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7Å Phase in the Sancheong Kaolin : 7Å-Halloysite or Kaolinite ?

(산청 고령토중의 7Å 상에 대한 연구 : 7Å-할로이사이트 또는 캐올리나이트?)

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ABSTRACT: The X-ray diffraction and electron microscopy study of the kaolin sample from Sancheong area show that the halloysite occurs as hydrated 10 Å form. It implies that the 7 Å reflection and hk-line splitting in the X-ray diffractogram are ascribed to kaolinite. Kaolinite in Sancheong kaolin is of a disordered type. It tends to be enriched in the colored part of kaolin samples. Quantitative analyses show that kaolin contains 16-57% halloysite and 10-55% kaolinite.

요약 : 산청지역에서 산출되는 고령토에 대하여 X-선 회절분석과 전자현미경 분석연구를 시행한 결과, 할로이사이트는 수화된 상태로 존재하며 회절도상의 7Å 회절선 및 hk-선의 갈라짐은 캐올리나이트에 의한 것이다. 캐올리나이트는 결정도가 낮은 유형에 속하며 착색된 고령토에 많이 함유되는 경향이 있다. 고령토 원시료의 구성광물에 대한 정량분석 결과 할로이사이트가 10~57%, 캐올리나이트가 10~57% 함유되어 있다.

INTRODUCTION

Kaolin in the weathering environment mainly consists of halloysite and/or kaolinite. It is well known that the fully hydrated 10Å-halloysite transforms to 7Å-halloysite on dehydration (Alexander *et al.*, 1943; Churchman, 1970). Dehydrated halloysite does not rehydrate.Therefore, it is difficult to distinguish 7Å-halloysite from poorly crystallized kaolinite in a mixture since both have very similar X-ray diffraction patterns.

Kaolinite has a wide range of structural disorder owing to the displacement of Al vacancy and $\frac{b}{3}$ translations (Brindley, 1980; Plançon and Tchoubar, 1977 I, II). In the extreme case of disordering, X-ray diffraction patterns are very similar to those of 7Å-halloysite.

The kaolin deposits generally occur at shallow depths of the anorthositic rocks. They are generally concentrated on gentle slopes of less than 17° between 100 (the local base) and 350m in altitude. The surface of deposits are covered by reddish brown soil. Below this soil, weathering profiles are developed from 5 to 30 m in depth. The profile is generally divided into three zones; the lower white sandy kaolin zone, the middle mature white kaolin zone, and the upper pink, reddish brown kaolin zone stained by iron oxides. Kaolin chiefly consists of kaolinite group minerals with minor amount of illite, vermiculite, chlorite/vermiculite, chlorite, smectite, plagioclase, amphibole, gibbsite,and iron oxides (Jeong, 1987). The white kaolin in the middle zone is often stained by iron oxides.

Previous studies (Kim and Kim, 1964; Sang *et al.*, 1972; Lee *et al.*, 1977; Sang, 1982) show that the kaolin from Sancheong area consists mainly of 10Å- and 7Å-halloysite without kaolinite, and all the 7Å-reflections in the X-ray diffraction pattern of kaolin have been regarded as 7Å-halloysite.

X-ray diffraction patterns of bulk kaolin specimens show both 10Å and 7Å reflections in various intensity ratios. 10Å reflections disappear upon heating to 100°C, resulting in stronger 7Å reflections. It suggests that 10Å reflections in this case is due to 10Å-halloysite. In order to find out whether the 7Å reflection in X-ray diffractograms is due to the naturally dehydrated

7Å-halloysite or kaolinite, X-ray diffraction and electron microscopic studies were made for both the natural moist and artificially dried specimens of size-fractionated kaolin.

EXPERIMENTAL

From Keumseo- and Danseong-Myeon of Sancheong-Gun, Kyeongsangnam-Do, Korea, samples with different color, texture, and depth were collected systematically in the field. The collected samples were tightly packed in the polyethylene bags to prevent dehydration and carefully transported to avoid the destruction of their textures. Raw kaolin samples were disaggregated in distilled water with magnetic stirrer. The suspension was processed with ultrasonic agitation after removal of sandy material, and then decanted in a 2-liter cylinder for gravity settling. Samples were fractionated to 10μ, 2μ, 0.5μ sizes for further analysis. Two oriented samples were prepared by smearing the suspension on the slide glass. One was X-rayed after 100°C over drying and the other in the untreated wet state.

X-ray diffraction patterns of samples were obtained using JEOL JDX-5P diffractometer at the Mineralogical Laboratory of Seoul National University with Cu Kα radiation. The normal slit condition was 1°–0.2 mm –2° and the scanning speed was adjusted for the purpose of measurement. For an accurate measurement of d-value, quartz was used as an internal standard. Quantitative X-ray diffraction analysis was carried out adopting internal standard method proposed by Chung (1974). The mineral samples to calculate the values of relative intensity ratio (RIR) were separated from the Sancheong kaolins by size-fractionation and hand-picking under stereomicroscope. The RIR values were obtained by comparing the intensity of representative reflection of the mineral with that of 113 reflection of corundum in a 1:1 mixture of the mineral and 1μ corundum powder. Effect of preferred orientation was minimized by careful sample loading and dilution by corundum powder, and the same mounting procedure was exercised throughout the experiment. The count data was input into personal computer, and the integrated peak area was measured as a peak intensity subtracting the background. Randomly oriented samples containing 20% corundum powder were run at the scanning speed of 0.5°/min, slit size of 1° –0.1mm –2°, time constant of 2 sec. with 30KV, 20mA conditions.

Transmission electron micrographs were taken using JEOL JEM 200CX electron microscope operated at 160 KV at the Material Testing Center of Seoul National University. Dispersed clay particles in distilled water were loaded on a carbon film for transmission electron microscopy observations.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the naturally occurring 10Å-halloysite and their dehydrated sample at 100°C are shown in Fig. 1, and also their diffraction data are given in Table 1. 10Å-halloysite shows intense (001), weak (003) reflection and also (02, 11), (20, 13), (24, 31, 15), (33, 06) diffraction bands with low angle terminations. On these diffuse bands, no other distinct reflection is observed. Artificial dehydration resulted in the change of basal reflections, so that (001) reflection at 10Å collapsed to 7.25Å, (003) reflection at 3.35Å to 2.39Å. (002) reflection appeared newly at 3.62Å. hk- diffraction bands did not change peak positions and intensities after dehydration. It is noticed that the intensity of (001) reflection of 7Å-halloysite is about one third of that of the original 10Å-halloysite. Therefore, careful attention is needed in interpretating the content of 10Å-halloysite from the X-ray diffraction patterns of mixture. It is likely to overestimate the 10Å-halloysite.

X-ray diffraction patterns of three common kaolin ores are shown in Fig. 2. They are very similar to those of 10Å-halloysite plus 7Å-

Table 1. X-ray diffraction data of halloysite (C-10).

10Å-halloysite			7Å-halloysite		
d(Å)	hkl	I/I_o	d(Å)	hkl	I/I_o
9.97	001	100	7.25	001	65
4.41	02,11	45	4.39	02,11	100
3.35	003	20	3.62	002	35
2.55	20,13	20	2,55	20,13	25
1.678	24,31,15	5	2.39	003	25
1.485	33,06	10	1.675	24,31,15	10
1.283	40,26	5	1.486	33,06	20
			1.283	40,26	10

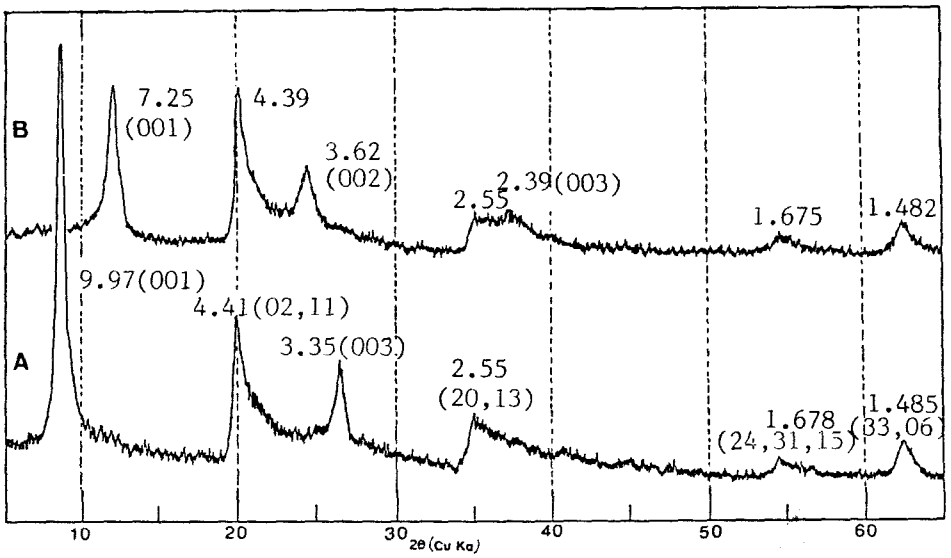

Fig. 1. X-ray diffraction patterns of 10Å-halloysite (A) and their dehydrated forms(B).

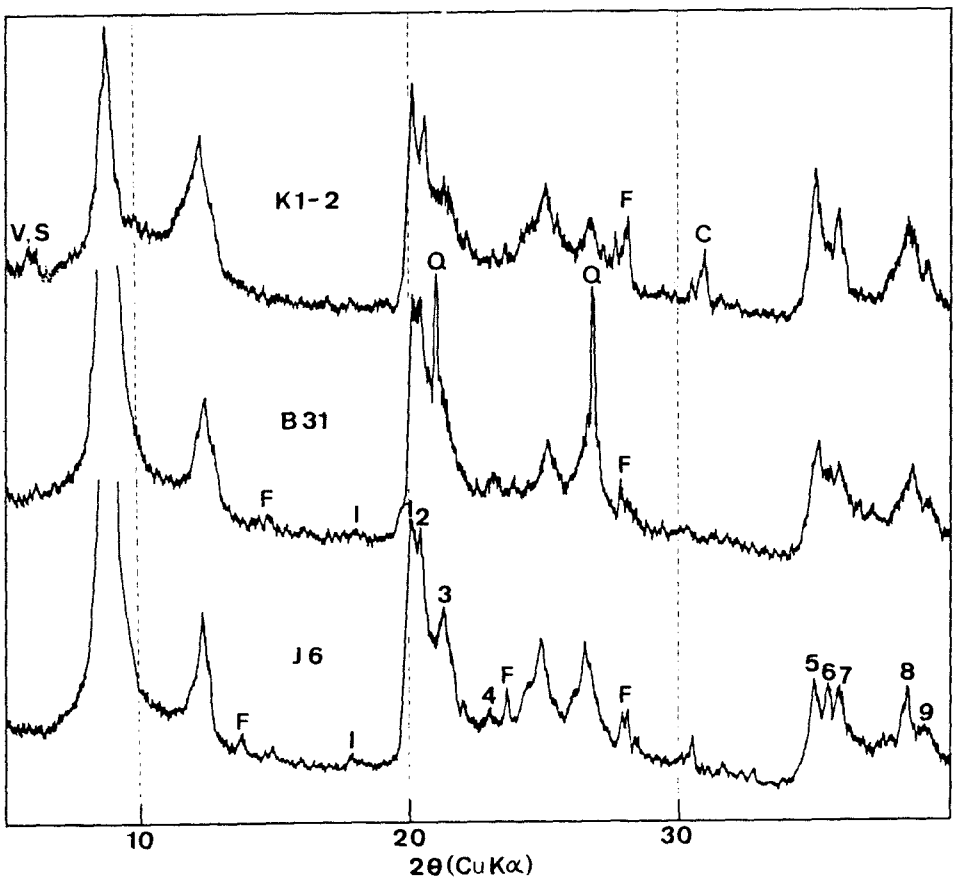

Fig. 2. X-ray diffraction patterns of some kaolins. V: vermiculite, S: smectite, I: illite, F: feldspar, C: clinozoisite, Q: quartz. Numbers indicate the reflections due to kaolinite as follows; 1:(020), 2:(110), 3:(111), 4:(021), 5(130)+(201), 6:(131), 7:(131)+(200), 8: (202)+(131), 9:(131)

halloysite shown in Fig. 1. 10Å reflection is certainly ascribed to 10Å- halloysite, but it is uncertain whether 7Å reflection is ascribed to 7Å-halloysite or kaolinite because highly disordered kaolinite is low in the intensity of basal reflection, and its hk reflections tend to diffuse like halloysite. However, a few reflections and shoulders are superimposed on the diffraction bands of (02, 11), (20, 13), which are not observed in pure halloysite (See Fig. 1). These reflections are indexed as hkl reflections of kaolinite which are (020), (110), (111), (021), (130)+(201), (131), (131)+(200), (202)+(131), and (131) (indicated as numbers in Fig. 2). The splitting of hk- diffraction bands as shown in Fig. 2 suggests that 7Å reflection is due in part to kaolinite rather than 7Å-halloysite.

X-ray analyses of size-fractionated specimens (Fig. 3) give further informations on the nature of 7Å-reflections. The diffraction pattern (1), (2), and (3) are those of kaolin specimens dried after fractionation, whereas (4) is wet specimen of the finest fraction (3) which has not undergone any prior drying.

X-ray diffraction patterns of each fraction were obtained for random and oriented specimens. (02, 11), (20, 13) bands were resolved in coarse fraction (1), suggesting that there exist some kaolinite contributing to the splitting of hk band. It is supported by the fact that SEM micrograph and photomicrograph of coarse fraction (1) shows many books and vermiforms (Fig. 4). Coarse fraction is mainly composed of these books and flakes of kaolinite and detrital plagioclase, so that no orientation effect is found in the oriented specimen. The splitting of bands in more finer fraction (2) is reduced as compared with fraction (1), and there is slight orientation

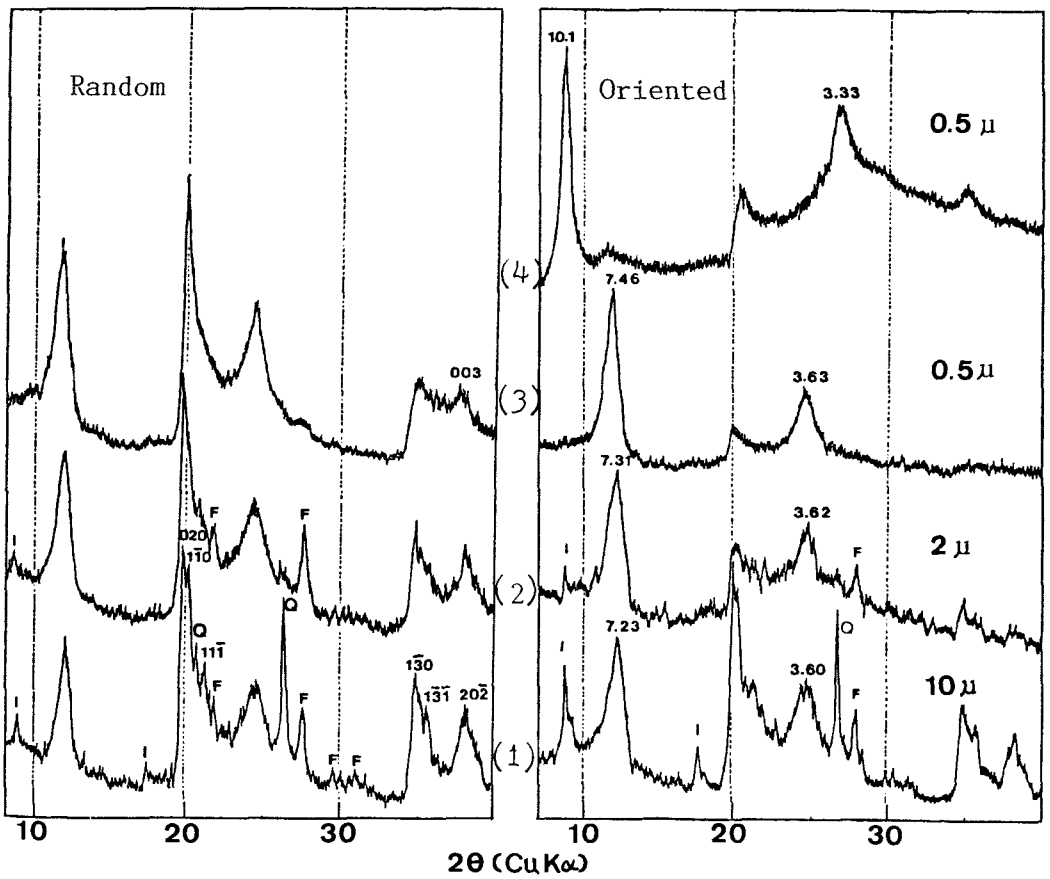

Fig. 3. X-ray diffraction patterns of size-fractionated kaolins (C-2). (1), (2), and (3) were dried at the 100°C after fractionation. (4) is not-dried equivalent of (3). I:illite, F: feldspar, Q: quartz.

effect. Finally, fraction (3) below 0.5μ is almost pure halloysite, and its diffraction pattern is the same as that of pure dehydrated halloysite as shown in Fig. 1. The intensive orientation effect is observed in fraction (3). The transmission electron micrographs of fraction (3) (Fig. 5) show many elongated tubes with various length and thickness. The significant enhancement of basal reflections of the oriented specimens implies that many of the elongated halloysite grains are not complete tube but incompletely rolled or flattened tube.

Sample (4), the wet equivalent of fraction (3) which was not dried after size-fractionation, gives an important information on the hydration state of halloysite in nature. The diffractograph

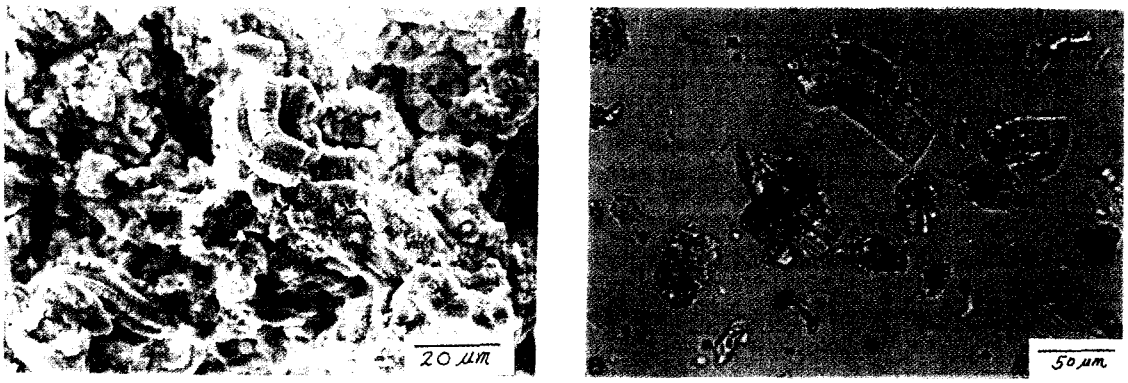

Fig. 4. A: SEM photograph of vermiform kaolinite, B: Photomicrograph of aggregate of kaolinite books (open nicol).

Fig. 5. Transmission electron micrograph of the finest fraction (No.3 in Fig. 3) shows halloysite tubes with various length and thickness.

(4) taken at the wet state shows mainly of 10Å-phase with a trace of 7Å-phase. The same patterns were obtained from other samples. Considering that dehydrated halloysite does not rehydrate, the diffractograph (4) implies that most of halloysite exist as 10Å state rather than 7Å state in nature so that 7Å-peak in common kaolin is not due to 7Å halloysite but to kaolinite. The week 7Å reflection in the pattern (4) may be due to fine-grained kaolinite. Nagasawa and Miyazaki (1975) who investigated many halloysites of different origins observed no naturally dehydrated 7Å-halloysite. From the present work, it has been known that the halloysite in the kaolin occurs in the hydrated state, and 7Å-reflection is due to kaolinite.

Kaolinite must have been ignored or underestimated in the previous works because of misidentification and false sample preparation for electron microscopy. Disordered kaolinite is so large as compared to halloysite that it is easily precipitated before loading the suspension on the carbon film. Furthermore, electron does not transmit those thick particles. On the other hand, halloysite is commonly fine-grained tube less than 0.1μm in width and 2μm in length, so that it is more easily laid on the substrate and more dominantly observed under electron microscope. Therefore, transmission electron microscope does not reveal real relative abundance of halloysite and kaolinite because of the different dimensions.

It is found that kaolinite is often concentrated in the red or reddish brown spots which consist of 10Å-halloysite, vermiculite, amphibole, gibbsite, and hematite. The kaolinite(E5) was handpicked from the red spots, and their X-ray diffraction pattern was shown in Fig. 6. The Georgia

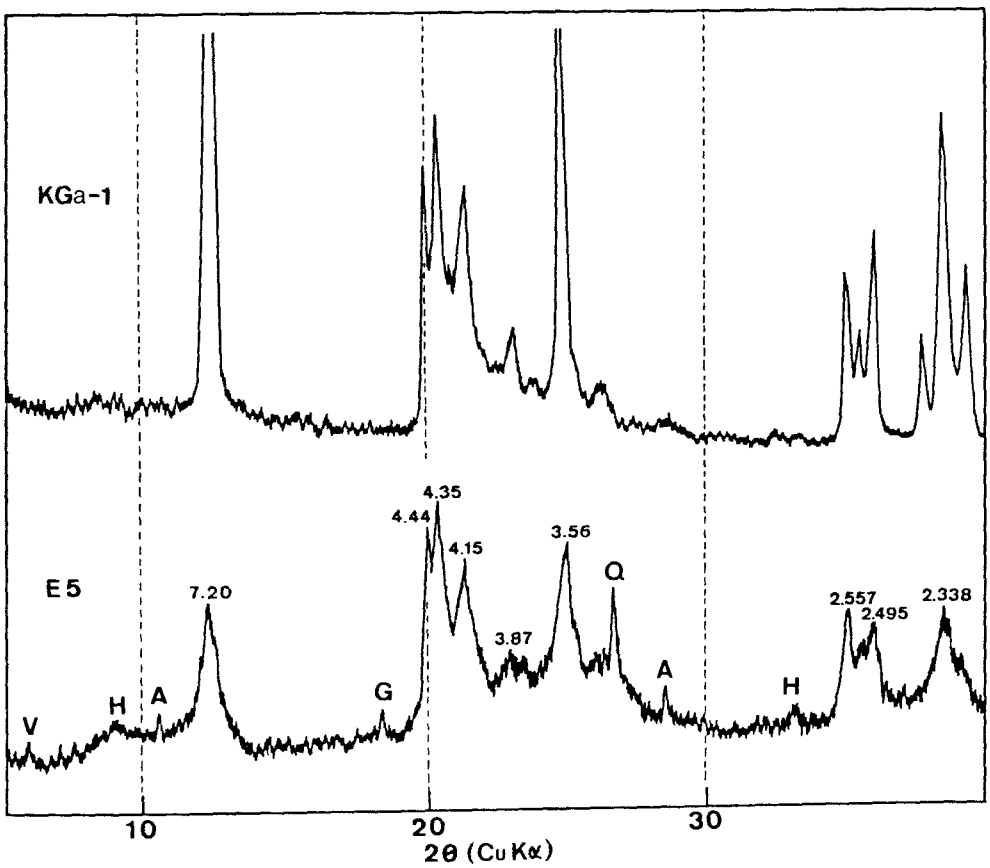

Fig. 6. X-ray diffraction pattern of kaolinites. KGa-1: Georgia kaolinite, E5: Sancheong kaolinite

kaolinite (KGa-1) purchased from the Source Clay of Clay Minerals Society was compared in Fig. 6. The diffraction pattern of Sancheong kaolinite sample(E5) well matches with that of the Source Clay sample(KGa-1) in the region of (02, 11) and (20, 13) diffraction bands, but the hkl peaks of E5 are weaker and broader than that of KGa-1. Brindley *et al.* (1986) compiled 24 diverse kaolinite specimens with various degree of disorder ranging from well-ordered Keokuk specimens to highly disordered Pugu specimens. Their Hinckley indices (HI) range from 1.72 for well-ordered kaolinite to 0.18 for the highly disordered one. The HI of E5 (0.64) located between the two end values implies that E5 kaolinite belongs to structurally disordered form. It is notable that the basal reflection of E5 is very weak and broad as compared to that of KGa-1 although the two have similar diffraction bands in the regions of 19 to 24(2θ), and 34 to 50(2θ). The broadness of the basal reflection is related to the z-dimension of the coherent scattering domain. The number of layers within coherent scattering domain can be calculated by Scherrer equation (Brindley, 1980) from the measurement of half height width. The measured numbers range from 11 layers to 25 layers, and averaged to 17 layer (about 122 Å). The extremely low intensity and broadness of basal reflection due to very small scattreing domain is distinct feature from other kaolinites of which HIs are similar to that of E5.

Quantitative X-ray diffraction analyses were carried out for some selected kaolin samples. 10Å halloysite from white veinlets and kaolinite from red spots of kaolin sample were used as a standard for the measurement of RIR values of the two minerals. 10Å-halloysite was nearly pure, but kaolinite standard contains some impurities such as vermiculite, 10Å-halloysite, gibbsite, and hematite. The measured RIR values of 10Å reflection of halloysite and 7Å reflection of kaolinite are 1.32 (±0.06) and 0.43 (±0.06), respectively. Halloysite exposed to air loses its interlayer water with various rate according to the packing state and humidity. There is a possibility that some of the interlayer water is lost during one hour of air drying in the process of homogeneous mixing of sample and corundum. However, no significant decrease of 10Å-reflection was observed in that short time period throughout the experiment. The representativity and purity of the standard, orientation effect, and accuracy of background level determination can affect the accuracy of the quantitative analysis of kaolin.

Apparent trend observed from quantitative analyses (Table 2) is that the reddish brown

Table 2. Quantitative analyses of some kaolins

sample	color	halloysite	kaolinite	others[1)]	total[2)]
S102	white	53	10	18	81
C 11	white	53	24	12	91
P 5	white	57	38	3	98
G2-1	green spotted white	44	32	12	88
E 5	white	57	19	15	91
H 11	green spotted white	25	41	21	87
B 31	yellowish brown	15	45	21	81
K1-2	greenish yellow	10	50	24	84
J 6	yellow	20	55	19	94
B 28	yellowish brown	20	40	20	80
C12-2	reddish brown	18	50	23	91

1) Others include following minerals; illite, vermiculite, C/V, plagioclase, iron oxide, amphibole, quartz, and gibbsite

2) The deficiency in total is ascribed to amorphous material

spotted kaolin sample contains a significant amount of kaolinite ranginges from 10 to 55% whereas the white kaolin sample consists of halloysite above 50%. The yellowish brown spots have more kaolinite than white part of the same sample. In any case, the kaolin sample from Sancheong area contains a significant amount of kaolinite.

CONCLUSIONS

X-ray diffraction patterns and transmission electron microscopic study of moist and dried specimens of size-fractionated kaolin samples show that 7Å-reflection arises from the kaolinite, whereas 10Å reflection from hydrated halloysite. It turned out that halloysite occurs as the hydrated 10Å form. Kaolinite can be simply identified by its 7Å-reflection and the splitting of hk- bands. Halloysite occurs usually as small tubes below 0.5μ in size, whereas kaolinite as book forms whose sizes are usually above 10μ. The kaolinite is a disordered type of about 0.64 HI and average layer number 17. Quantitative analyses show that a significant amount of disordered kaolinite is contained in kaolin, and that more weathered reddish brown kaolins tend to contain much more. The content of kaolinite tends to enrich in colored kaolin.

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