

# SIGNIFICANCE OF KAOLINITE INTERSALATION IN CLAY MINERAL ANALYSIS

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## ABSTRACT

Recent development of the intersalation method by which kaolinite (as well as dickite and halloysite) is expanded makes possible the application of X-ray diffraction to qualitative and semiquantitative determinations of these mineral species. It also permits their distinction from the X-ray-thermally similar intergradient 2:1-2:2 layer silicates which are not affected by the treatment. Intergradient 2:1-2:2 layer silicates are developed by interlayer precipitation of hydroxides of aluminum, iron, and magnesium during pedogeochemical weathering and probably also during burial in sediments. The *quantitative* determination of kaolinite-halloysite by NaOH differential dissolution is completely corroborated by the qualitative, semiquantitative X-ray diffraction intersalation technique with respect to their clear differentiation from chlorite and intergradient clays.

## INTRODUCTION

This brief paper reviews and discusses some recent literature (1959-1960, with one reference to 1958, and two references to 1961-2, in press) on the three topics: (1) the intersalation of kaolinite (and dickite) lattices by interlayer penetration of K and  $\text{NH}_4$  salts and a comparison to intersalation of halloysite which permits a differentiation between these dioctahedral layer silicates; (2) Al and Fe hydroxide interlayering in expansible layer silicates (resulting in intergrade 2:1-2:2 or "chloritelike" minerals) as a function of pedogeochemical weathering of micas and other 2:1 layer silicates and the reverse of these reactions in sediments; and (3) the concordance found between the *qualitative* and semiquantitative X-ray diffraction-intersalation technique and the *quantitative* heating-NaOH differential dissolution analysis method for the differentiation of the 1:1 dioctahedral-type layer silicates from true chlorites and also from 2:1-2:2 intergrade layer silicates.

Incomplete Al and Fe hydroxide interlayers of expansible layer silicates are thermally unstable in the range 400-500 °C, and therefore the loss of the 7 Å 002 diffraction peak concurrent with collapse of the 14 Å spacing

to 10 Å (unlike true chlorite) causes confusion in the X-ray thermal differentiation of the 7 Å diffraction peak of kaolinite and halloysite from that of 2:1-2:2 intergradient minerals. The differentiation of these two classes of minerals is scientifically important because of widespread occurrence of mixtures of kaolinite and halloysite with pedogenically interlayered 2:1-2:2 intergrade clays.

### INTERSALATION OF 1:1 DIOCTAHEDRAL LAYER SILICATES

Wada (1958, 1959a, 1959b) found that K and  $\text{NH}_4$  salts, including neutral  $(\text{NH}_4)_2\text{HPO}_4$ , formed layers between halloysite layers (his manuscripts were lent to the present writer by Dr. S. Aomine in 1956). The intersalation reaction was also shown with halloysite by Garrett and Walker (1959). Wada (1961) showed a similar "intersalting" or intersalation of pure kaolinites. Andrew, Jackson, and Wada (1960) showed the same reaction for dickite, kaolinite, and the kaolinite of soil clays. In the procedure of Andrew, Jackson and Wada (1960), potassium acetate crystals are added to clay in the proportion of 60 mg of  $\text{KCH}_3\text{COO}$  to 40 mg of clay and triturated in an agate mortar as moisture is gathered by deliquescence of the salt. It was shown by Hanna and Jackson (in manuscript) and by Andrew, Jackson and Wada (1960) that allowing the moist mixture to stand overnight at 70 percent relative humidity allows a major increase in the development of the salt interlayer with a minimum of grinding. Also, it was observed that the K salt interlayer develops in the kaolinite of many soil clays without any mortaring at all. The interlayering is characterized by a 14 Å X-ray diffraction peak shown by this mixture.

The procedure (Andrew, Jackson and Wada, 1960) calls for transfer of the slurry to a centrifuge tube by 10 N  $\text{NH}_4\text{NO}_3$  washings followed by five centrifuge washings with this solution. The tube is drained by inversion over a towel. A portion of the drained clay cake is smeared on a glass slide with the salt solution still present. It is X-rayed moist or after drying at 100 °C for 2 hr. Kaolinite, halloysite, and dickite thus intersalated with  $\text{NH}_4\text{NO}_3$  give an 11.6 Å X-ray diffraction peak and its higher orders; these are diagnostic of 1:1 dioctahedral layer silicates. Kaolinite remains at 11.6 Å after washings with 6 N  $\text{NH}_4\text{NO}_3$  solution while a dickite collapses to 7 Å by these washings, thus differentiating these two species. Finally, the remaining portion of clay in the tube is washed three times with distilled water and an X-ray slide is prepared, dried in a desiccator at 70 percent R.H., and X-rayed. Kaolinite and dickite show a 7 Å peak and halloysite shows a 10 Å peak, thus differentiating these species.

In order to distinguish kaolinite and halloysite in a mixture of layer silicates of soil clay involving the presence also of vermiculite and interstratified vermiculite-chlorite (Dr. Saatci of this laboratory has noted such

a mixture of layer silicates in a Turkish Terra Rossa soil), the water-washed specimen is heated to 200 °C to collapse the halloysite while leaving the K and NH<sub>4</sub>-collapsed vermiculite at 10 Å.

The quantitative determination of the halloysite content of a clay sample is based (Jackson, 1960a) on the H<sub>2</sub>O content increment of the halloysite between the dehydrated and intersalation-hydrated condition resulting from the above procedure.

It is of interest to note that salt solution-clay slurry preparations were used by Barshad (1960) for X-ray diffraction, and the 14 Å and 18 Å spacings reported for vermiculite and montmorillonite, respectively, were also shown by Andrew, Jackson and Wada (1960) for these components in the NH<sub>4</sub>NO<sub>3</sub> preparation.

### INTERGRADIENT 2:1-2:2 LAYER SILICATES

Occurrence of incomplete aluminum-iron (and possibly magnesium) hydroxide layers in the interlayer position of the expansible layer silicates vermiculite and montmorillonite, results in properties of the clays that are intergradient between those of the 14 Å spaced expansible minerals and 14 Å spaced chlorite minerals. The term intergrade (from the dictionary) is applicable (Dixon and Jackson, 1959) to this type of mixing in the *X* and *Y* crystallographic planes. The cation exchange capacity and specific planar surface properties as well as thermal collapse properties (400°-500 °C) are intergradient between those of the expansible layer silicates and true chlorite. Such intergrades are apparently products of pedogeochemical weathering in the soils and mantle rocks as reviewed elsewhere (Dixon and Jackson, 1959; Glenn *et al.*, 1960; Dixon and Jackson, 1962; Jackson, 1960b). That iron can coprecipitate with aluminum in intergrade soil clays has been indicated by Sawhney (1960). Simultaneous occurrence of the *X*-*Y* intergrade with *Z*-axis interstratification has been reported by Dixon and Jackson (1960, 1962).

Weathering of chlorite and illite in shale-derived profiles (Harrison and Murray, 1959) resulted in the development of interstratified or intergradient mixed-layer minerals at the soil surface from the chlorite component found at depth; at the same time, the removal of interlayer K from certain illite cleavages formed interstratified expansible interlayers in the assemblage. Increase in the proportion of expansible planes in illitic clays (Hensel and White, 1960) occurred with proximity to the soil surface and with increasing age of the glacial till in Indiana and Ohio.

The full complement of K for true mica was found (Mehra and Jackson, 1959a) in a series of nineteen samples including six underclay fractions and two glauconite fractions. The interlayer planes that were filled with K ranged from 1 to 76 percent of the total, while those interlayer planes *not* filled

with K were found to be freely expansible by glycerol. The sorption planes plus the K-filled planes summed to a constant, the unit cell planar total. Laboratory hydrothermal synthesis of clays (Warsaw, 1960) from mixtures having the elemental composition insufficient in K for mica formation gave mixed layer assemblages, indicating that the K is not uniformly distributed but goes into certain micallike planes and leaves other planes free to expand, like the natural mixtures of mica with expansible lattices found by the above workers.

Nonetheless, in pedogeochemical weathering the cleavage space tends to become cluttered with precipitates of aluminum-iron-magnesium hydroxides (Jackson, 1960b). Laboratory-prepared montmorillonite plus aluminum hydroxide (Slaughter and Milne, 1960) is glycol expansible ("swelling chlorite") initially but "cannot be re-expanded once it has been collapsed" by drying. A characteristic 14.7 Å spacing was obtained from some preparations. Some of the aluminum hydroxide-montmorillonite complexes showed collapse to 9.7 Å at 250 °C while others collapsed much less completely even at 600 °C. The magnesium hydroxide interlayer that developed in montmorillonite gave a strong 002 reflection at 7.4 Å, equal to the 001 intensity, while the nickel hydroxide interlayer gave a very strong 002 at 7.3 Å and near absence of the 001 at 14.7 Å. The latter preparation might aptly be termed a "7 Å chlorite."

Magnesium of sea water accumulated in the exchange positions of montmorillonite (Carroll and Starkey, 1960) and this suggests a pathway to chloritization of expansible layer silicates deposited in the sea (pH 7.4-8.5), corresponding to the alkali soil chloritization reported by Jackson (1960b). At the same time, the mobilization of silica from clays in contact with sea water (Carroll and Starkey, 1960) reflects the type of chemical reaction that would be required to upgrade the layer charge (Al for Si) to hold the full mica level of K in interlayers, noted by Mehra and Jackson (1959a).

Pinsak and Murray (1960) concluded that the main control on clay mineral content of Recent sediments is the clay mineralogy of the source area. This concurs with Burst (1959) and Weaver (1959) for materials not involved in deep burial. Expanded clay minerals appear to be partially contracted by the time they have been buried 10,000-15,000 ft (Weaver, 1959), and illite was found to be the dominant clay mineral in Mississippian and older sediments. A study of less ancient sediment, the Eocene Wilcox formation (Burst, 1959), showed that burial to a depth of 12,000-14,000 ft correlated closely with the loss of montmorillonite swelling characteristics and concurrent increase in heat-stable 14 Å spacing and glycol-stable 10 Å spacing.

It should not be inferred that pedogeochemical weathering is simply a matter of expansion and contraction of layer silicates with attendant plus-or-minus interlayering with K or hydroxides. The presence of a deep mor (organic acid, humus) layer under kauri trees of New Zealand produced

an  $A_2$  horizon of the soil having a clay fraction that was 95 percent  $\text{SiO}_2$  in the form of quartz and cristobalite (Swindale and Jackson, 1960). The destruction of layer lattice clays was observed to be in the reverse order of weathering stability in the absence of cheluviation (a part of the process of podzolization), the rates of destruction being in the order: iron oxides > gibbsite > kaolinite > 2:2 and 2:1 layer silicates > quartz-cristobalite.

### DIFFERENTIAL DISSOLUTION ANALYSIS CORROBORATED

The heating-NaOH method was proposed (Hashimoto and Jackson, 1960) for differential dissolution analysis (DDA) of kaolinite + halloysite from clay samples, leaving the chlorite and intergradient 2:1-2:2 minerals undissolved. Heat collapsible intergrade of soils appeared to be only slightly dissolved while kaolinite and halloysite were dissolved (Dixon and Jackson, 1960, 1962). The intersalation method provides an ideal qualitative and semiquantitative tool to check the validity of the quantitative method. It was found (Andrew, Jackson and Wada, 1960) that complete corroboration was obtained; namely, clays having little or no kaolinite or halloysite by DDA gave no 11.6 Å peak by intersalation; such soils as Crosby coarse clay with 15 percent kaolinite and halloysite by DDA (Dixon and Jackson, 1959) gave a noticeable 11.6 Å peak. Those high in kaolinite-halloysite (Dixon and Jackson, 1960, 1962) gave a relatively strong 11.6 Å peak (Andrew, Jackson and Wada, 1960, Fig. 1).

It should be pointed out that the amorphous materials including free oxides and allophane (Hashimoto and Jackson, 1960) and, for the most precise work the 400 °C-soluble intergrade aluminum (Dixon and Jackson, 1959) must be dissolved from the sample prior to the kaolinite + halloysite determination. The content of allophane can be determined quantitatively by cation exchange capacity hysteresis or delta value (Aomine and Jackson, 1959). The quantity of montmorillonite, as distinct from vermiculite, can be determined quantitatively, whether as discrete crystals or as an interstratified component, by the duo-interlayer specific surface method (Mehra and Jackson, 1959b). Thus much more quantitative analysis of clay is possible by the several methods than can ever be achieved by X-ray diffraction alone.

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