

CLAY MINERAL WORK PROCEEDING IN JAPAN

By

TOSHIO SUDO

Tokyo University of Education

ABSTRACT

Studies on clays in Japan were begun about 1900. Modern clay mineralogical work began about 1940 and is being developed in the following scientific and industrial branches: geology, mineralogy, chemistry, ceramics, soil sciences, soil mechanics, etc. Recent important items are as follows: (a) Order-disorder problems of clay minerals. (b) Studies of clay minerals by electron micrographs and electron diffraction methods. (c) Mixed-layer minerals. (d) Studies on alteration products of volcanic glass. (e) Studies on sedimentary rocks and recent sediments. (f) Clay minerals associated with various kinds of ore deposits, and particularly wall-rock alterations. (g) Soil clay minerals, particularly of volcanic ash soils, paddy soils, etc. (h) Mineralogical and colloid-chemical studies of bentonites and acid clays. (i) Clay deposits for ceramic uses. (j) Studies of complexes between clay minerals and organic reagents. (k) X-ray studies on transformation of kaolin minerals.

The results emphasize certain general characters of Japanese clays such as a complex mode of association among clay minerals, or prevalent occurrence of minerals having a lower degree of crystallinity.

INTRODUCTION

Studies on clays were begun in Japan before 1900. The late Professor S. Koza and his collaborators of Tohoku University first carried out thermal studies, including differential thermal analysis of ceramic clay materials. This, together with excellent work on feldspar problems, is still appreciated. The late Professor K. Kobayashi of Waseda University first discovered an interesting clay from Niigata Prefecture in 1899, which he named an acid clay and which he investigated from the chemical-industrial viewpoint. His work was developed especially by K. Yamamoto, Y. Otsubo and others of Waseda University. The studies of Japanese bentonite by M. Uchida, and of glauconite by J. Takahashi and T. Yagi of Tohoku University are also important contributions. Although studies on clays are advancing daily, we still appreciate the work of these early investigators who initiated clay mineral studies in Japan and facilitated subsequent developments.

Clay mineral studies based on modern concepts were begun about 1940, mostly by the writer and his collaborators. This activity was encouraged especially by industrial concerns which considered that properties of clays will never be made clear fundamentally unless they are studied in detail. This recent progress has been facilitated by the development of modern scientific techniques and also by clay research in many different scientific fields. Recent clay mineral studies in Japan have taken place in the fields of geology, mineralogy, chemistry, physics, soil chemistry, soil mechanics, chemical industry, and ceramics. A short summary of recent work is given.

STACKING DISORDER

Stacking disorders in the layer structures of Japanese clay minerals, particularly kaolin minerals, sericite and montmorillonite, have been dealt with by M. Nakahira (1949, 1951, 1952) and M. Nakahira and S. Iwai (1949, 1953). These studies are based on x-ray diffraction data obtained from clay powders and/or thin films formed by drying water-suspensions of clays. The conclusions were based mostly on sharpness, diffuseness, and indices of the powder lines or diffraction spots obtained. Generally speaking, the results indicate a wide range of stacking disorders from nearly ordered, to partially disordered with random displacements of $\pm 1/3 b_0$, to fully disordered with random displacements of $\pm 1/3 b_0$, to random layer structures.

MIXED-LAYER MINERALS

Recently the writer and his collaborators confirmed the presence of long spacings in the powder patterns of certain clays from Japan. Clays with long spacings are also being found in several other localities suggesting that this feature is less rare than we hitherto anticipated (Sudo, Takahashi, and Matsui, 1954, 1954a; Sudo and Hayashi, 1955). The writer and his collaborators found that some so-called acid clay shows x-ray powder photographs with a total absence of basal reflections, and suggested that their properties were caused by a sort of random mixed-layering (unpublished).

ELECTRON DIFFRACTION DIAGRAMS

Advances in techniques of electron microscopy have facilitated the study of clay minerals, giving many clear electron micrographs; Professor C. Kawashima of the Tokyo Institute of Technology is a pioneer in the morphological study of clay minerals by the electron microscope. Recently a three-stage electron microscope has shown clearly the electron diffraction diagram of a single clay crystal observed in the electron microscope (Ito and Ito, 1953). Professor G. Honjo and his collaborators in the same institute studied the electron diffraction diagrams of chrysotile and halloysite and confirmed the following: (a) Of 160 crystallites of Hong Kong kaolin examined, eight had [1,0], three had [3,1] and the remainder had [0,1] as their tube axes. For tubular kaolin, [0,1] seems to be the predominating tube axis. (b) Continuous intensity distributions along layer lines were more or less indicated in the diffraction diagrams of reference specimens (Hong Kong and Spruce Pine kaolins). For these kaolins, intensity peaks corresponding to a well developed three-dimensional structure were sometimes more predominant. The intensity peaks are due to a structure having a period of about 14.4 kX perpendicular to the kaolin layer. Even where the continuous intensity distributions were considerable and three-dimensional peaks were less defined, at least the existence of an 021 reflection was always recognized (Honjo and Mihama, 1954).

CHESTNUT SHELL-LIKE SHAPE OF CERTAIN CLAYS REVEALED IN ELECTRON MICROGRAPHS

In 1949, an interesting clay was discovered which has mineralogical properties similar to hydrated halloysite except that its electron micrograph shows

rounded grains. Such a clay from Shichinohe-machi, Aomori Prefecture, was studied mineralogically (Sudo, Minato, and Nagasawa, 1951), with x-rays (Nakahira, Iwai, and Suzuki, 1951); it was also compared with Japanese fire clays (Muraoka, 1952) and studied by thermal methods (Sudo and Otsuka, 1952). On examination with the electron microscope, the writer found, in most preparations, rounded grains in close association with elongated crystals of halloysite minerals, which frequently project from the central rounded grain and are shaped like chestnut shells (Sudo, 1953a). The writer and his collaborators (Sudo, 1953, 1954; Takahashi, 1955) are studying this variety of clay and are suggesting a crystallization course of volcanic glass. Kinoshita and Muchi (1954) have reached the same conclusion in their study of bauxitic clay from Kyushu.

CLAY MINERALS ALTERED FROM TUFFS AND VOLCANIC ROCKS

Tuff and tuffaceous sediments are widely distributed in Japan and commonly have suffered intense alteration to clay materials. The writer first pointed out the importance of clay-mineral study of the alteration of tuff and related rocks. Nearly all kinds of clay minerals are found as alteration products, taking into account those formed by weathering processes and by hydrothermal action. The principal alteration products considered to have been formed from volcanic glass by weathering processes are as follows: (a) kaolin minerals, (b) montmorillonite minerals, and (c) mica clay minerals. The kaolin minerals included kaolinite, halloysite (dehydrated), hydrated halloysite, allophane, and the white kaolin clays showing the chestnut-shell shape mentioned above. Montmorillonite minerals are the principal components of most so-called bentonites and some so-called acid clay. Among the mica clay minerals, celadonite and related materials are dominant in replacing pumice fragments in so-called green vitric tuff. The origin of the celadonite is not obvious. The writer considers that the mineral possibly may be formed by weathering under sea water; however, it may also be explained by hot-spring action (Sudo, 1951).

The writer illustrated the alteration products formed by weathering processes from vitric tuff as indicated above. However, in many cases it is considered that hot-spring action may have an important role in the formation of clays from tuff. Some bentonites and acid clays, particularly those developed around ore deposits, are in this category. Quartz and cristobalite can be detected commonly in bentonite or acid clay by x-rays; the cristobalite is considered to have been derived from opaline silica. Furthermore, zeolite is commonly found in a certain bentonite (Sudo, 1949). Iron-montmorillonite was found in the montmorillonite zone developed around an ore deposit (Sudo, 1950). A special iron-rich variety of montmorillonite was found as an alteration product from volcanic rock fragments included in Oya-ishi which is a thick vitric tuff used as an important building stone (Sudo and Ota, 1952). The origin of the montmorillonite is uncertain. The writer believes that this special alteration may have been caused by a kind of autometamorphism of the volcanic rock by volcanic vapor trapped in fragments during rapid formation of the thick tuffaceous rock.

Altered volcanic rocks (andesitic or basaltic) and pyroclastic rocks are widely distributed in the Tertiary formations; some of them are described as green tuff. The alteration products are sericite from felsic minerals, and chlorites

from mafic minerals and groundmass. It is noteworthy that iron-rich saponite is considered to be widely distributed in these rocks. The Tertiary iron sand beds are commonly associated with altered basalt and andesite, and in these rocks iron-rich saponite is commonly enriched (Sudo, 1954a). Recently Yagishita carried out clay-mineral studies on green tuff and showed that the alteration products are mica clay minerals, montmorillonite minerals (including iron-saponite), and kaolin minerals. He indicated that two-layer minerals are commonly dominant in nonmarine facies whereas three-layer minerals are dominant in marine facies (Yagishita, 1952, 1953a, 1954, 1954a; Yagishita and Araki, 1953).

RECENT MARINE SEDIMENTS

The clay minerals of recent marine sediments have been studied. Yamanouchi and Tanaka (1954) identified illite and montmorillonite in the marine clays in the region north of Kyushu. Kitazaki and Suzuki (1954) found that blue muds are composed largely of amorphous materials plus small amounts of quartz and illite.

CLAY MINERALS ASSOCIATED WITH ORE DEPOSITS WITH SPECIAL REFERENCE TO WALL-ROCK ALTERATIONS

Various kinds of clay minerals have been found in intensely altered clay zones adjacent to ore bodies. Special attention is being given by clay workers to the problem of wall-rock alterations. Almost all the principal clay minerals are found in the various kinds of ore deposits. The writer (Sudo, 1954b) suggested a somewhat regular mode of association between metallic minerals and clay minerals which are found in close association with the metallic minerals and are considered to have been formed essentially contemporaneously with metallization. The types of association are as follows: gold ore (kaolin minerals, montmorillonite), silver ore (montmorillonite), mercury, tellurium, and antimony ores (kaolin minerals and sericite), copper ore (sericite and chlorite), lead and zinc ores (chlorite and sericite). Chamosite is associated with certain copper ores (Sudo, 1943, 1954b). Numerous reports have been published concerning sericite which commonly predominates as a clay mineral associated with metallic ores of the epithermal type. Its mineralogical properties are nearly the same as those of muscovite in specimens of sericite schist; however, sericite is slightly different from muscovite, having less potassium, more water, and lower degree of crystallinity (Honda, 1951; Hashimoto, 1953, 1954; Kitazaki, 1952; Yagishita, 1953). Special varieties, such as iron-sericite and magnesium-sericite, were found by Minato and Takano (1952) and were studied in relation to wall-rock alteration (Iwao, 1953).

Clay mineral studies of wall-rock alteration have clearly shown the development of clay zones around ore bodies. The following zonal arrangements, from unaltered country rocks progressing toward ore areas, were confirmed. In sulfur deposits the following sequence is found: so-called propylite, including iron saponite; sericite; halloysite minerals; kaolin minerals, limonite; kaolin minerals; alunite; opal; sulfur, pyrite; sulfur (Mukaiyama, 1954, 1954a). The hornblende andesite near Beppu, Kyushu, is associated with the following zones:

hornblende andesite, kaolin minerals, alunite, silicious zone (Kinoshita and Muta, 1953). This silicious zone is composed largely of opaline silica which is easily dissolved by alkalis and is used as a raw material for cement. A similar zonal arrangement occurs in the rocks of the Kasuga mine, namely: so-called propylite; kaolinite; limonite, kaolinite; dickite; alunite; silicious zone, including gold (Tokunaga, 1955). The kaolinite of this mine has previously been examined mineralogically (Muta, 1952). It is also noteworthy that dickite is associated with certain antimony deposits in the same mine (Matsukuma and Tanaka, 1955).

A detailed study of the wall-rock alteration of the Kosaka mine was made by S. Iwao, F. Kishimoto, and K. Takahashi (1954). The ore deposit of this mine is one of the principal "Kuroko" deposits—a hydrothermal replacement deposit consisting of pyrite, chalcopyrite, galena, zinblende, and gypsum. This rock is widely distributed in northeastern Japan. This ore deposit shows a zonal arrangement as follows: unaltered wall rock, montmorillonite; main clayey zone; silicious zone. The writer made a detailed mineralogical study of the altered area of an ore body of the Hanaoka mine, which is also a typical "Kuroko" deposit, and found the following zonal arrangement: unaltered wall rock; montmorillonite; chlorite, sericite, kaolin minerals; ore bodies. It is noteworthy that clay minerals having long spacings were found in the clay zone of chlorite, sericite, kaolin minerals; the chlorite is generally of a magnesium variety. Leuchtenbergite has been identified in the chlorite zone developed around the gypsum deposit of the Wanibuchi mine, Shimane Prefecture.

So-called propylite is very commonly found in the wall rock of metallic deposits (Sudo and Sekine, 1951). Mineralogical studies of the altered area formed by a copper vein in propylite were undertaken by Sudo, Nagasawa, Iwao, and Omori (1953).

CLAY MINERALS ASSOCIATED WITH COAL

Recently the mineralogy of the clays associated with coal measures has been studied. Large quantities of bentonite are associated with certain coal measures of Kyushu; the bentonite is composed of montmorillonite and illite (Kinoshita and Tanaka, 1949). Kaolin minerals and montmorillonite are two principal alteration products from the sediments associated with certain coal measures in Hokkaido. It was inferred that three-layer minerals may be dominant in marine sediments and two-layer minerals in nonmarine sediments (Araki, 1953; Suzuki, 1954, 1954a; Suzuki and Kitazaki, 1954a). N. Obara (1954) in an interesting study of the underclays associated with the Ishikari coal field in Hokkaido, identified kaolin minerals and montmorillonite and suggested that kaolin minerals may have been formed in a warmer climate and montmorillonite in a cooler one. He also considered the underclays from the geochemical point of view, tracing the relationship between the silica:alumina ratio and the content of organic carbon in reference specimens of the underclays.

SOIL CLAY MINERALS

Japanese soils were examined by chemical and x-ray methods by Professors M. Shioiri, T. Seki, K. Kawamura, S. Funabiki, and others. Recent studies dealt with clays in paddy soils (Uchiyama and Onikura, 1954, 1954a), upland soils

(Egawa, Watanabe, and Sato, 1955), and volcanic ash soils (Aomine and Yoshinaga, 1955; Nozawa, 1953). The genesis of soil clays was discussed in detail for the soil derived from granodiorite, Fukushima Prefecture (Masui, 1954, 1954a). Generally, indistinct thermal reactions and diffuse x-ray diffractions prevent detailed conclusions. However, it seems that paddy soils are composed largely of mixed-layer minerals (random or regular) between montmorillonite and kaolin mineral lattices. Diffuse reflections with long spacings of 20 to 30A were detected. In upland positions, allophane is the principal clay material in volcanic ash soils, and kaolin minerals predominate in the other soils (Diluvium and Tertiary soils). It is worth noting that T. Harada and K. Kutsuna (1954, 1955, 1955a) found a soil containing vermiculite near Yahatahama, Shikoku, and carried out detailed studies on this material.

CERAMIC RAW MATERIALS

For many years the Geological Survey of Japan has contributed to geological and mineralogical studies of argillaceous ceramic raw materials, and considerable information has been published. The most recent report is listed here along with the summarizing reports (Ando, 1952; Muraoka and Tanemura, 1954; Tanemura, 1954, 1954a), in which clay mineral work was described. Pyrophyllite deposits are distributed mostly in the Chugoku district and are associated with kaolinite, dickite, diaspore, and corundum in highly aluminous clays occurring as hydrothermal replacement bodies; Mitsuishi pyrophyllite has long been famous (Kimura, 1951). Sedimentary kaolin deposits (the so-called "Kibushi" and "Gaerome" clays) are distributed widely in the Chubu district. These clays have been used for whiteware and fire clay. The clay deposits of the lower Quaternary were formerly thought to have been formed by weathering processes from granitic rocks; recently, however, volcanic ash is being considered as a source (Nozawa, 1953a, 1953b). Underclays as, for example, Iwate clay and Iwaki clay, have been used as important fire clays (Muraoka, 1952). Bauxitic clays, including gibbsite, are found in Kyushu. The Yame clay is an example; it is thought to have been formed from tuffaceous beds by weathering processes, but its origin is not yet perfectly understood (Muraoka, 1952). Some kaolin deposits formed by hydrothermal action (e.g., Kampaku kaolin from Tochigi Prefecture) are commercially important (Mutho, 1952). In general the ceramic argillaceous raw materials of Japan are of Quaternary or Tertiary age, regardless of their sedimentary or hydrothermal origin. Small-scale deposits are common; however, they are not uniform in either their mineralogical or their ceramic properties.

CHEMISTRY OF BENTONITE AND ACID CLAY

Studies of acid clays are among the most important clay studies in Japan. These were begun by the late Professor K. Kobayashi of Waseda University, and have been continued by many workers, including Professors K. Ishikawa, Y. Otsubo and others. These studies have been carried out mostly in the chemical industries and they make use of modern techniques, such as differential thermal analysis. The method of arriving at the structural formula of montmorillonite minerals has been applied to the chemical composition of acid clays (not necessarily monomineralic), and it was shown that most acid clays may be expressed

as a structural formula of montmorillonite plus certain percentages of excess silica. In short, acid clays are considered to be a complex of colloidal silica and a clay derivative. Montmorillonite is considered to change to a complex of colloidal silica and an acid clay by the process of activation (Otsubo and Kato, 1950, 1953; Otsubo, 1950, 1951). A hydrothermal synthesis of acid clay is reported (Otsubo and Kato, 1952). Sasaki (1952, 1952a) studied geological, mineralogical, and colloid-chemical properties of an acid clay (Itoigawa clay) and showed that this clay is largely a kaolin mineral. Further studies of acid clay and bentonite will be developed more from the mineralogical standpoint.

Recently H. Takahashi (1955a) studied the complex of montmorillonite and benzidine. Mainly from detailed x-ray study, he pointed out that benzidine and montmorillonite may form a complex which is blue in the presence of interlayer water. The blue color disappears when the clay is dehydrated and reappears when it is moistened. Recently also the kinetics of color development of some clay mineral sols with benzidine was studied (Shirai and Ishibashi, 1954). B. Tamamushi studied the physico-chemical properties of sericite, especially the rheological behavior of sericite suspensions in water, electrolyte solution, and carbon tetrachloride. In certain specimens, he reported beautiful interference colors which were attributed to the formation of multiple layers when the flaky sericite particles arranged themselves parallel to each other and separated by distances of the order of 2000 Å to 4000 Å (Tamamushi and Shirai, 1954).

MISCELLANEOUS AND UNPUBLISHED STUDIES (AS OF JULY 1955)

Hydrated halloysite from Ishikawa Prefecture, and garnierite from Fukui Prefecture were studied mineralogically (Sugiura, 1955; Kinoshita, Tanaka, and Miyashita, 1949). Trace elements in the residual kaolin clays from Aichi Prefecture were studied by K. Fukuo (1949). In regard to the genesis of clay minerals, reference is made to T. Sakamoto's (1954) paper. He reviewed data on the profiles of residual clays and discussed the environmental conditions of their formation. M. Nakahira (1954) recently published a crystal-structural view of the thermal transformation of kaolinite and halloysite on the basis of their dehydration curves. He stated that the dehydroxylation of well-ordered kaolinite takes place in two steps whereas halloysite dehydrates in one stage. The firing product in the first stage is not necessarily amorphous but is a pseudo-crystalline mineral.

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