

CHLORITES DIFFERENTIATED FROM INTERGRADE SMECTITES AND VERMICULITES BY SOLUTION STABILITY CRITERIA¹

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 14.0 Å 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.

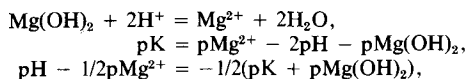
The concept of intergrade minerals is mainly based upon a gradation in physical properties (especially X-ray diffraction) between smectites or vermiculites and chlorites. The purpose of this investigation is to compare some important chemical properties of hydroxy interlayers in intergrade materials 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 Mg²⁺ or Al³⁺ 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:

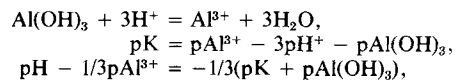


where K is the equilibrium constant, p is the negative log of the activity, and the activity of water is assumed to be unity. The larger the value of pH - 1/2pMg²⁺, the more soluble (less stable) is the Mg(OH)₂ phase. Recent solubility determinations on two high-Mg and two high-Fe chlorites indicate an equilibrium pH - 1/2pMg²⁺ 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 sta-

bility 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:



where the activity of water is assumed to be unity. The larger the value of pH - 1/3pAl³⁺, 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 - 1/3pAl³⁺ 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 - 1/3pAl³⁺ 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

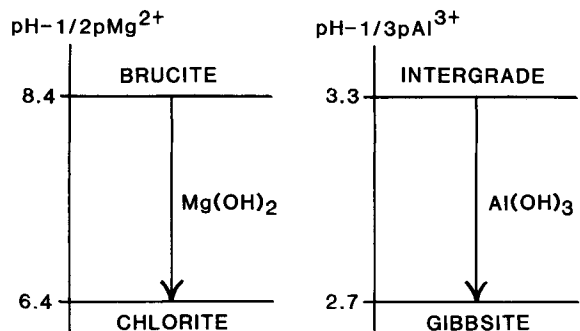


Figure 1. Equilibrium stability of Mg(OH)₂ in chlorite compared to brucite (left) and Al(OH)₃ in gibbsite compared to intergrade smectite or vermiculite (right). Lower solution parameters indicate greater stability. Arrows indicate direction of predicted change.

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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 $\text{Al}(\text{OH})_3$ 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 chlorite 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 $\text{pH} - 1/2\text{pMg}^{2+}$ 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 $\text{Mg}(\text{OH})_2$ sheet in true chlorites appears to be stable relative to separate-phase $\text{Mg}(\text{OH})_2$ (brucite) and chlorite equilibria are controlled by a single solid phase of bulk chlorite composition. In contrast to this behavior, the $\text{Al}(\text{OH})_3$ sheet in intergrade smectites and vermiculites acts as a separate solubility unit and is unstable relative to separate-phase $\text{Al}(\text{OH})_3$ (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.

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