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Mineral Composition of Clay from the Minami-Shiraoi mine, Southwestern Hokkaido*

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Abstract

The results of X-ray diffraction, DTA, and infrared absorption spectroscopy showed that kaoline clay from an altered green tuff of the Neogene Tertiary, forming the basement of the Kuroko-type Minami-Shiraoi ore deposit, consisted mainly of kaolinite, quartz, and pyrite. On the basis of both normative composition in the raw clay sample and X-ray reflection intensities characteristic of the major minerals, quantitative mineral compositions in six successive particle-size fractions were estimated. Kaolinite was abundant in the coarser fractions, reaching 84% by weight in the 10-5 μ fraction, while a small but significant amount of pyrite remained even in the <3 μ fraction. It is inferred from X-ray fluorescence, DTA, and chemical analysis that material containing heavy metals, probably in the form of sulphide or sulfate, are concentrated in the <3 μ region. To efficiently purify kaolinite in the clay by flotation, it is necessary to first remove the sulphides in the fine fractions, particularly in the <3 μ fraction. Physical elimination of these sulphides is beneficial in order to avoid environmental contamination by such heavy metals as Cu, Zn, Pb, Ni, and As, which are concentrated in the <3 μ fraction.

Introduction

The Minami-shiraoi mine, which is located about 13km northeast of the National railroad station at Shiraoi in southwestern Hokkaido, has yielded barite and kaoline clay. In the past barite, after purification by hand-picking and flotation, has been supplied as a material for chemical reagents, while attention had not been paid to the use of kaoline clay until several years ago. Today, however, the clay has become of major importance at the mine. The mined clay ore is separated from most of the sulphide minerals contained in it by flotation, since the presence of the sulphides greatly reduces value of the clay. Chemical treatment with a sodium hydrochlorite solution is also employed to eliminate the sulphides remaining in the flotation product as well as to whiten it. In 1976 raw clay ore was mined at the rate of about 1800 tons a month, and the purified kaoline clay was shipped at the rate of about 700 tons a month to a paper-making factory. The grain-size distribution of clay used in the manufacture of paper is required to be within a relatively narrow range, and the amount of

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halloysite or metahalloysite, which is frequently found in kaoline clay, needs to be sufficiently low that the quality of the clay is not adversely affected. Data on grain-size distribution of principal minerals in the clay is essential not only for effectively separating kaoline from other minerals but also for more extensive utilization of kaoline clay.

For these reasons, we began to determine the quantitative mineral composition of the black clay mined recently at Minami-Shiraoi. The results which appear in later sections, are not conclusive because of the necessity for more extensive examination. This paper, however, provides fundamental data for the purification of kaoline.

Outline of geology of the ore deposit

The Minami-Shiraoi ore deposit is of the Kuroko type. Lenticular ore bodies, consisting of sulphide minerals and silicate minerals associated with barite, occur in a green tuff of the Neogene Tertiary. The major ore body, consisting of barite and silicate minerals, is elongated in the direction of N40-50°E and dips towards the SE. Small sulphide bodies also occur in the kaoline zone underlying the main ore. The green tuff surrounding the ore bodies was altered to clay containing kaolinite and montmorillonite by a hydrothermal solution at the time the ore deposit was emplaced. Welded tuff of the Quarternary period unconformably overlies the green tuff. Although Sugimoto^{1,2)} and Sugimoto and Shoya³⁾ consider that the ore deposit is of a hydrothermal metasomatic type, Sato and Aragane⁴⁾ suggests that it is also possible to infer a syngenetic origin. The dominant mineral in clay zone of the northeastern part of the silicate-barite ore body is montmorillonite. While kaoline minerals are predominant in the southwestern part. In the basement of the ore bodies there are two distinctive clays, a white and a black: the former exists near to the ore bodies; the latter occurs in a deeper zone. The boundary between them is not well-defined, though there are scattered white clay lenses in the black clay zone adjacent to the white zone.

Sample preparation and mineral analysis

Sample preparation. Clay samples were collected from several spots on outcrops of the black clay layer at a depth of about 20 meters below the ground surface. The consolidated clay specimens were loosened and well-mixed with water in a tank equipped with a rotator. The mineral particles under 44μ in diameter were then sieved in water. To determine the mineral composition of individual grain-size fractions, the sieved materials under 44μ were divided into a series of particle-size ranges: $44-30\mu$, $30-20\mu$, $20-10\mu$, $10-5\mu$, $5-3\mu$, and $<3\mu$. The settling-tube method was employed for this separation, and meta-sodium phosphoric acid was used as a dispersion reagent. The mineral particles, suspended in a dilute solution in the tube, were transferred to a beaker with an andreasen pipet after sufficient settling time for separation into each grain-size fraction. Samples were then dried in air at room temperature.

Mineral identification. X-ray powder diffraction data indicates the clay from the black

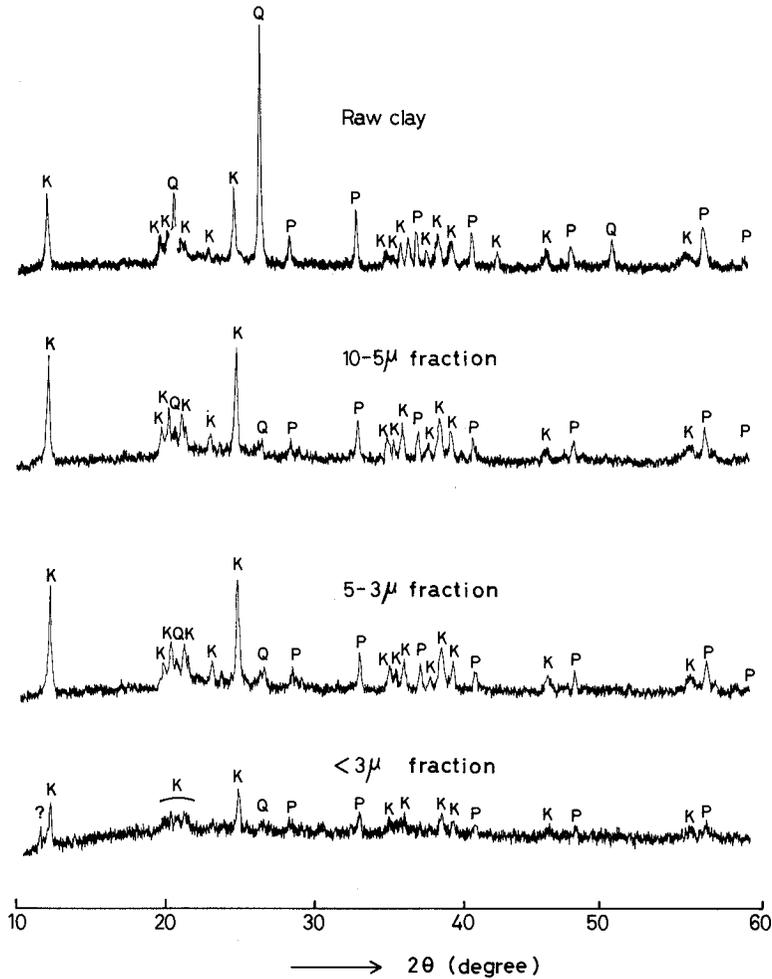


Fig. 1 X-ray diffraction patterns of raw clay and its grain-size fractions from the Minami-Shiraoi ore deposit.

The letters stand for the minerals in the samples :

K for kaolinite, Q for quartz, and P for pyrite. Experimental condition : Cu K α (Ni), 35KV, 15mA, Slits 1°-0.15mm-1°, Time constant 2sec., Full scale count 1000 cps, Scanning speed 1°/min.

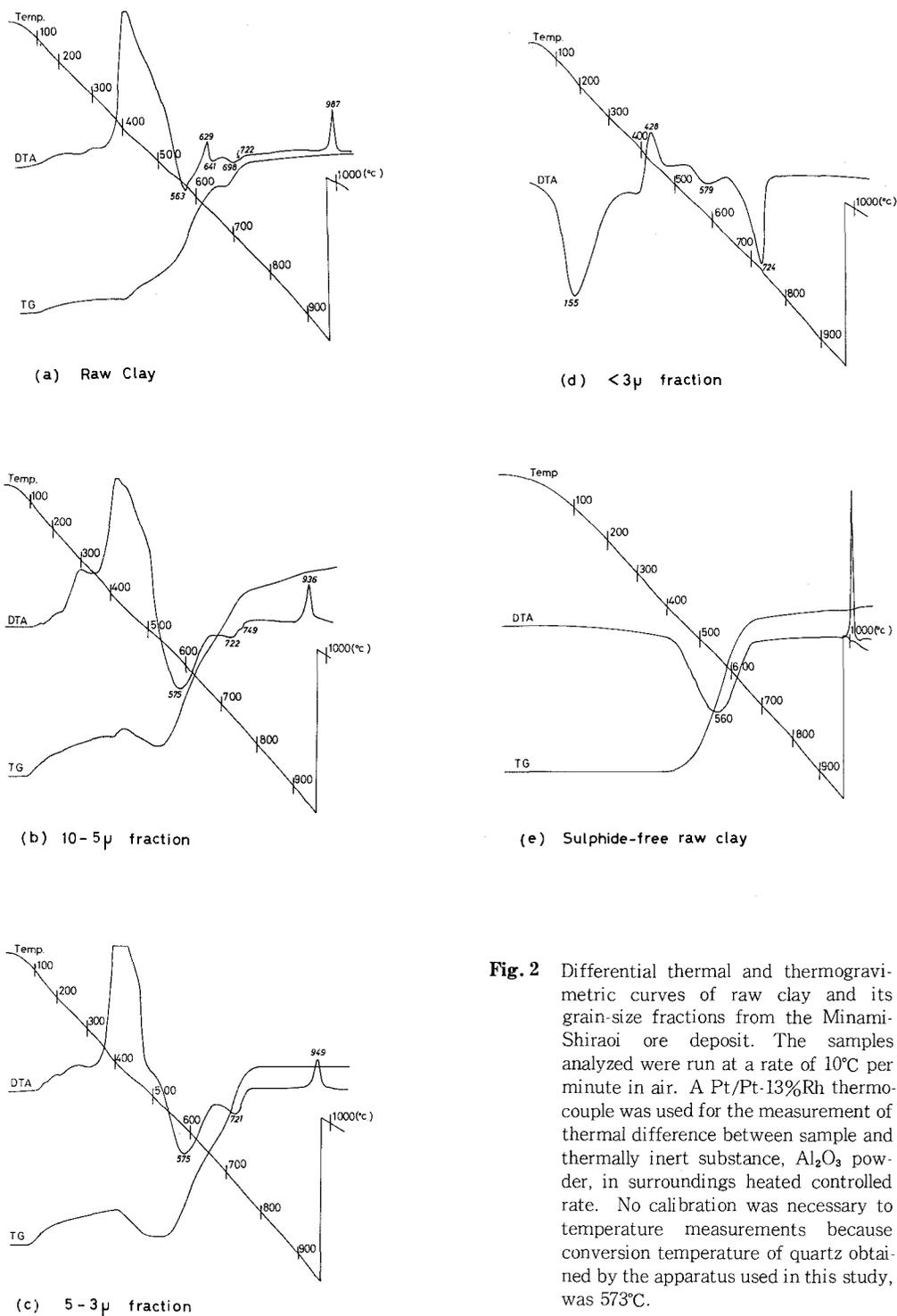


Fig. 2 Differential thermal and thermogravimetric curves of raw clay and its grain-size fractions from the Minami-Shirai ore deposit. The samples analyzed were run at a rate of 10°C per minute in air. A Pt/Pt-13%Rh thermocouple was used for the measurement of thermal difference between sample and thermally inert substance, Al_2O_3 powder, in surroundings heated controlled rate. No calibration was necessary to temperature measurements because conversion temperature of quartz obtained by the apparatus used in this study, was 573°C.

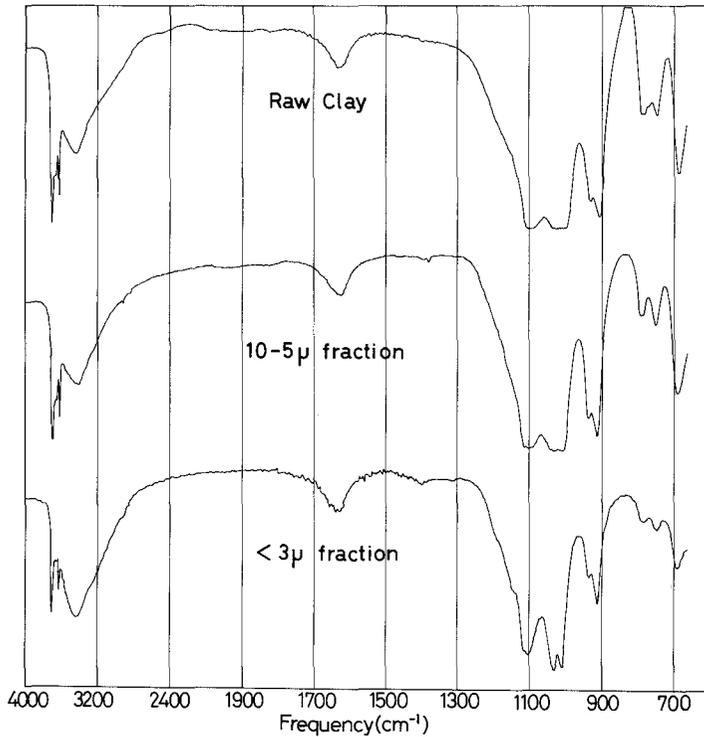


Fig. 3a Infrared absorption spectra of selected clay samples.

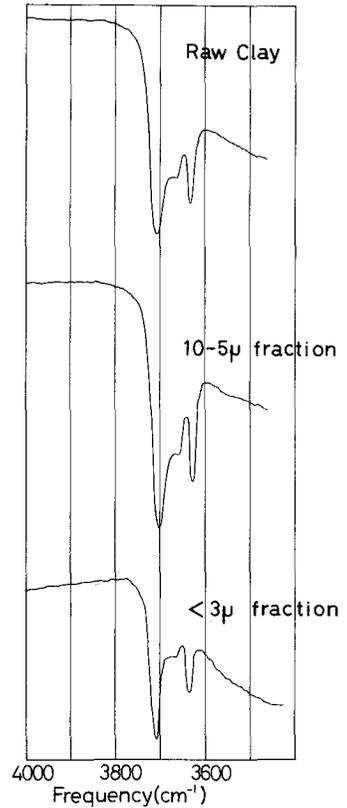


Fig. 3b Infrared absorption spectra of selected clay samples in the range of 4000 to 3400 cm^{-1} .

zone is composed mainly of kaolinite, quartz, pyrite, and occasionally marcasite (Fig. 1). Although Ushizawa^{5,6} reported that, in addition to kaolinite, dickite and nacrite were contained in clays from the ore deposit, differential thermal curves in air of samples from the black clay zone show the endothermic peak in the 560-580°C region to be dehydroxylation of kaolinite (Fig. 2). The hydroxyl water of kaolinite is dehydrated at a somewhat lower temperature than that of dickite and nacrite^{7,8,9}. Typical dehydroxylation for kaolinite, dickite and nacrite appears to take place in the respective ranges of 550-600°C, 600-650°C, and around 700°C¹⁰. The DTA for a portion of the raw clay sample, in which the sulphides had been chemically removed after purification by flotation, reveals the typical pattern of kaolinite. The infrared absorption spectra (Fig. 3a) of clay samples clearly show the characteristic vibration profile of kaolinite. The hydroxyl stretching bands of the kaolinite subgroup within range from 3700 to 3600 cm^{-1} occur at 3697, 3669, 3652, and 3620 cm^{-1} in kaolinite; 3704, and 3622 cm^{-1} in dickite; and 3701, 3652, and 3622 cm^{-1} in nacrite¹¹. Moreover, in

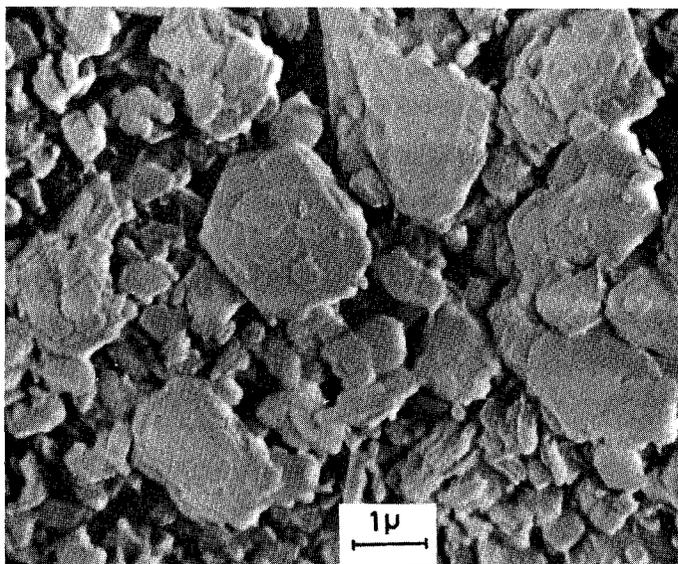


Fig. 4 Scanning electron microphotograph of kaolinite in the $< 3 \mu$ fraction.

kaolinite the O-H stretching band at about 3700cm^{-1} is the strongest peak among the four, whereas in dickite and in nacrite the absorption band at 3622cm^{-1} becomes deeper than that at 3700cm^{-1} ¹²⁾. In spite of the apparent lack of a 3669cm^{-1} peak, the O-H vibration patterns represented in Fig. 3b can nevertheless be ascribed to the characteristic pattern of kaolinite. The spectrum of the $<3\mu$ fraction has a tiny absorption band comparable to the 3669cm^{-1} band. Scanning electron microphotography (Fig. 4) suggests this kaolinite is relatively thick. This is a possible explanation for the lack of a 3669cm^{-1} peak.

The X-ray powder diffraction pattern of the $<3\mu$ sample records several reflection peaks which can not be assigned to the major minerals. These peaks can not yet be positively identified with reflections of specific clay minerals nor sulphides until a more extensive examination is completed.

Chemical analysis. A combination of classical wet chemistry ¹³⁾ and atomic absorption spectrophotometric method ¹⁴⁾ for Ca, Mg, Na and K was applied to the chemical analysis of the clay. Sulphide sulphur was analyzed by a gravimetric technique: sulphur was precipitated as BaSO_4 by adding a dilute BaCl_2 solution to the weakly acidified sample solution, which had previously been extracted with a mixture of liquid bromine and carbon tetrachloride; ferric iron in the solution was removed as iron-hydroxylate; the small amounts of sulphur dissolved from the BaSO_4 precipitates during washing with hot water were also recovered from the washings. The results given in Table 1 imply that the clay consists of relatively pure kaolinite since the concentrations of alkali and alkaline earth metals are very low. Normative composition based on the ideal formulas of possible coexisting minerals in the clay, was calculated from chemical analysis, and is tabulated in Table 1. The small

excess of sulphur remaining after the allocation of an appropriate amount to make normative FeS₂ may denote the presence of other sulphides or sulfates. In fact, relatively strong peaks of chalcophile heavy metals, such as Pb, Ni, Zn, Cu, and As were detected in the X-ray fluorescence spectrum of the raw clay (Fig. 5).

Estimate of quantitative mineral composition in respective particle size regions

The quantitative major mineral composition of the particular particle-size fractions chosen for this study was estimated by a comparison between X-ray diffraction intensities of

Table 2 Relationship between the coefficient of variation (C.V.) for X-ray intensity measurements and the counting time interval.

Time	Average*	Range	C. P. S.	C. V.(%)
10 sec	4394 cpm	4229-4648 cpm	439.4	14.6
20	8566	8494-8621	428.3	2.4
30	13004	12909-13153	434.5	3.2
40	17293	17110-17471	432.3	3.5
50	21568	21274-21782	431.4	3.5
60	25813	25618-25921	430.2	1.7
120	51624	51245-52051	430.2	2.2

Table 3 Reproducibility of X-ray intensity on specific reflection peaks during repeated mountings of the clay sample on the same Al-holder.

No.	Average *	Range	C. P. S.	C. V.(%)
1	24340 cpm	23994-24569 cpm	406	1.7
2	24212	24052-24394	404	1.7
3	24387	24258-24471	406	1.7
4	25438	25307-25609	424	1.7
5	24454	24400-24562	408	1.7
6	24145	23938-24278	402	1.7
7	24506	24444-24597	408	1.7
8	23818	23690-23888	397	1.7
9	24324	24290-24445	405	1.7
10	24869	24769-24967	414	1.7

* Each number is mean value of 10 runs and is subtracted from background which is averaged over both X-ray counts on high and low-angle baselines close to the peak measured.

minerals in the raw clay and those in sample powders of various size fractions. All the clay samples except the $5\text{-}3\mu$ and the $<3\mu$ fractions were ground to $<5\mu$ in an agate mortar to minimize possible error due to the effects of particle-size on the intensity measurement of reflected X-ray peaks¹⁵⁾. The fixed-time counting method was employed for the measurement of the peak height at the (002) spacing plane in kaolinite, the (1011) in quartz, and the (002) in pyrite. In the clay samples, the diffracted peaks of these lattice planes were free from interferences that were due to the presence of other closely spaced peaks. The intensity of every reflection in each of these three minerals was measured by using a Geiger-counter at the peak maximum as determined by stepwise scanning at an interval of 0.02 degrees (2θ). To find a suitable counting-time interval, the coefficient of variation of the count intensity of the basal plane (002) of kaolinite was examined at various running intervals. A sixty second counting-time gave about 2% in C.V.(Table 2). The reproducibility of a given X-ray diffraction peak intensity was also checked by a sample powder mounted repeatedly onto an Al-specimen holder. The $10\text{-}5\mu$ clay powder was put onto an Al-holder, which had been placed on a finely flosted glass plate; pressed with a finger as tightly as possible; set on a goniometer; and then the intensity on the peak maximum of the (002) of kaolinite was counted for 60 seconds. The number obtained was subtracted from an estimated background strength that was averaged over backgrounds of both low and high-angle site of the (002) peak. As given in Table 3, this procedure can be expected to yield an accuracy of about 2 per cent in the measurement of a given reflection line. The peak height of the particular diffraction-peak intensity of kaolinite, quartz, and pyrite in the clay powder was determined by this method. The results are tabulated in Table 4. The estimated

Table 4 X-ray intensity count of characteristic reflections of kaolinite, quartz and pyrite.

Sample	Kaolinite(002)	Quartz(1011)	Pyrite(002)
Raw clay	13451 cpm	42161 cpm	10744 cpm
44-30 μ	14944	19180	13224
30-20	18972	9140	12189
20-10	20464	6186	11302
10-5	22016	2053	7750
5-3	18900	3044	7451
<3	9061	1687	3278

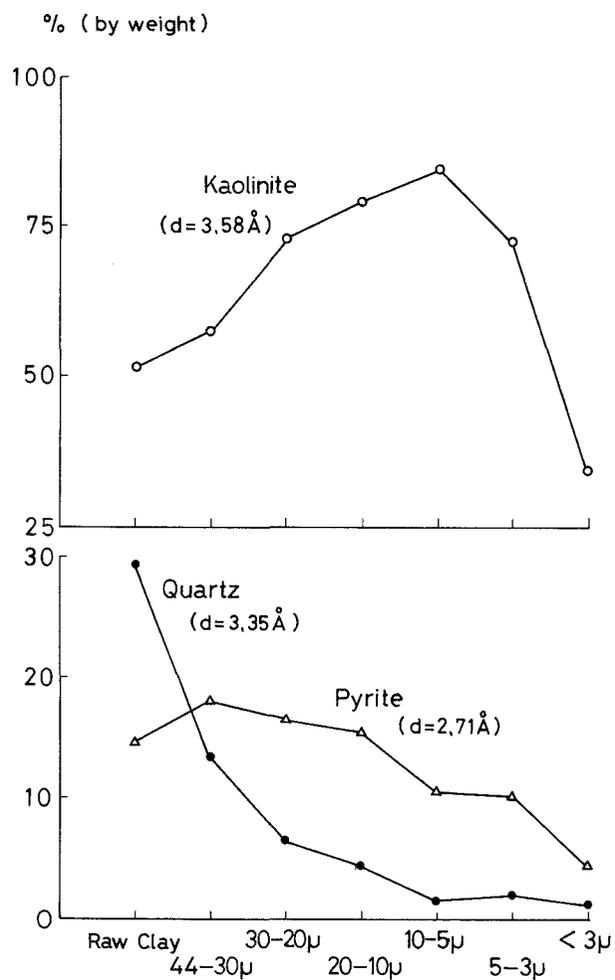
Each number is mean value of 10 runs and is corrected for average background.

Experimental condition: Radiation $\text{CuK}\alpha$ (Ni filter), 35KV, 15mA, Slits $1^\circ\text{-}0.15\text{mm}\text{-}1^\circ$, Time constant 2sec., Fixed-time count 60sec.

Table 5 Concentrations of Cu, Pb, Zn and Ni in raw clay and <math><3\mu</math> fraction samples.

	Raw clay	<math><3\mu</math> fraction
Cu	490 $\mu\text{g/g}$	46000 $\mu\text{g/g}$
Pb	350	310
Zn	81	3400
Ni	27	54

The metals in the samples were analyzed by using atomic absorption spectrometry.

**Fig. 6** Variation in the estimated quantities of the principal minerals in clay from the Minami-Shiraoi ore deposit.

quantity of these minerals in the samples was obtained by multiplying the ratio of an X-ray count(cpm) on a chosen line in a sample to the corresponding count in the raw clay by its normative concentration(%). Figure 6 demonstrates that the concentration of kaolinite increases with a decrease in the particle size up to the 10-5 μ fraction, where it reaches 84% by weight; that a subsequent steep depletion of kaolinite on the variation curve occurs in finer regions; and that the amount of quartz decreases from about 30% in the 44-30 μ fraction to 1 or 2% in the 10-5 μ through <3 μ fraction. While becoming gradually depleted among smaller particle-size fractions, the quantity of pyrite in both the 10-5 μ and the 5-3 μ fractions, was slightly enriched. It is significant that small amounts of pyrite still remain in the <3 μ , because the elimination of sulphides by flotation is of great difficulty in fine regions.

Conclusion

By an examination of the X-ray, DTA, and infrared absorption spectra of a clay sample collected from the black clay zone underlying both the main barite-silicate ore body and the small sulphide ores, it was determined that the major mineral components were kaolinite, quartz, and pyrite. Kaolinite in the sample was largely distributed among the coarser particle-size fractions, reaching 84% by weight in the 10-5 μ fraction. Scanning electron microphotography suggests that the kaolinite is relatively thick. The amount of quartz in the <10 μ fraction was less than 2%. The presence of a small but significant quantity of pyrite in the fine particle fraction, particularly in the <3 μ size range, will seriously complicate the purification of the kaoline clay if only simple flotation is used. The concentrations of Cu, Zn, Ni, and probably As (Fig. 5) were enriched markedly in the <3 μ fraction, compared to those in the raw clay (Table 5). A large quantity of Cu in the <3 μ region is likely to be in the form of sulphide or sulfate. It is clearly not advantageous, therefore, to carelessly employ chemical treatments for the further purification of the clay because of the obvious hazard of environmental contamination by the heavy metals. Instead, physical removal before flotation of material containing heavy metals in the <3 fraction would be more beneficial in purifying the kaoline clay, partly because a more efficient separation would be expected by flotation, and partly because the employment of chemical treatments could then be minimized. In order to use the purified kaoline as a coating material for paper, it is necessary to reduce its grain size to under 5 μ (preferably <2 μ) since the coarser distribution of grain size adversely affects the degree of gloss, the strength of coating, the reflectivity, and the resistivity of the product to abrasion¹⁶⁾.

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