

Some Concepts of the Relationship Between the Chemical Compositions and Structures of Clay Minerals*

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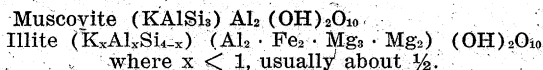
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The common clay minerals which have been investigated up to the present time can be classified in one or the other of two general structural types. The first type may be thought of as resulting from the condensation of an hexagonal net of silica tetrahedra with a layer of hydrargillite giving rise to a double layer of composition $(\text{OH})_4\text{Al}_2\text{Si}_2\text{O}_6$. The second type arises from the condensation of two such silica nets, one above and one below, with one hydrargillite layer, giving rise to a triple layer of composition $(\text{OH})_2\text{Al}_2\text{Si}_4\text{O}_{10}$.

Of these two types the first seems to be the less variable. It includes kaolinite, nacrite, dickite, and the halloysites. The second type is subject to many significant variations in chemical composition with concomitant effects on physical properties. In this group are found montmorillonite, beidellite, nontronite, illite, and perhaps several others. It has been suggested by several investigators, notably Linus Pauling¹ and C. E. Marshall² that the broader chemical freedom of the second type is due to the greater stability of its symmetrical configuration. It is with the inferential relationships between the chemical composition and properties of the second type that this paper is concerned.

In these two idealized types, each silicon ion is located in the interstice between four oxygen ions in tetrahedral configuration, and each aluminum ion in the interstice between six oxygen (or hydroxyl) ions in octahedral configuration. On the basis of various proven structures for silicate minerals, the following substitutions have been suggested as possible: tetrahedral positions may be occupied by Al^{+++} or by P^{++++} ; octahedral positions may be occupied by Mg^{++} , Fe^{++} , Fe^{+++} , Ti^{++++} , or Li^+ .

By far the most common, the best authenticated replacement, is that of Al^{+++} for Si^{++++} , as it occurs in muscovite.³ One fourth of the Si^{++++} positions are occupied by Al^{+++} , and the excess (—) charge resulting is compensated by the presence of one K^+ ion in 12-coordination between triple layers. Muscovite builds a rigid stable crystal with perfect cleavage between layers. Its rigidity is attributed to the attractive power of the K^+ ions for each of the adjacent triple layers. Illite, perhaps the most widely distributed clay mineral in Illinois, exhibits the same crystal structure as does muscovite. It differs in having a lower K_2O content, a higher relative content of SiO_2 , and in the exhibition of moderate base-exchange properties. Whereas the ratio of Si^{++++} to Al^{+++} in the tetrahedral layers for muscovite is 3, and one K^+ ion is required for each set of 4 such positions, the similar ratio for illite may be 6 or 7 or higher, and only about one K^+ ion is required for two sets of 4 such positions. Thus the illite, being subject to only about one-half the attractive forces responsible for the crystal habit of muscovite, occurs as a clay rather than as macro-crystals. The analogy between the two minerals is perhaps better illustrated by examination of "structural formulae" for each:



A second common, and significant, replacement is that of Mg^{++} (or Fe^{++}) for Al^{+++} in octahedral positions. This replacement, presumably can occur in either of two ways, as has been implied in the above formula.

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Three Mg^{++} ions may perform the role of two Al^{+++} ions as has been deduced in the case of several biotite micas, and of talc, without the introduction of any unbalanced charges, or one Mg^{++} ion may directly replace one Al^{+++} ion with the appearance of one excess (—) charge per replacement. Such a (—) charge, however, differs from that observed in the case of muscovite in that, whereas, the muscovite charge is localized at the surface of a unit and can be readily balanced by an adjacent K^+ ion, this second sort occurs in the middle of a stable structural unit. Observations on specimens of montmorillonite have shown that the number of this sort of charges approximates the base exchange capacity. Montmorillonite is a soft, finely crystalline, and very readily dispersed clay with high base exchange capacity.

Nonttronite is a name applied to several clays with physical characteristics quite similar to those of montmorillonite, but with more or less Fe_2O_3 content. These are presumed to arise from substitution of Fe^{+++} ion for Al^{+++} ion in octahedral positions, a substitution which does not effect electrical neutrality. Both nonttronite and another similar clay, beidellite, are commonly distinguished from montmorillonite on the basis of lower $SiO_2:R_2O_3$ ratios, but neither is fully characterized at present.

No natural clay has yet been observed where only one sort of replacement could be shown to be active. However, these qualitative considerations of the relations between physical properties, structure, and chemical composition lead to the suggestions that in cases where the first sort of substitution predominates one finds the illites, with stable lattice dimensions, moderate plasticity, and moderate base exchange capacities; where the second sort of substitution predominates the clays swell on addition of water, disperse readily to extremely small particle sizes, and exhibit high base exchange capacities.

LITERATURE CITED

1. L. Pauling, *Proc. Nat'l Acad. Sci.* **16**, 123-9, 578-82 (1930).
2. C. E. Marshall, *Zeit. Krist.* **91**, 433-49 (1936).
3. W. W. Jackson and J. West, *Zeit. Krist.* **76**, 211-27 (1930).