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MINERALOGY OF HALLOYSITE FROM SURYUN, KOREA

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ABSTRACT

The halloysite in Suryun area, Seongju-Gun, Kyeongsang Buk- do-Korea, occurs as a distinctive kaolin mineral and has formed as a weathering product of feldspar in late Precambrian anorthositic rocks.

X-ray diffraction studies showed that the halloysite occurs naturally as a 10A° or hydrated form which on exposure to atmospheric conditions transformed to 7A° or dehydrated form. The stability of interlayer water shows variation from sample to sample due to particle size. Scanning electron microscopy displayed that the halloysite occurs in tabular form growing in aggregates or in bundles in weathered plagioclase feldspar. Under transmission electron microscope the tubes show variable dimensions. Electron microprobe analyses show slight substitution of Al for Si in tetrahedral site of halloysite structure.

INTRODUCTION

Halloysite usually occur in two types according to their shapes: tubular (Parham, 1969; Eswaran and Bin, 1978; Tazaki, 1982; Nagasawa and Noro, 1987), and spherical (Minato and Utada, 1969). In Korea halloysite has been reported to occur in mostly tubular form (Lee, Kim and Jeong, 1977; Jeong, 1987; Kim and Chang, 1987) and rarely in spherical form (Jeong, 1987; Kim, 1989). The Suryun halloysite form the predominant mineral of kaolin deposits of Korea, and is commonly associated with minor kaolinite, illite and iron oxide minerals.

This paper describes the mineralogical characters of Suryun halloysite which is a weathering product of feldspar in anorthositic rocks.

MATERIALS AND METHODS

Samples were collected form upper, middle and lower zones of weathering profile of Buntonggol kaolin deposit (Fig. 1) in Suryun area. The particle size of the samples were determined by wet seiving and by the sedimentation method. Fe-oxide impurities were removed by the method of Mehra and Jackson (1968) and pure sample of halloysite was obtained by centrifuge. XRD pattern was obtained using fully computerized Rigaku RAD-C diffractometer operated at 30 KV, 10 mA with Ni filtered CuKα radiation.

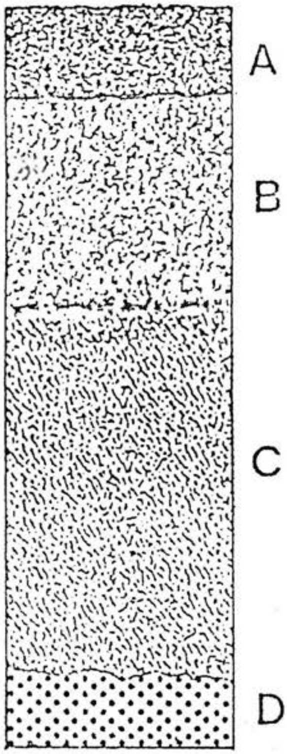

Fig 1. Generalized columnar section of the Buntonggol residual kaolin deposit of Suryun area. A: Upper reddish brown zone, B: Middle pink zone, C: Lower white zone, D: Host anorthositic rock. Scale: Vertical thickness equals to 6 m.

A JEOL model JEM 200CX, transmission electron microscope operated at 160 KV and JEOL JSM-35 scanning electron microscope were used for electron microscopy. Pellets of purified halloysite samples coated with carbon were analysed by JEOL JCXA 733 superprobe for chemical analyses. The instrument was operated with beam current of 10 mA and beam diameter of 2 μm. DTA curves were recorded by using Rigaku instrument at a heating rate of 10^{o} C/min, a Al_2O_3 was used as reference material.

X-Ray Diffraction Analyses

The X-ray diffraction analyses illustrate that the Suryun halloy site occurs in natural state as 10A° or hydrated form which on losing interlayer water has transformed into dehydrated form or 7A° halloysite. Fig. 2 shows the diffractograms of naturally occuring halloysite at stages in the drying process under room temperature conditions. The oriented sample shows continuous loss of interlayer water and formation of some intermediate unstable hydration phases as reported by Kohyama et al. (1978).

The stability of interlayer water of halloysite varies from sample to sample as shown in X-ray diffractogram (Fig. 3). The stability ratio (height of the 10A° peak)/(area of the basal reflection in the range of 7A° - 10A°) as described by Nagasawa and Miyazaki (1875) give value ranges from 0.24 to 0.84. For oriented samples C-7 and D-2 it is 0.2. The particle size of the samples seems to affect the stability of interlayer water. Fine size samples (B2, TI) are more stable in relation to coarse size samples (D2, C7).

Thermal Analyses

The DTA curves of halloysite are shown in Fig. 4. The endothermic peaks at 110° C and 550° C show the removal of interlayer water and dehydroxylation, respectively. The exothermic peak at 950° C shows recrystallization and formation of mullite. The asymmetry of the endothermal peak and its high slope ratio of 3.3 is strongly suggestive of halloysite (Brammao et al., 1957). The slope ratio of the main endothermal peak at 500 - 600° C varies between 2.2 and 2.8.

Morphology

The scanning electron micrograph of halloysite is shown in Fig. 5A. The halloysite occurs in elongated tubes that formed in aggregates or bundles from weathered fledspar. The transmission electron micrograph in Fig. 5B also displays tubular morphology. The thickness of the tubes ranges from 0.1 to 0.3 μm and length from 1-12 μm. The tubes are short and thick or long and thin, a few showing crinckled morphoogy.

Chemical Analyses

More than 50 analyses of halloysite were obtained by using electron microprobe. The selected and average chemical composition of halloysites from Suryun kaolin are given in Table 1. The Al:Si ratio of 2 μm fractions range from 0.958 to 1.027. The former value shows little substitution of Al for Si in the tetrahedral site.

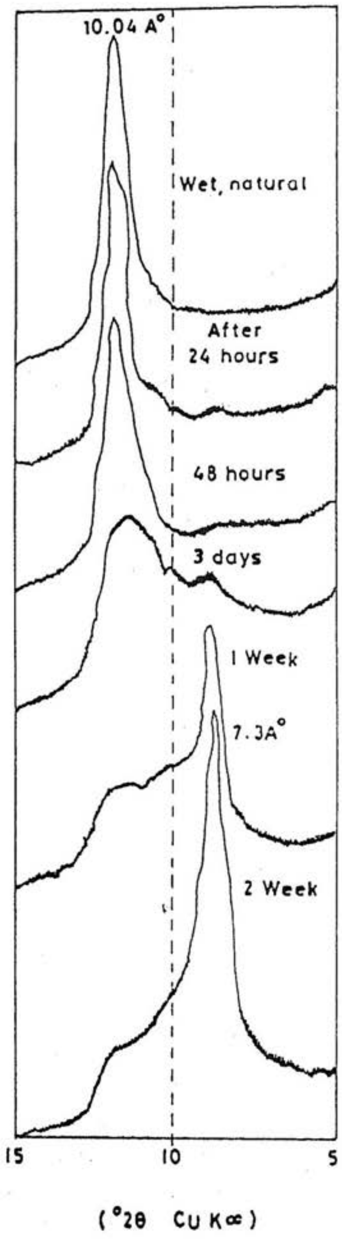

Fig. 2 (Left). X-ray diffractograms of halloysite sample showing variation of 10A° peak with increasing dehydration under room temperature condition.

Fig. 3 (Right). X-ray diffractograms showing stability of interlayer water in different raw halloysite samples.

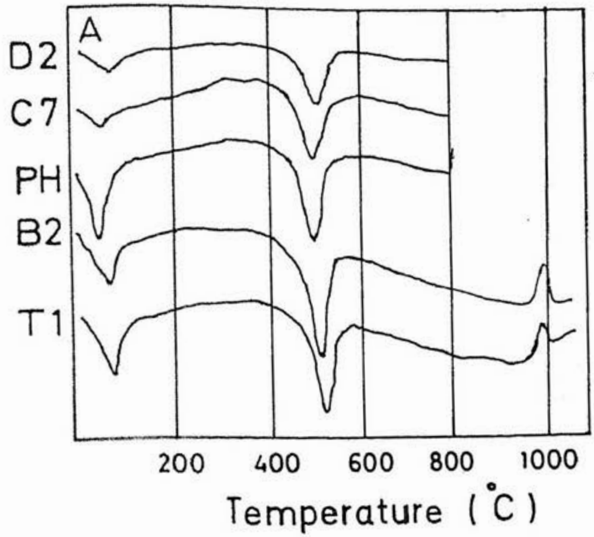

Fig. 4. Differential thermal analysis curves of Suryun halloysite. T1 and C7: Lower zone, PH, B2, and D2: Middle zone.

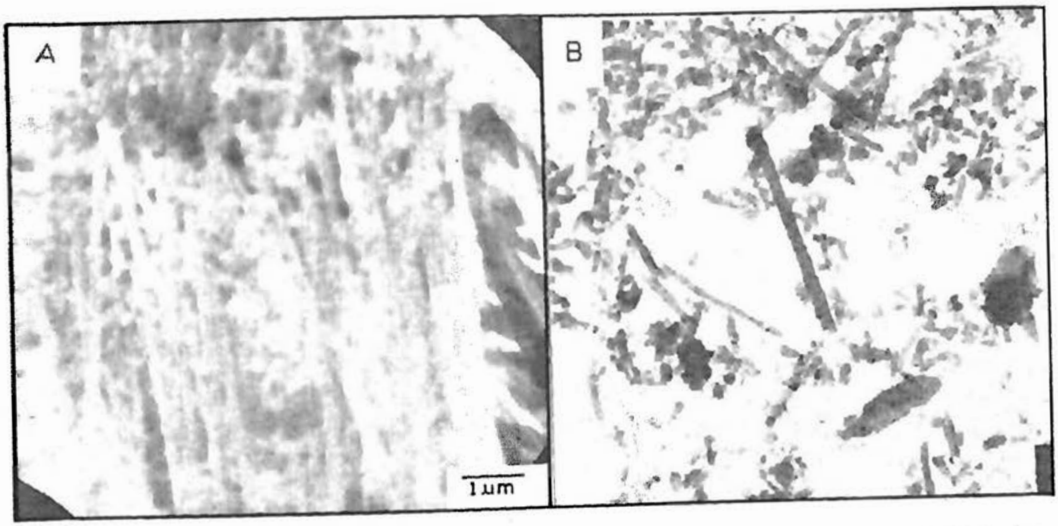

Fig. 5. Electron micrograph of Suryun halloysite. A: Scanning electron micrograph. Halloysite showing tubular morphology and growing in aggregate or in bundles. B: Transmission electron micrograph of halloysite showing varied dimensions: short and thick to long and thin tubes.

TABLE 1. ELECTRON MICROPROBE ANALYSES OF SURYUN HALLOYSITE.

Sample #	Theoretical	T1 (4)	B2 (6)	PH (3)	C7 (5)	D2 (3)
SiO_2	46.55	45.52	46.20	45.59	45.42	46.22
Al_2O_3	39.49	40.32	38.15	38.15	38.56	38.15
TiO_2	0.00	0.07	1.16	0.16	0.00	0.04
Cr_2O_3	0.00	0.26	0.74	0.74	0.25	0.29
FeO	0.00	0.00	0.00	0.00	0.13	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.02
MgO	0.00	0.06	0.16	0.16	0.08	0.04
CaO	0.00	0.17	0.00	0.00	0.17	0.15
Na_2O	0.00	0.10	0.54	0.54	0.02	0.14
K_2O	0.00	0.27	0.77	o.77	0.49	0.45
Total	86.04	86.77	86.72	86.11	85.12	85.50

Numbers of cations on the basis of 14 Oxygens

Si	4.000	3.903	3.987	3.864	3.973	4.020
Al	4.000	4.075	3.881	3.910	3.975	3.911
Ti	0.000	0.005	0.010	0.010	‘0.000	0.003
Cr	0.000	0.018	0.050	0.051	0.017	0.020
Fe	0.000	0.000	0.000	0.000	0.010	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.001
Mg	0.000	0.008	0.021	0.021	0.010	0.005
Ca	0.000	0.016	0.000	0.000	0.016	0.014
Na	0.000	0.017	0.090	0.091	0.003	0.024
K	0.000	0.030	0.085	0.085	0.055	0.054
Si/Al	1.000	0.958	1.027	1.013	1.009	1.027
R^{3+}/Si	1.000	1.049	0.985	1.000	1.004	0.978

Total Fe as FeO

Sample numbers are the same as in Figure i.e. T1 & B2: lower zone; PH, C7 & D2: middle zone. Numbers in parenthesis indicate total count for average with standard deviation of $\pm$ 0.002.

CONCLUSIONS

The Suryun halloysite is weathering product of anorthositic rocks. It occurs in natural state as 10A° halloysite, which on dehydration is transformed into 7A° form. On heating to 900° C total destruction of original mineral takes place. At 950° C, a new phase, mullite, is formed. Scanning electron microscopy shows that the halloysite has a tubular morphology and occurs as aggre gates or bundles. Transmission electron microscopy shows that the tubes range from 0.1 to 0.3 μm in diameter and 1-12 μm in length. Some tubes show crinckled morphology. Slight substitution of Al for Si in the tetrahedral site of halloysite structure occurs as revealed by electron microprobe analyses.

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