Clays and Clay Minerals, Vol. 31, No. 4, 317–318, 1983.

CHLORITES DIFFERENTIATED FROM INTERGRADE SMECTITES AND VERMICULITES BY SOLUTION STABILITY CRITERIA[1]

Key Words—Chlorite, Intergrade, Smectite, Solubility, Vermiculite.

Those who investigate the mineralogy of soils and sediments quickly find less-than-perfect minerals to be commonplace. Chemical compositions are usually unknown and physical properties commonly depart from available standards. These investigators tend to adopt operational definitions of minerals based mainly upon readily measured X-ray diffraction characteristics. Chlorite, *operationally defined*, might be a mineral that produces a 001 spacing of about 14.0Å on an X-ray powder diffraction pattern of an oriented sample. The 14-Å peak does not expand with addition of glycerol or ethylene glycol, nor does it contract when K-saturated and heated to 300°C. It remains at least partially expanded at 550°C. This definition will include some members of what might be considered to be a gradational series between chlorite at one end and smectite or vermiculite at the other, with hydroxy interlayered minerals in between (e.g., Barnhisel, 1977, p. 331). Whether the hydroxy interlayer materials are smectite-like or vermiculite-like is determined by X-ray powder diffraction after the hydroxy interlayers are removed. A second view might regard the hydroxy interlayer material as "contaminants" that merely prop open adjacent vermiculite or smectite sheets (e.g., MacEwan and Wilson, 1980, p. 234). These materials would thus be considered "contaminated" smectite or vermiculite, but not chlorite or chlorite intergrades.

The concept of intergrade minerals is mainly based upon a gradation in physical properties (especially X-ray diffraction) between smectites or vermiculites and chlorites. The purpose of this investigation is to compare some important chemical properties of hydroxy interlayers in intergrade materials and chlorites, in order to evaluate the desirability of classifying intergrade materials as chlorites.

SOLUBILITY OF HYDROXY INTERLAYERS

The relative stability of solid-phase Mg or Al hydroxide interlayers is most simply obtained by considering pH and Mg^{2+} or Al^{3+} activities in the equilibrium solution. Comparing resultant solution solubilities avoids the necessity of directly considering the complex factors that influence the activity of the solid phase.

Magnesium hydroxide interlayers in chlorite

The solubility of $Mg(OH)_2$ may be expressed as follows:

$$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O,$$
$$pK = pMg^{2+} - 2pH - pMg(OH)_2,$$
$$pH - 1/2pMg^{2+} = -1/2(pK + pMg(OH)_2),$$

where K is the equilibrium constant, p is the negative log of the activity, and the activity of water is assumed to be unity. The larger the value of $pH - 1/2pMg^{2+}$, the more soluble (less stable) is the $Mg(OH)_2$ phase. Recent solubility determinations on two high-Mg and two high-Fe chlorites indicate an equilibrium $pH - 1/2pMg^{2+}$ value of approximately 6.4 for chlorite as compared to 8.4 for brucite (Kittrick, 1982). Thus, to the extent that these four chlorites represent chlorite in general, the brucite sheet in chlorite acts as a stable part of the structure relative to separate-phase brucite (Figure 1). There are no stability determinations on dioctahedral-interlayer chlorites, but it is instructive to contrast the stable chemical behavior of trioctahedral chlorite interlayers with that of the dioctahedral interlayer of intergrade materials.

Aluminum hydroxide interlayers in smectite and vermiculite

The solubility of $Al(OH)_3$ may be expressed as follows:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O,$$
$$pK = pAl^{3+} - 3pH^+ - pAl(OH)_3,$$
$$pH - 1/3pAl^{3+} = -1/3(pK + pAl(OH)_3),$$

where the activity of water is assumed to be unity. The larger the value of $pH - 1/3pAl^{3+}$, the more soluble (less stable) is the $Al(OH)_3$ phase. Of the multitude of investigations on hydroxy interlayers in smectites and vermiculites, only a few have included the necessary solution measurements for estimating the solubility of the hydroxide interlayer. These investigations involved $Al(OH)_3$ sheets that had previously been formed as interlayers in smectite and vermiculite in the laboratory. In the absence of any solubility information on natural intergrade materials, it must be assumed that the natural materials are represented by these few synthetic ones. It was found that $pH - 1/3pAl^{3+}$ was greater for $Al(OH)_3$ interlayers in smectites than for gibbsite (Figure 1) (Turner and Brydon, 1965, 1967; Singh and Brydon, 1967). Thus, in contrast to $Mg(OH)_2$ sheets in trioctahedral-interlayer chlorites, the $Al(OH)_3$ sheets in intergrade smectites are more soluble than their separate-phase counterpart. In fact, it was found that when the $pH - 1/3pAl^{3+}$ of the system was lowered to that of gibbsite, all of the $Al(OH)_3$ interlayers were removed from the smectites and converted to separate-phase gibbsite (Turner and Brydon, 1965; Singh and Brydon, 1967).

Brydon and Turner (1972) found a similar situation with $Al(OH)_3$ sheets in vermiculite. Initially, the $Al(OH)_3$ sheets were more soluble than gibbsite. With time the $Al(OH)_3$ sheets approached the solubility of gibbsite and were removed from the vermiculite. Unlike smectite interlayers, the $Al(OH)_3$ sheets were not completely removed during the time period of the experiments (285 days). The removal of $Al(OH)_3$ sheets from

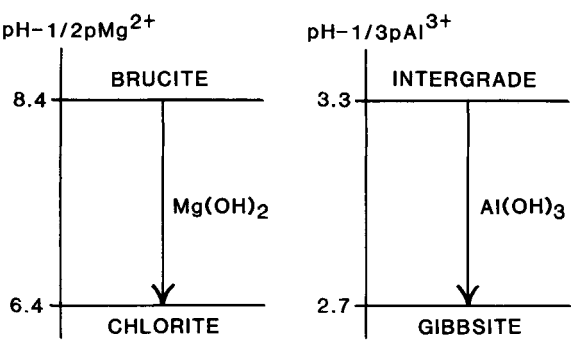


Figure 1. Equilibrium stability of $Mg(OH)_2$ in chlorite compared to brucite (left) and $Al(OH)_3$ in gibbsite compared to intergrade smectite or vermiculite (right). Lower solution parameters indicate greater stability. Arrows indicate direction of predicted change.

[1] Scientific Paper No. 6366. College of Agriculture Research Center, Washington State University, Pullman, Washington, Project 0511.

Copyright © 1983, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1983.0310412 Published online by Cambridge University Press

synthetic intergrade smectites and vermiculites (be it rapid or gradual) indicates a dynamic process. If this is true of natural intergrade materials, the interlayers must be constantly replenished in order to maintain a level of interlayers characteristic of a particular environment.

Contrasting stability of intergrades and chlorites

The dynamic formation and dissolution of $Al(OH)_3$ interlayers in intergrade materials distinguishes them as solubility units that are independent of the 2:1 silicate layers. This behavior contrasts sharply with trioctahedral-interlayer chlorites where the 2:1 layer and the interlayer act as a single solubility unit (Kittrick, 1982). That is, equilibrium solubility determinations for cholorite lie along a single stability line derived from bulk chlorite composition, rather than at the intersection of independent 2:1 layer silicate and hydroxy interlayer stability lines.

Perhaps the greatest chemical contrast between intergrade materials and chlorites is their pH stability. Natural aluminum hydroxy interlayers seem to form best at approximately pH 5. Assuming that chlorites maintain a $pH - 1/2pMg^{2+}$ value of approximately 6.4, at pH 5.0 the Mg^{2+} activity in the equilibrium soil solution would have to be 631 M! This means that authigenic soil chlorites (such as described by Rich and Bonnet, 1975) will be found only in alkaline soils. For example, a calcareous soil with a pH of 8.3 would require a solution Mg^{2+} activity of only 1.6×10^{-4} M in order to be in equilibrium with chlorite. Thus, aluminum hydroxy interlayers and chlorites are likely to form only in entirely separate pH environments.

SUMMARY AND CONCLUSIONS

To the extent that a relatively few samples represent nature, and as long as trioctahedral-interlayer chlorites can be appropriately compared to dioctahedral-intergrade 2:1 minerals, the $Mg(OH)_2$ sheet in true chlorites appears to be stable relative to separate-phase $Mg(OH)_2$ (brucite) and chlorite equilibria are controlled by a single solid phase of bulk chlorite composition. In contrast to this behavior, the $Al(OH)_3$ sheet in intergrade smectites and vermiculites acts as a separate solubility unit and is unstable relative to separate-phase $Al(OH)_3$ (gibbsite). As equilibrium with gibbsite is approached, the hydroxy aluminum is preferentially removed from the interlayer position. Furthermore, hydroxy aluminum interlayers and chlorites form in soils of distinctly separate pH environments. It is therefore concluded that intergrade smectites and vermiculites are chemically distinct from chlorites. This is not nullified by the fact that the hydroxy sheets in intergrade smectites and vermiculites give these minerals physical properties whereby they might be classified as chlorites by operational definitions, such as a 14-Å X-ray diffraction peak unaffected by polar liquids, K-saturation, or moderate heat. Chemically, these hydroxy sheets are best considered thermodynamically non-stable "contaminants" in what are otherwise ordinary smectites and vermiculites. It is unusual, perhaps unique, to consider stability information as a criterion for application of a mineral name. Mineralogists must decide whether it is a sufficiently important distinction in this case.

Department of Agronomy and Soils J. A. KITTRICK
Washington State University
Pullman, Washington 99164

REFERENCES

Barnhisel, R. I. (1977) Chlorites and hydroxy interlayered vermiculite and smectite: in *Minerals in Soil Environments*, J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 331–356.

Brydon, J. E. and Turner, R. C. (1972) The nature of Kenya vermiculite and its aluminum hydroxide complexes: *Clays & Clay Minerals* **20,** 1–11.

Kittrick, J.A. (1982) Solubility of two high-Mg and two high-Fe chlorites using multiple equilibria: *Clays & Clay Minerals* **30,** 167–179.

MacEwan, D. M. C. and Wilson, M. J. (1980) Interlayers and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 197–248.

Rich, C. I. and Bonnet, J.A. (1975) Swelling chlorite in a soil of the Dominican Republic: *Clays & Clay Minerals* **23,** 97–102.

Singh, S. S. and Brydon, J. E. (1967) Precipitation of aluminum by calcium hydroxide in the presence of Wyoming bentonite and sulfate ions: *Soil Sci.* **103,** 162–167.

Turner, R. C. and Brydon, J. E. (1965) Factors affecting the solubility of $Al(OH)_3$ precipated in the presence of montmorillonite: *Soil Sci.* **100,** 176–181.

Turner, R. C. and Brydon, J. E. (1967) Effect of length of time of reaction on some properties of suspensions of Arizona bentonite, illite, and kaolinite in which aluminum hydroxide is precipitated: *Soil Sci.* **103,** 111–117.

(Received 12 November 1982; accepted 4 February 1983)

https://doi.org/10.1346/CCMN.1983.0310412 Published online by Cambridge University Press