

SOIL HYDROXY-INTERLAYERED MINERALS: A RE-INTERPRETATION OF THEIR CRYSTALLOCHEMICAL PROPERTIES

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Abstract—Hydroxy-interlayered minerals (HIMs) are typical of moderately acidic soils. Barnhisel and Bertsch (1989) defined the hydroxy-interlayered clay minerals as a solid-solution series between smectite, vermiculite and pedogenic or aluminous chlorite end-members. Their experimental data for the relationship between the decrease in cation exchange capacity (CEC) and the amount of Al fixed in the interlayers of smectites and vermiculites is reinterpreted using calculated structural, chemical and X-ray diffraction (XRD) evidence. The adsorbed Al ions are in a 6-fold coordination state: $[\text{Al}(\text{OH})_x(\text{H}_2\text{O})_y]^{(3-x)+}$ with $x+y=6$. The polymerization process occurs before saturation of the exchange sites by Al ions. Some of the adsorbed Al ions form polynuclear cations keeping a constant positive charge.

X-ray diffraction patterns of oriented preparations in the ethylene glycol-solvated state suggest that HIMs consist of randomly interstratified expandable and chlorite-like layers (17 and 14.2 Å). Chlorite-like layers result from the selective adsorption of Al complex ions in specific interlayer zones that behave similarly to Al-chlorite (donbassite-like) with incomplete (60%) ‘gibbsite-like’ sheets (chlorite₆₀). Using this framework, HIM XRD patterns can be interpreted by comparison with calculated chlorite₆₀-dismectite mixed-layer mineral patterns using the NEWMOD software.

Key Words—Adsorption, Aluminum, Hydroxy-interlayered, Polymerization, Soil Clays.

INTRODUCTION

Hydroxy-interlayered minerals (HIMs) are found to be stable in moderately acidic and oxidizing conditions in soil horizons with low organic matter content and frequent wetting and drying cycles (Rich, 1968). They have been most commonly identified in Alfisols and Ultisols (see the pioneering work of Jackson, 1964). These minerals are formed by adsorption and polymerization of Al ions in the interlayer region of expandable clay minerals and form in moderately acidic soils. The polymerization of Al hydroxides in the interlayer region produces ‘gibbsite-like’ islands (Dixon and Jackson, 1962) which modify the expansion or the collapse of the layers after ethylene glycol solvation, K saturation or heat treatment. The chemical composition of hydroxy-interlayered vermiculites (HIV) has been established in the pioneering work of Kirkland and Hajek (1972). The Al ions fixed in the interlayer region of smectites and vermiculite can be liberated in acid solutions (April *et al.*, 2004). This process is accelerated in natural environments by acid rain (see the Acid Rain Workshop, 42nd annual Meeting of the CMS; McDonald *et al.*, 1998).

Based on their XRD patterns, HIMs have been classified in three different mineral families: pedogenic or aluminous chlorites, hydroxy-interlayered smectites (HIS) and hydroxy-interlayered vermiculites (HIV). The

essential characteristics of the three mineral families were summarized in a review by Barnhisel and Bertsch (1989). Because of a continuous variation in the swelling properties and the CEC, those authors considered the hydroxy-interlayered clay minerals as a solid-solution series between smectite, vermiculite and pedogenic or aluminous chlorite end-members. They concluded their review with the model of Dixon and Jackson (1962) which proposed an ‘atoll arrangement’ of hydroxy-Al-polymers in the interlayer zone of smectite or vermiculite.

The proposed solid-solution model is not self coherent. Several problems remain unresolved. Firstly, how Al ions are adsorbed and polymerized in the interlayer zones is not clear. The relationship between the decrease in the CEC with increasing amount of fixed Al could be used to analyze these processes, thereby improving the structural formulae proposed for HIMs. Secondly, the interpretation of XRD patterns for HIMs remains empirical because the crystallographic structure of HIMs is not correctly explained by the solid-solution model. The goal of the present study is to re-examine the crystallographic structure of the soil hydroxy-interlayered minerals in order to take into account the specific XRD properties of these minerals. The work is based on the data compiled in the paper by Barnhisel and Bertsch (1989).

OBSERVATIONS AND ANALYSIS

The CEC of hydroxy-interlayered minerals

The crystallochemical properties of HIMs formed in natural conditions are difficult to study because they are

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mixed with other clay minerals in soils. Other than rare exceptions (Harris and Hollien, 1988), they cannot be sufficiently purified to measure their chemical composition and their CEC or to characterize their crystal structure. Consequently, it is almost impossible to understand how they form. This is why experimental systems are needed. However, the experiments should closely simulate the natural conditions under which Al interlayers are formed. This rules out results obtained from pillared clay experiments. The unique polycation species which could be of importance for HIMs in soils is the Al_{13} polycation. Its presence, which has been discussed by Bertsch (1987), will be re-examined further. The most important result obtained from experiments which could be compared to natural conditions is the relationship between CEC vs. fixed Al (Barnhisel and Bertsch, 1989, p. 773).

The CEC decreases with increasing amount of fixed Al (Figure 1):

$$\Delta_{CEC} = -0.07 + 0.01X_{Al}$$

where Δ_{CEC} and X_{Al} represent the decrease in the CEC (mol kg^{-1}) and the quantity of Al fixed in the interlayer zone (mg g^{-1}), respectively. The relationship implies: (1) that most HIMs have both exchangeable and fixed Al forms in the interlayer zone; and (2) that the relative proportions of the two types of Al are inversely related.

The above equation can be used to calculate how many fixed Al ions are needed for a decrease of 1 cmol kg^{-1} . For simplicity, assume that the clay mineral structure is represented by montmorillonite, *i.e.* $Si_4O_{10}Al_{1.9}Mg_{0.3}(OH)_2Na_{0.3}$ (mass of half unit-cell: 367 g mol^{-1}), 1 mg g^{-1} of fixed Al is equivalent to

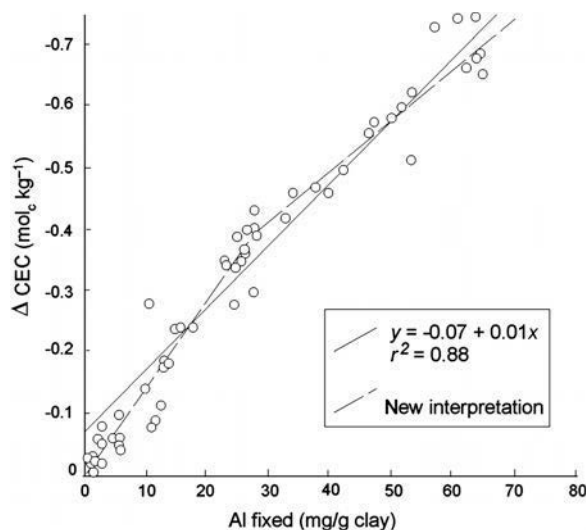


Figure 1. Relationships between Al fixed by clays and the resultant decrease in cation exchange capacity (from Barnhisel and Bertsch, 1989, p. 773). Solid line: relation calculated by Barnhisel and Bertsch; stippled line: new interpretation of the relationship between Δ_{CEC} vs. the amount of fixed Al.

$367/26.98 \times 10^{-3} \text{ atom mol}^{-1}$ or $0.014 \text{ atom mol}^{-1}$. Thus, a Δ_{CEC} variation of 1 cmol kg^{-1} corresponds to the fixation of $0.14 \text{ atom mol}^{-1}$ of Al. Theoretically, the 2:1 layer negative charge (-0.3) is compensated by 0.3 monovalent cations per half unit-cell. Here, assuming a 6-fold coordination state with a trivalent configuration for each adsorbed ion ($[Al(H_2O)_6]^{3+}$), a maximum positive charge of $+0.42$ would result from the 0.14 Al ions adsorbed in the interlayer. This mismatch between the theoretical and calculated positive charges could be due to several reasons: (1) the montmorillonite assumption is an oversimplification of the clay composition; (2) the equation in the Barnhisel and Bertsch (1989) review is an approximation; (3) the $[Al(OH)_n(H_2O)_{6-n}]^{6-n+}$ complex ion is not systematically trivalent; (4) other Al complex ions such as Al_{13} could be present.

Despite its uncertainties, the Barnhisel and Bertsch equation can be used to investigate the way in which Al ions are fixed in place of exchangeable ones in the interlayer region of smectites and vermiculites. Here, fixation means that the Al polynuclear cations become non-exchangeable due to the formation of hydrogen bonds with the basal oxygens as is the case for chlorites.

The Δ_{CEC} and X_{Al} parameters used in the equation represent the average chemical composition of the HIM interlayer zones. They do not give any information on the cation distribution in the interlayer zone. Thus, two structural models can be envisaged: (1) fixed Al-polynuclears co-exist with exchangeable cations (Ca^{2+} , Mg^{2+} , Na^+ ...) inside a single interlayer zone (mixed-site model); and (2) fixed Al-polynuclear and exchangeable cations are concentrated in separated interlayer zones (mixed-layer model). Most studies devoted to the cation exchange processes in smectites have shown that cationic species are preferentially adsorbed in specific interlayer zones. Knowing that the competition between two ionic species leads to the formation of a mixed-layer-like structure (Glaeser and Méring, 1954; Mamy and Gaultier, 1979; Ferrage *et al.*, 2005), it is probable that the exchangeable and the fixed ions or Al-polynuclears are segregated in separate layers. Consequently, it is important to check if the mixed-layer model is really compatible with HIM XRD patterns.

XRD properties of hydroxy-interlayered minerals

Hydroxy-interlayered minerals have similar basal 'spacings' in their natural state. They all present a relatively narrow peak at 14.2 \AA . The full width at half maximum intensity (FWHM) of that peak is $<0.9^\circ 2\theta \text{ CuK}\alpha$. When saturated with bivalent cations, low-charge smectites expand to 15 \AA and 17 \AA under ambient conditions in the air-dried and ethylene glycol solvation states, respectively. These spacings are dictated by the presence of two water or two ethylene glycol layer-cation complexes in the interlayer sites. This is not the case for HIS. Without chemical treatment, *e.g.*

Table 1. Position (Å) of the 001 reflection for chlorite, vermiculite and smectite and their equivalent in the hydroxy-interlayered species.

| | Air-dried (Sr, Ca, Mg) | Glycol | K-saturated | Heated (300°C) |
|--------------------|------------------------|--------|-------------|----------------|
| Chlorite | 14.2 | 14.2 | 14.2 | 14.2 |
| Vermiculite | >14.5 | 16 | 10 | 10 |
| Smectite | 15 | 17 | 10 | 10 |
| HIS | 14.2 | 15 | 12 | 10–11 |
| HIV | 14.2 | 14.2 | 14.2 | 12–13 |
| Aluminous chlorite | 14.2 | 14.2 | 14.2 | 14.2 |

extraction of Fe and/or Al hydroxides, hydroxy inter-layered smectites do not fully expand with glycol treatment. Additionally, the first-order peak is intense while the other 00 l peaks are much less intense if not absent in the XRD patterns. This effect is due to less scattering intensity because of the incomplete structure of 'gibbsite-like' sheets in the mineral.

It is not uncommon to find normally expandable smectites and HIMs in the same soil sample (April *et al.*, 2004). Hence, the identification or determination of the behavior of the individual mineral species becomes difficult. In general, smectites have a larger peak centered near 15 Å while HIMs are centered at 14.2 Å but the best identification test is K saturation and thermal treatment. Harris and Hollien (1988) showed that the 001 peak of HIVs broadens and shifts to ~12 Å. After thermal treatment, the crystal structure of HISs collapses as indicated by the shift in the 001 peak towards 10–11 Å (Ransom *et al.*, 1988).

Vermiculite minerals are high-charge expandable clays, the d_{001} of which shifts from 14–15 Å in the air-dried state to ~16 Å after saturation with ethylene glycol (Douglas, 1989). Soil vermiculite is a term used in the past to describe non- or poorly expanding soil clay minerals with a basal spacing between 14 and 15 Å (Wilson, 1987). The poor expandability is often due to the presence of polymerized Al ions in the interlayer zone. Criteria for the identification of HIS, HIV and aluminous chlorite using XRD have been summarized by Barnhisel and Bertsch (1989), and are presented in Table 1.

The position and intensity of the diagnostic peaks for HIMs are quite well reproduced using NEWMOD calculations (Reynolds, 1985) assuming that the 'solid-solution' can be considered as due to an aluminous chlorite and expandable layer interstratification. The chemical composition of the soil aluminous chlorite is not known. However, some properties can be deduced from HIV studies (Kirkland and Hajek 1972; Arousseau *et al.*, 1983): HIVs are dioctahedral Al-rich minerals in which the negative layer charge is compensated by exchangeable and Al cations in the interlayer. Then, the soil aluminous chlorite is necessarily di-dioctahedral (donbassite type). Using NEWMOD software, it appears that the very weak intensity of the 002 diffraction is obtained for an incomplete 'gibbsite sheet' (60%,

Figure 2). The parameters used for the calculation are indicated in the Appendix.

The interlayering of Al₆₀-chlorite with a dioctahedral smectite has been used to mimic a HIS mixed-layered mineral series. The computed results show that the position and intensity of the 002 and the intensity of the 003 peaks vary with the amount of expandable layers (Figure 3a,b).

DISCUSSION

Before considering the crystallochemical structure of HIMs (structural formula), two problems have to be resolved: (1) the incorporation of Al ions in the interlayer zone. Whatever the polymer state in solution,

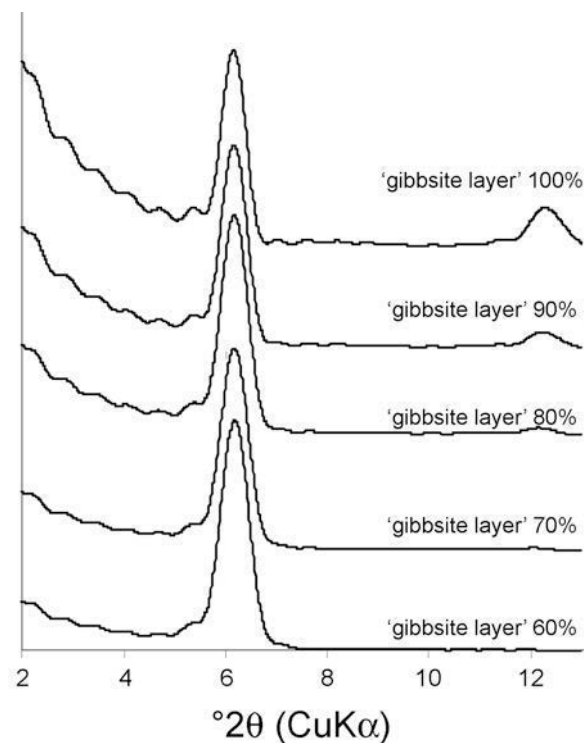


Figure 2. Calculated XRD patterns using NEWMOD (Reynolds, 1985), CuK α , of di-dichlorite (Si1Fe: 0; N: 3–10) with 100 to 60% of the 'gibbsite-like' sheet. The chlorite₆₀ is considered to be the 'chlorite' component of the chlorite-smectite mixed layers used for HIM XRD pattern re-interpretation.

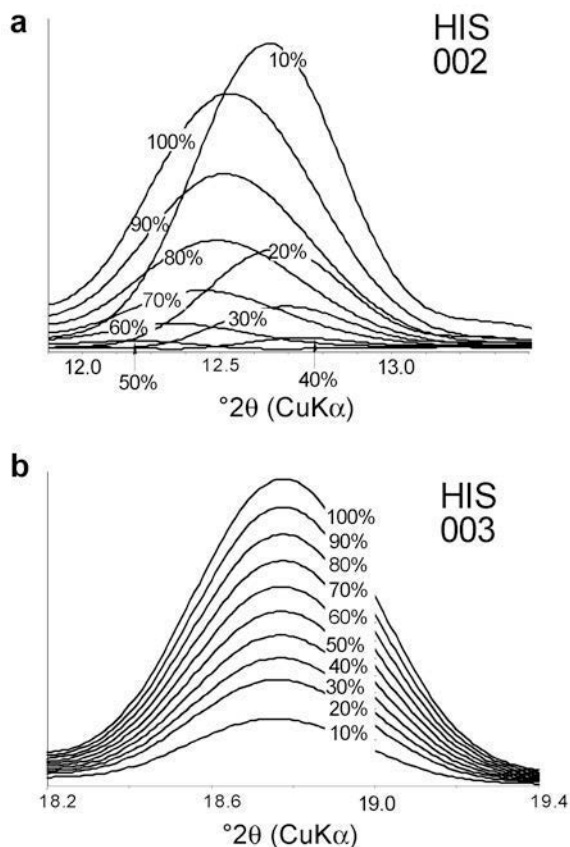


Figure 3. Calculated XRD patterns using NEWMOD (Reynolds, 1985), CuK α , of chlorite₆₀-dismectite. Mixed-layered minerals from 0 to 100% expandable layers (di-dismectite with Fe = 0 and $N = 3-10$). (a) Variation in the position and the intensity of the 002 diffraction peak in the range 11.9–13.4°2 θ . (b) Intensity variation in the 003 peak in the range 18.2–19.4°2 θ .

the incorporation of Al ions in the interlayer zone is controlled by a cation-exchange mechanism. The question is: how are the negatively charged sites on the 2:1 layers neutralized by the Al-polynuclears? (2) The polymerization of the adsorbed Al ions in the interlayer sheet of HIV or HIS minerals. Because the 2:1 layer has a defined negative charge, the polymerization occurs at a constant positive charge on the polymer. The question is: how is the incomplete 'gibbsite sheet' formed in the interlayers of smectites or vermiculites?

The incorporation of Al ions in the interlayer region of HIMs

The origin of Al-polymers was debated in the 1980s because of evidence for the presence of the $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ complex ions (or Al_{13}) in solution as well as in the interlayer zone of experimentally prepared pillared clays (Plee *et al.*, 1985; Schultz *et al.*, 1987; Montargies *et al.*, 1995). The Al_{13} complex ion is composed of two hexagonal rings of Al octahedra linked by an Al ion in tetrahedral coordination. However, Bertsch (1987) showed that this complex ion

would not form readily in natural environments and that the HIV and HIS found in soils are not similar to artificially prepared pillared clays. The d_{001} values of pillared clays with interlayer Al_{13} complexes varies between 17 and 19 Å (Montargies *et al.*, 1995) which is incompatible with the measured 14.2 Å d_{001} value typical of HIMs. Besides, there is no evidence for the presence of tetrahedrally coordinated Al ions inside the interlayer zone. Consequently, when adsorbed, Al ions should be in a 6-fold coordination state $[\text{Al}_n(\text{OH})_x(\text{H}_2\text{O})_y]^{x+y}$, with $x+y$ depending on n and on the type of polymer (linear or cyclic). Whatever the value taken by n , the thickness of the polymer formed from 6-fold coordinated Al ions must not exceed that of a 'gibbsite-like' sheet in a chlorite-type structure.

The competition between ions leads to their segregation in specific interlayers. Thus, the problem is to examine how the Al ions which are adsorbed in a given interlayer progressively form a 'pseudo-gibbsite sheets'. The maximum number of 6-fold coordinated Al ions in the interlayer position that are housed in a unit-cell is 4 (Figure 4a). Of course they are fixed on isolated negatively charged sites of the 2:1 unit surface, and their size is not limited to the unit-cell area. Al ions may form bigger polymers (>4 ions) if two conditions are met: (1) the positive charge of the polymer must remain constant. Thus, the relative proportions of OH groups and water molecules are adjusted to compensate the local negative charge on the 2:1 layer surface (Figure 4b); (2) the maximum number of Al cations in the polymer is determined by the surroundings of the local negative charge, i.e. the relative location of the negative charges on the 2:1 layer surface (isolated, clustered).

The maximum positive charge per Al ion decreases with the degree of polymerization (Figure 5) and is always higher for linear polymers than for cyclic ones. In both species, the positive charge is reduced through the replacement of water molecules by OH groups.

Because of steric constraints, the notion of Al-polymers inside the interlayer space of smectites or vermiculites under natural conditions (1 or 2 water layers) is made possible if their size is comparable to that of hydrated cations. Thus, only monomers or dimers are available for adsorption on the exchange sites of the 2:1 layer surface. Theoretically, the slope of the linear correlation between CEC and fixed Al would indicate what Al-polymer type is adsorbed at first on the exchange sites (Figure 6a). The larger the slope, the smaller the polymer. It is highly probable that only Al-monomers are involved in the adsorption process in natural conditions. With increasing Al adsorption, the slope of the curve should decrease because some of the adsorbed Al is consumed by the polymerization process (Figure 6b). The greater the charge in the 2:1 layer, the greater the degree of polymerization. Thus, two steps should be considered during the formation of HIMs:

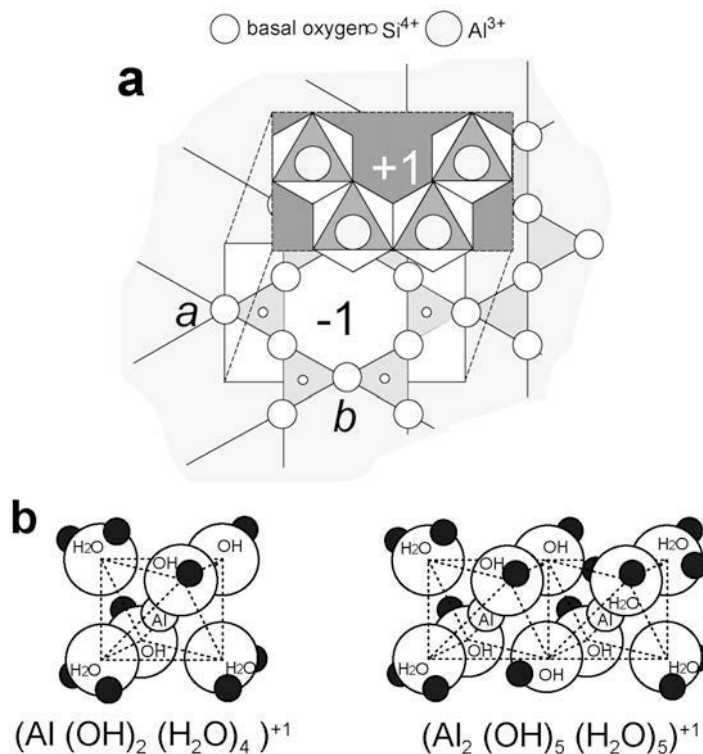


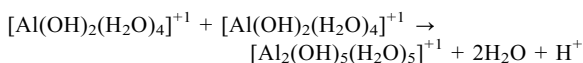
Figure 4. Position of the Al-polymer in the HIV interlayer region. (a) Maximum number of 6-fold coordinated Al ions per unit-cell. (b) The 6-fold Al ion coordination may be adjusted by a variable number of OH groups and water molecules.

(1) 1Al-monomer adsorption; (2) polymerization. Considering the limiting conditions, Δ_{CEC} must be null for no fixed Al, the fitting function for Δ_{CEC} vs. Al fixed plot (Figure 1) should start from the origin. Therefore, a non-linear or two-step linear function is proposed (stippled lines, Figure 1). This is coherent with a two-step exchange-polymerization process.

The polymerization process

Considering for simplification that Al ions are adsorbed as $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^{+1}$ monomers, the first step in the process is their exchange for alkali cations in the interlayer (t_1 in Figure 7). The exchange ratio depends on the activity of Al ions in the solution and the selectivity of the vermiculite or smectite layer inner surfaces for Al vs. alkali ions. In a second step (t_2 in Figure 7), the adsorption of additional Al ions from solution has two concomitant effects: (1) to increase the replacement of remaining exchangeable cations; and (2) to induce the polymerization process.

Because the polymer must compensate for local negative charge, the positive charge of the polymer must remain constant through the polymerization process. Thus, the polymerization reaction should be as follows:



How polymerization physically proceeds inside the interlayer zone remains unknown. It is probably controlled by processes similar to that of a crystal growth on (001) faces (migration of ions on the surface, formation of strong chemical bonds, rejection of impurities). At the end of the process (step 3), almost all the exchangeable alkali cations are replaced by Al-polymers that form rings or chains in the interlayer zone (t_3 in Figure 7). By coalescence, these rings and chains build a discontinuous gibbsite-like structure (dioctahedral sheet). At the end of the process, the gibbsite-like structure must have a positive charge that compensates the negative charge of the 2:1 layer.

The crystallochemical composition of HIMs

Barnhisel and Bertsch (1989) showed that the OH/Al ratio varies between 2.5 and 2.9. They suggested that HIV or HIS could be considered to form a solid-solution series with the pure end-members consisting of dioctahedral vermiculite or smectite on one end of the series and aluminous pedogenic chlorite on the other end of the series. The negative 2:1 layer charges in HIV and HIS are considered to be partially compensated by a $[\text{Al}_6(\text{OH})_{15}]^{3+}$ polymerized ring structure. Kirkland and Hajek (1972) presented an average HIV structural formula from the analysis of 12 Alabama soils: $[\text{Si}_{3.24}\text{Al}_{0.76}\text{O}_{10}(\text{Al}_{1.56}\text{Fe}_{0.24}\text{Mg}_{0.20})(\text{OH})_2[\text{Al}_{1.56}(\text{OH})_{3.79}]\text{K}_{0.24}\text{Ca}_{0.08}]$. Other HIM compositions have

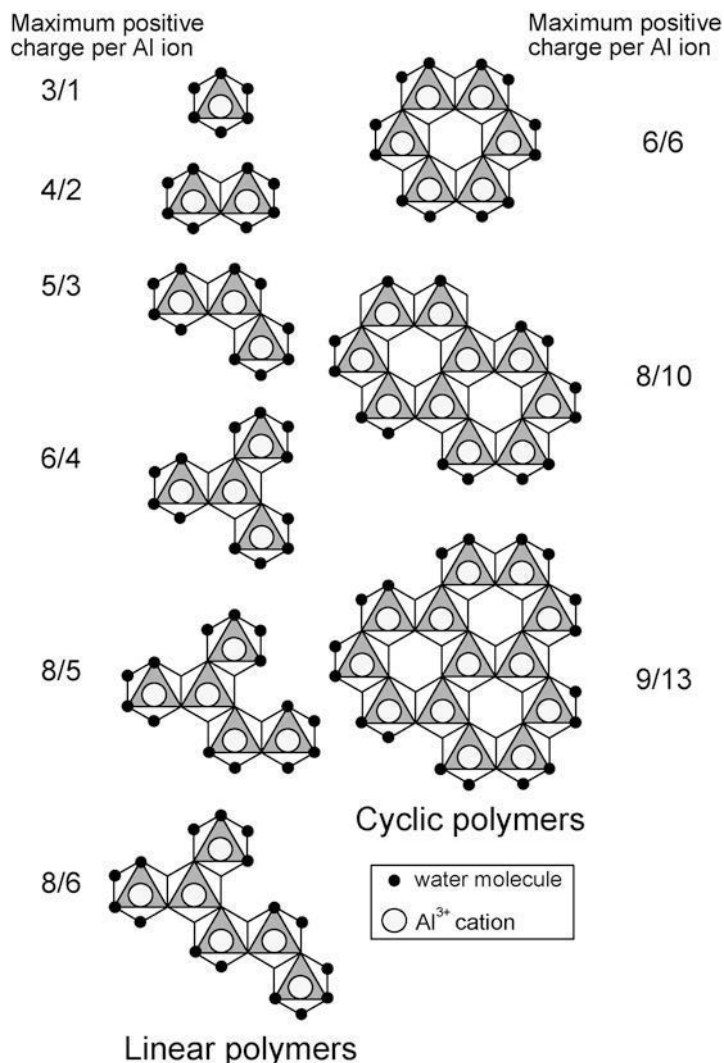


Figure 5. Schematic representation of the relationship between the positive charge and the degree of polymerization when water molecules are present in the 6-fold coordination of Al ions (maximum positive charge).

been proposed (see Barnhisel and Bertsch, 1989). However, all consider that the Al-polymer islands firmly bond the 2:1 layers and hold the interlayer region open in a sort of pseudo-zeolite structure. Even if the chemical composition of these minerals is highly variable (Barnhisel and Bertsch, 1989), the structural formula above is indicative of the pedogenic chlorite trend. The charge of the 2:1 layer is -0.96 per half unit-cell and is near the theoretical value of -1 for Si_4O_{10} encountered in chlorites. To be electrically neutral, the $[\text{Al}_{1.56}(\text{OH})_{3.79}]$ member should have a positive charge equal to $+0.56$. Additionally, to respect the 6-fold coordination of Al ions, neutral water molecules should be added to the formula. The question is, how are these Al-polymers integrated in the vermiculite interlayer region?

Because the $[\text{Al}_{1.56}(\text{OH})_{3.79}]$ member must have a positive charge equal to $+0.56$, any of the polymers

represented in Figure 4 should incorporate hydroxyls to reduce their positive charges. Consider for instance that the positive charge is brought by a linear 4-polymer (18 octahedron apices) as shown in Figure 4, then the formula of the $[\text{Al}_{1.56}(\text{OH})_{3.79}]$ member must be rewritten as follows: $[\text{Al}_4(\text{OH})_{10.56}\text{H}_2\text{O}_{7.44}]^{+1.44} \times 0.39$. What is the crystallographic meaning of the 0.39 ($1.56/4$) coefficient? If, for simplicity, one negative charge is considered to be located on a single hexagonal cavity, this coefficient is related to the degree of occupation of the cavities: 2.6 for 10 cavities. To be completely isolated, each charged cavity must be surrounded by six neutral ones. In such a case, the coefficient is equal to 0.14. Consequently, for a 2.6 coefficient, several linear 4-polymers are necessarily in contact making higher polymers.

The number of the polymers fixed in the interlayer region of the expandable minerals depends on their size

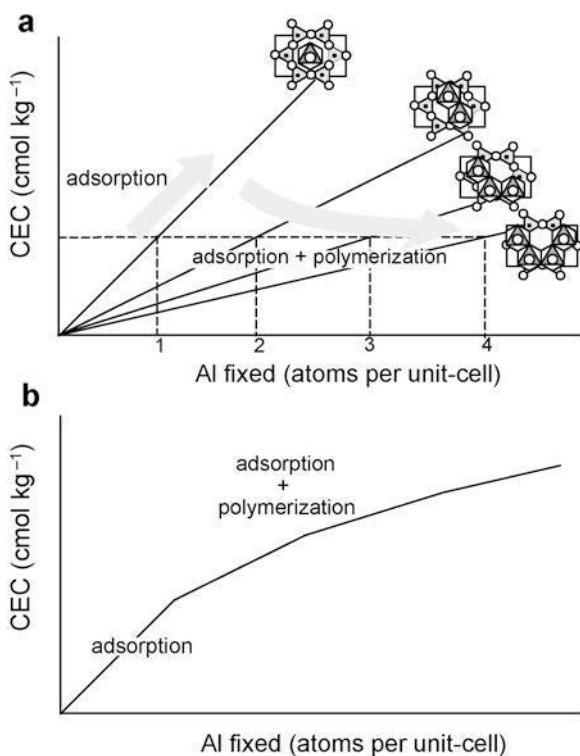


Figure 6. Theoretical representation of the CEC decrease vs. fixed Al ion relationships: (a) the adsorption and adsorption-polymerization steps; (b) variation of the curve slope with progressing saturation of the exchangeable sites by fixed Al ions.

(number of Al) and shape (linear or cyclic) and the layer charge. However, even if the above calculation is only a theoretical exercise, it clearly indicates that a continuous gibbsite-like sheet cannot be formed in HIMs because the positive charge becomes negligible when the polymer covers hundreds of unit-cells. This confirms the presence of 'Al islands' linked to water molecules in the interlayer zone of HIMs.

The mixed-layer model

During the adsorption process, the presence of mixed-site interlayers is unavoidable. Alkali and Al cations are surrounded by water molecules. However, it is not clear if the expandability of smectite or vermiculite is reduced at this early stage before Al ion polymerization. On the contrary, as soon as gibbsite-like chains or islands are formed, the smectite or vermiculite layer loses its expandability (chlorite-like d_{001} at 14.2 Å). Thus, HIMs can be considered as interlayered minerals as schematically represented in Figure 8. Their expandability depends on the proportions of 'chlorite-like' layers. This effect is demonstrated by the shift in the 001 peak in the ethylene glycol-solvated state from 17 to 14.2 Å.

Expandable layers collapse to 10 Å after K saturation and heating to 300°C while the d_{001} of the non-expandable layers (Al-chlorite) remains at 14.2 Å,

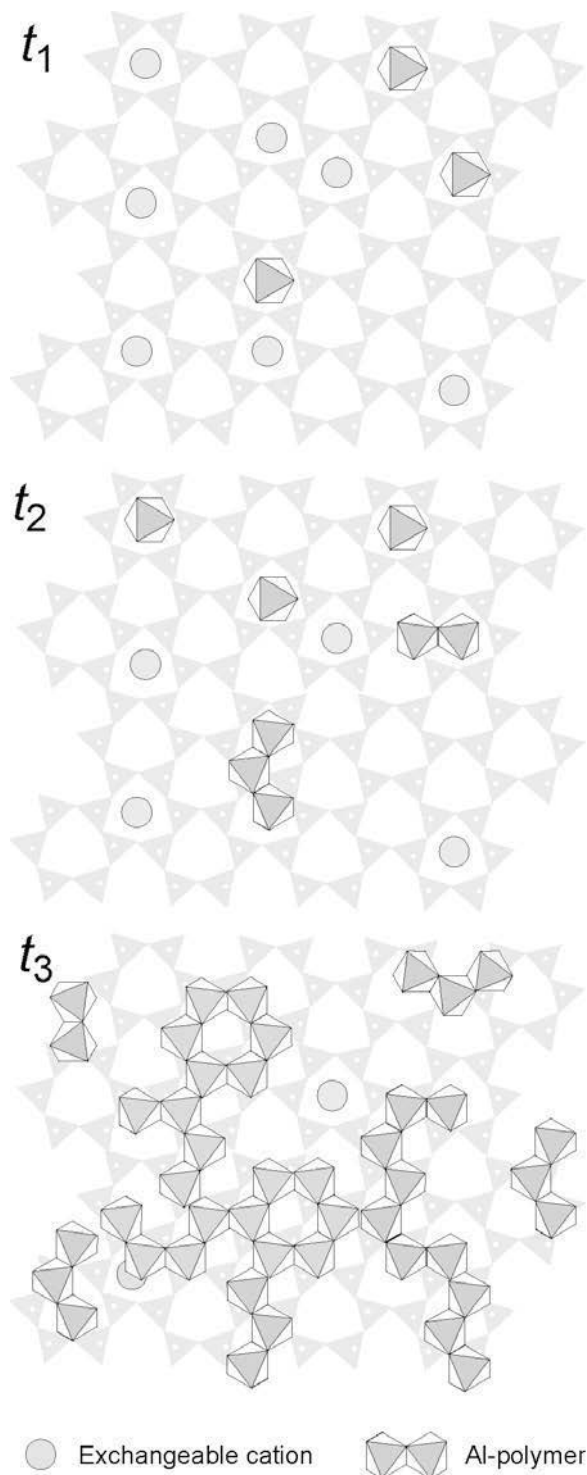


Figure 7. Schematic representation of the Al ion adsorption and polymerization in the interlayer zone of vermiculite or smectite. For simplification, Al ions are considered to be adsorbed in a monomer state. t_1 : the amount of adsorbed Al ions is controlled by the CEC. t_2 : some of the additionally adsorbed Al ions are consumed in the polymerization process. t_3 : almost all the alkali exchangeable cations are replaced by Al polymers which form chains or rings in the interlayer zone.

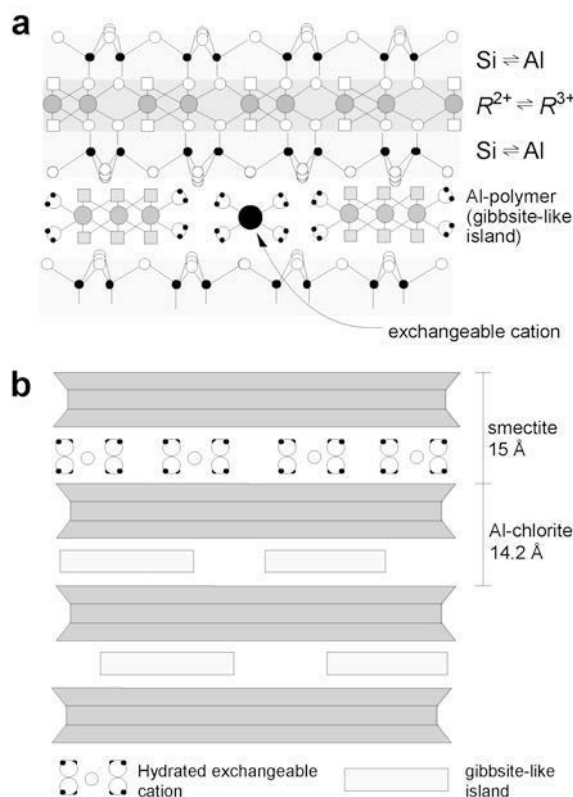


Figure 8. The mixed-layered model for the interpretation of the XRD patterns for HIMs. (a) The 'gibbsite' interlayer is discontinuous and hydrated exchangeable cations are still present. (b) Schematic representation of the stacking of expanding and non-expanding layers in HIMs.

whatever the treatment. Consequently, after that treatment, the position of the 001 peak of HIMs is intermediate between 14.2 and 10 Å. With higher thermal treatment, the peak shifts towards 10–11 Å. Concomitantly, it widens and loses intensity, indicating that the 'chlorite-like' layers are deformed inducing defects in the stacking.

This discussion still ignores the proportion of fixed Al necessary for a given layer to lose its expandability and behave like chlorite. Fortunately, these data are not absolutely necessary for a first approach to the interpretation of XRD patterns from HIMs because the fixed Al influences only the intensities of the 002 and 003 peaks and not their position. Thus, the variability of the HIS and HIV described in natural soils can be acceptably approximated by a series of 17–14.2 Å and 16–14.2 Å randomly ordered mixed layers, respectively.

CONCLUSION AND OUTLOOKS

The re-interpretation of Barnhisel and Bertsch's data leads to a possibility that HIMs behave as mixed-layer minerals. The interlayering of non-expandable layers (14.2 Å) with expandable ones results from the selective

adsorption of Al complex ions on specific interlayer zones. The 'gibbsite-like' sheets of the aluminous chlorite are certainly not complete but we still do not know how they are organized inside the interlayer. Because of their importance for soil chemical properties, a detailed study of the HIM crystal structures is needed. In particular, their XRD patterns should be investigated using modern modeling techniques. This analysis would help to answer the following questions: (1) how does the Al ion polymerization proceed inside the interlayer zone? Why is it limited to incomplete 'gibbsite-like' sheets? (2) As the 'gibbsite-like' sheet is necessarily incomplete, what is the minimum proportion for the interlayer expandability to be lost? (3) Where are water molecules located within the interlayer zone?

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APPENDIX (NEWMOD CALCULATION)

Aluminous chlorite

Selection of the clay type: di-dichlorite (SiFe = 0; hydroxide Fe = 0)

Hydroxide sheet: variation from 1 to 0.6

Reichweite: R0

Proportions: 1–99%

Size of the coherent domain: 3–10 layers

Chlorite60-smectite mixed-layer minerals

Selection of the clay type: (1) di-dichlorite (SiFe = 0; hydroxide Fe = 0, hydroxide = 0.6); (2) dismectite 2Gly (Fe = 0)

Reichweite: R0

Proportions of smectite: variable from 0 to 100%

Size of the coherent domain: 3–10 layers