
Procedure of clay mineral analysis

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Introduction

Recent advance of clay mineralogy has revealed subtle variations of properties even in individual clay minerals, and it is a general belief that detailed studies to clarify variations of properties of clay minerals are important not only from scientific viewpoints but also for industrial problems. Hence, it is necessary to develop a method of clay mineral analysis which is able to explain structural attributes and to show subtle variations of individual clay minerals; simple methods are usually useless. The purpose of this short report is to summarize a routine procedure used for such analyses.

Preparation of specimens

About 50 g of sample is placed in a porcelain dish and distilled water is added to make a paste, which is further kneaded and transferred into a 1000 ml graduated cylinder. Distilled water is added to the cylinder to make the volume 1000 ml, and then 1 ml NH₄OH-solution (about 5 N) is added as a dispersing reagent. The inhalt of the cylinder is stirred with a glass rod, and the minus-two-micron fraction (e. s. d.) is pipetted after a predetermined settling time of eight hours. The suspension is transferred into the centrifuge bottle and the suspending particles are collected and dried up at room tem-
perature.

The cylinder is refilled with distilled water, adding with ammonia solution, and the suspension obtained is pipetted after eight hours of settling. This procedure is repeated until a clear supernatant liquid is obtained.

In the case of volcanic ash soils particularly containing allophane, it has been well known that the maximum dispersion can be attained by HCl-treatment rather than by NH₄OH-treatment. Detailed discussion was made(1) by KANNO. The result hitherto obtained in our laboratory is briefly stated in the paper of KURAHAYASHI and TSUCHIYA (this Journal).

In the case of consolidated samples such as sedimentary rocks, the raw sample is disaggregated in a steel mortar to be passed through a 60 mesh sieve so as to remove sand grains. About 20-50 g of the pulverized sample, after passing through the sieve, is taken, and the minus-two-micron (e. s. d.) fraction is obtained as stated above. This fraction is used chiefly for clay mineral analyses including chemical, thermal, and X-ray analyses, and for electron micrographic investigations.

Even in investigations of qualitative features of clay minerals, it is desirable to carry out the procedure under a fixed condition in each sample, but it may not be necessary to carry out the procedure under so strictly fixed condition as in the case of quantitative studies.

**X-ray analysis**

X-ray analysis was usually carried out with well-oriented aggregates which are made by gently pouring a dilute suspension of the sample over a glass-slide and settled and dried up at room temperature.

(a) **X-ray examination of heated samples** Well-oriented aggregates are made on a silica-glass slide.

In the first step, X-ray powder diffraction effects are recorded at room temperature. In the next step the silica-glass slide is heated at every temperature stepwise as 100°C, 200°C,  . . . 1000°C for one hour, and air quenched, and X-ray diffraction effects are examined imme-
diately after each step of heating. In case there is a time gap between the removal of the slide from the furnace and the radiation by X-ray, the slide is placed in a decicator to prevent rehydration.

As is known well, investigations on diffraction effects after heating are helpful not only for differentiation of clay minerals but also for confirmation of subtle variations of heat effects even in individual clay minerals, as in the case of chlorite. Depending upon its chemical composition and also on crystallinity, the temperature where chlorites lose diffraction effects by heating ranges about 450°C to 700°C. Some chlorites in Recent marine sediments lose diffraction effects after heated at 450°C and immediately quenched as noticed by JOHNS, GRIM, et al. (2) It has been accepted that the dehydration of well-crystallized chlorites is completed mostly after heated at 850°C-900°C. No kaolinite has been found yet which decomposes after heated at 450°C; it usually decomposes after heated at 600°C. Although temperatures of decomposition of clay minerals depend on hours of heating, this procedure may be very helpful for differentiation of clay minerals when it is carried out under a fixed condition.

(b) X-ray examination of samples treated by organic reagents Oriented aggregates are made on another slide and immersed with a few drops of ethylene glycol or glycerol, and the wet film thus obtained is radiated by X-ray. In this treatment, preferred orientation is usually disturbed, so that a paste of clay powder obtained by immersing with glycerol is pressed between two slides, and each of them is pulled toward the opposite directions by pressing for the purpose of bringing the aggregates to well-oriented state again. However, even if such a procedure is taken, we met with cases where such treatments fail to make stronger basal reflections again. (3) Expansion of expanding lattices is usually well attained when the sample is converted to Ca-clay by passing it through a calcium ion-exchange resin column before treating it with glycerol. This treatment is very necessary for detection of the presence of expanding lattices. But, WALKER (4) recently pointed out the very complex attitudes of vermiculites and montmorillonite minerals concerning formation of glycerol and ethylene glycol complexes. He
suggested that the glycerol test can be applied to the differentiation between these two mineral groups in the case of homoionic specimens.

(c) X-ray examinations of samples treated by inorganic reagents

Treatment with ammonium nitrate solution for detection of Mg-vermiculite. Oriented aggregates are made with the sample which was boiled in 1N ammonium nitrate solution for ten minutes, washed by distilled water, and dried up at room temperature. It was reported by WALKER that this treatment usually caused the 14 Å reflection of vermiculite to be replaced by the 10 Å reflection.\(^\text{(5)}\)

Treatment with sodium citrate, calcium chloride, and glycerol for confirmation of dioctahedral analogue of vermiculite.\(^\text{(6):7)}\) It was reported for the first time by BROWN\(^\text{(6)}\) that the persistency of the 14 Å reflection after treatment with ammonium nitrate solution is not necessarily due to chlorite; interlayer contaminants such as aluminum ions may prevent the contraction of lattices. TAMURA\(^\text{(7)}\) extended the procedure of the confirmation of dioctahedral analogue of vermiculite by removing aluminum ions by treating it with citrate solutions.

Treatment with magnesium acetate solution to know the degree of weathering of illite.\(^\text{(8)}\) Oriented aggregates are made with the sample boiled in 1 N solution for one hour on a water-bath, washed with distilled water, and dried up at room temperature.

Treatment with hydrochloric acid to decompose chlorites. Oriented aggregates are made with the sample warmed in about 6 N hydrochloric acid on a water-bath for one hour, washed with distilled water, and dried up at room temperature. This treatment is helpful to detect kaolinite in a mixture of it and chlorite, because chlorites, particularly iron-rich types, decompose by this treatment.

Differential thermal analysis

Differential thermal analysis curves are recorded with the samples less than two microns in natural state or treated with piperidine. The procedure, as reported by ALLAWAYS,\(^\text{(9)}\) is very effective to detect the presence of a small amount of montmorillonite. The procedure
used in our laboratory is as follows: the sample is soaked into piperidine for about 30 minutes and dried up on a water-bath.

**Electron micrographic methods**

The sample of minus-two-micron is immersed with a few drops of distilled water to make a paste, and a piece of it is placed on a film-coated grid. A jet of water is sprayed on the paste on the grid to make a dilute suspension film covering the surface of the grid.

The steps of the procedures as mentioned above are summarized in the following Table.

<table>
<thead>
<tr>
<th>Raw specimens</th>
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<tr>
<td>(Disaggregation, sieving, dispersion)</td>
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<td>(Centrifugation, decantation)</td>
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<tr>
<td>Sand and silt</td>
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<td>Clay (&lt; 2 μm)</td>
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**Sand grains:**
- (1) Microscopic observations of coarse grains; polished surface of opaque grains; and thin sections.
- (2) X-ray, chemical, and differential thermal analyses.

**Clay fractions:**
- (1) X-ray analysis of specimens:
  - (a) untreated.
  - (b) heated at 100°C, 200°C, ..., 1000°C.
  - (c) treated with ethylene glycol or glycerol.
  - (d) treated with ammonium nitrate solution (1 N).
  - (e) treated with hydrochloric acid (6 N).
  - (f) treated with magnesium acetate solution (1 N).
  - (g) treated with sodium citrate, calcium chloride, and glycerol.
- (2) Differential thermal analysis of specimens:
  - (a) untreated.
  - (b) treated with piperidine.
- (3) Chemical analysis.
- (4) Electron micrographic observation.
- (5) Staining test.

**References**

Amorphous clay allophane separated from subsoils of volcanic ash origin in Japan, when treated with H-saturated cation exchange resin and OH-saturated anion exchange resin, or electrodialyzed, has relatively high ultimate pH and shows no titrable exchange acidity. In addition, allophane dispersed by hydrochloric acid (above pH 4), settled by an addition of sodium chloride and washed with 80% ethanol until practically free from chloride, liberates during electrodialysis considerable amounts of chloride ion but little cations, while when the clay is dispersed in acid media, settled by neutralization about to pH 7 and washed with distilled water until it become chloride-free, the situation of ion adsorption is reversed.

From these observations, the following two facts may be deduced: firstly, allophane has nature of an ampholytoid with relatively high pH of isoelectric point, secondly, when treated with a neutral salt solution (N-KCl in this case) H⁺ and OH⁻ dissociate simultaneously from allophane surface canceling the exchange acidity and alkalinity one another. Even silica gel shows an appreciable exchange acidity.

Several results of the more detailed investigations on these properties of allophane will be described.