite and vermiculite, and (2) titration of NaOH into these mixtures while stirring rapidly with a magnetic stirrer to give final solutions of 0·2N in Hg ions and OH/cation ratios of 0·0, 2·0 and 2·4 for both the montmorillonite and the vermiculite.

After intervals of 2, 7 and 21 weeks, aliquots from these suspensions were withdrawn. One aliquot was washed twice in distilled water and resuspended, dried on a glass slide and analyzed by X-ray diffraction using a Phillips X-ray diffractometer. The slide was then glycol vapor-treated overnight at 60°C and analyzed again. The same slide was then heated at 350 and 550°C for 1 hr and analyzed by diffraction after each heating. Another aliquot was heated overnight at 60°C in 1N KCl solution and washed several times to remove the excess salt. After resuspension in water the colloid was analyzed by X-ray diffraction following each treatment described above.

The pH of each of the hydroxy–cation suspensions was monitored with a Beckman model 76 pH meter 1 min, 1 day, and 2, 7 and 21 weeks after the reactions were started.

RESULTS AND DISCUSSION

The Hg–montmorillonite and vermiculite suspensions, neutralized to different degrees, flocculated immediately upon contact with the NaOH solution. Slaughter and Milne (1960) suggested that this rapid flocculation results in the early formation of a coating of cation–hydroxy complex material on the clay material which then moves into the interlayer position. This migration would suggest that a longer period of time is required to form hydroxy interlayers from the flocculated material than from a clear OH–cation solution, as is possible with Al (Sawhney, 1968).

Flocculation may not, however, retard the formation of OH-interlayers since hydroxy–Mg interlayers were developed, by the writer (unpublished work), from flocculated suspensions as rapidly as hydroxy–Al interlayers from unflocculated suspensions. After aging 2 weeks, the former were found to be significantly more stable thermally than were the latter. In addition, hydroxy–Mg interlayers which formed in vermiculite were more stable to temperature than those formed in montmorillonite during this aging period, as indicated by X-ray diffraction after the various treatments.

On the other hand, $d(001)$ values indicate that Hg failed to develop stable complex interlayers within the initial two week period in either the montmorillonite or vermiculite. What are believed to be stable Hg-complex interlayers

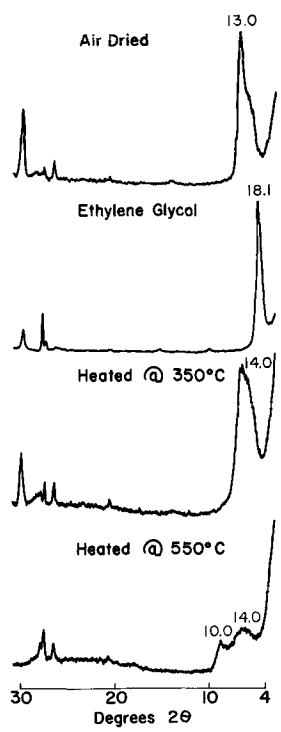


Fig. 1. X-ray diffraction tracings of montmorillonite aged 21 weeks in solutions of OH/Hg = 2·4.

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Table 1. pH of hydroxy–Hg suspensions after various time intervals

Scotland vermiculite	1 min	1 day	2 weeks	7 weeks	21 weeks
OH/Hg 0·0					
2·0	11·86	11·81	12·00	11·40	11·67
2·4	11·95	11·82	12·12	11·63	11·83
Upton montmorillonite					
	1 min	1 day	2 weeks	7 weeks	21 weeks
OH/Hg 0·0	4·77	5·10	5·53	5·23	5·05
2·0	11·91	11·88	12·03	11·50	11·75
2·4	11·99	12·00	12·11	11·67	11·91

were, however, formed in the montmorillonite but not in the vermiculite (Fig. 1), after aging 21 weeks.

pH

For the hydroxy–Hg suspensions, Table 1 shows an apparent increase in pH during the initial 2-week interval, which was followed by a drop in pH after aging 7 weeks to a value somewhat below that observed after 1 min. The pH then increased between 7 and 21 weeks to approximately the 1 min value. However, X-ray diffraction patterns made during the 21 week interval did not indicate a correlation between the development of the hydroxy-complex interlayers and the change in pH.

As indicated earlier stable Hg-complex interlayers were not developed in the vermiculite during the period investigated. The lack of interlayer development was indicated by a complete collapse to 10 Å when heated to 350° C. X-ray diffraction patterns of the montmorillonite hydroxy–Hg samples, after aging 2 weeks in the solutions, displayed only characteristic 17 Å glycol spacings which easily collapsed to 10·0 Å when heated to 350° C. After 7 weeks, hydroxy–Hg suspensions of OH/Hg ratios of 2·0 and 2·4 appeared to form weakly developed interlayer structures in the montmorillonite. However, the interlayers were represented only as a diffuse high-background in the low 2θ region of the diffraction pattern after heating to 350° C. Heating to 550° C resulted in a total collapse of the structure to 10 Å.

Glycolation of the OH/Hg 0·0 and 2·0 samples, aged 21 weeks, produced a basal spacing of 17·3 Å, while glycolation of the OH/Hg 2·4 sample gave an 18·1 Å spacing. The appearance of larger than normal montmorillonite spacings, similar to those observed in this study, have been reported in aluminum (Sawhney, 1968; Carstea, 1968) and magnesium interlayered montmorillonite (Caillére and Hénin, 1949). Upon heating (~ 100° C) these spacings were found to collapse to approximately 14 Å, suggesting the spacings to be, in part, a function of relative humidity. The larger than normal montmorillonite spacings in this study also appears to be a function of relative humidity since heating to 350° C caused a total collapse of the unneutralized sample and 14·5 and 14·0 Å spacings for the OH/Hg 2·0 and 2·4 samples, respectively. The OH/Hg 2·0 sample completely collapsed to 10 Å heating to 550° C, while the OH/Hg 2·4 sample gave 14·0 and 10·0 Å spacings at this temperature. The two peaks of the OH/Hg 2·4 sample probably indicate that some hydroxy-complex interlayers collapsed while others did not, which suggests that not all of the hydroxy-complex interlayers were developed to the same degree.

CONCLUSION

Interlayer Hg-hydroxy complexes were formed in the montmorillonite but not in the vermiculite. However, details of the composition and structure of the interlayer material are not known. To fully evaluate the composition as well as the effects of pH, mineral structure, and OH/cation ratio on the development of the Hg intergrades, a more exhaustive study will be required. However, the fact that Hg-complex intergrade material can form in montmorillonite indicates that it may occur in expansible soil clays. Depending on the stability and resistance to weathering of the interlayer Hg-complexes, this occurrence could be a problem in farming areas where seed grain treated with mercury fungicides have been used, since a small amount of mercury is taken up by the produce of the grain (Montague, 1971).

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