

The Place of X-Ray Diffraction in Clay Mineralogy*

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Studies in the mineralogy of clays have been unique in that the clay minerals are the only rather large group, mineralogically, in which optical and chemical data did not precede crystal structure data by one or more decades.

Various arbitrary definitions of clays have suggested that the term be reserved for materials made up of particles below 5 or 2 or 1μ . These magnitudes are of no significance in the present paper, but they readily explain why petrographers were forced to await twentieth century developments on the microscope before seriously attacking clay problems.

Almost contemporaneously with the optical characterization and naming of a number of apparently distinct clay mineral species, X-ray powder diffraction diagrams were registered for them, and these diffraction diagrams were used in a cataloguing sense as a criterion of identity additional to the optical data and chemical analyses. By 1930 six or eight rather common minerals and a somewhat greater number of rarer ones had been recognised. Since then additional work has resulted in the dropping of a few names as duplications, and in one or two additions.

In 1930, Linus Pauling presented before the National Academy of Sciences a series of papers outlining the general features of the crystal structures of several clay minerals and of the micas, chlorites, and talc. The minerals included in the scope of his work were all those common silicates exhibiting pronounced basal cleavage, and the series of layer structures proposed were consistent with this property. These papers, offered somewhat as predictions, virtually did predict all the work done in this field up to the present. Each structure is based upon hexagonally packed layers of oxygen atoms, adjacent layers being so displaced as to permit the presence at the interstices either of silicon atoms tetrahedrally surrounded, or aluminum atoms octahedrally surrounded. Various minor modifications are made to fit specific cases. For example, in the muscovite micas one-fourth of the tetrahedral positions are occupied by aluminum, and the resultant deficiency of positive charges is compensated for by an alkali ion in the nearest open space.

The resultant feature of the close family resemblance of this broad group of minerals is that many of the X-ray diffraction lines are common to the entire group. Only lines related to the respective stackings of layers or the distance between adjacent layers, are criteria of the identity of a species. Relatively pure minerals are not easily miscalled but among mixtures greater care must be exercised. Differences in particle size of two samples of the same mineral exhibit more superficial differences than do distinct species of equal particle size in the lower size group. Since many clays contain as much as one-fourth by weight of particles below $.1\mu$, identifications in this range cannot be avoided.

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Another feature of X-ray diffraction work which assumes prominence in patterns obtained from mixtures of clay minerals is absorption edges. These result from the fact that crystals diffract the general radiation of shorter wave lengths as well as the characteristic radiation being employed, and mark the limiting energies beyond which bromine and silver, respectively, in the sensitive plate or film do not absorb radiation. These edges are most commonly observed in powder diffractions in the same region where the diagnostic features of characteristic diffraction are observed. For example, the bromine absorption edge corresponding to the 4.45Å line common to all clays falls almost coincident with the 7.1 line characteristic of kaolinite.

Most of these uncertainties can be obviated by a recently developed modification of the powder diffraction method. A clay suspension is permitted to dry in a flat surface, resulting in an aggregate of particles having their basal planes more or less parallel to the plane of the surface. Diffraction from such a specimen takes the form of a "fibre diagram" familiar in textile researches. Lines related to the diagnostic basal distances are arranged in one simple series and all others are reflected to the sides.

In answer to the question, "How valid is an identification made on the basis of this single series of reflections?", flakes made up of 0.05μ particles have been mounted on an oscillating spectrograph permitting the registration of high orders of the basal plane reflections. Satisfactory agreement between observed and theoretical, (or one might say micro and macro crystal), relative intensities were observed through 16 orders for kaolinite and through 22 orders for illite, a muscovite mica. The evidence is therefore conclusive that even the finest grained clays exist as the same species which are observed optically among the coarser grained.