

Mineralogy and Genesis of the Sungsan Clay Deposits

聾山납석광상의 광물학적 및 성인적 연구

Hyen Goo Cho (조현구)*·Soo Jin Kim (김수진)**

*Department of Geology, Gyeongsang National University, Chinju 660-701, Korea
(경상대학교 지질학과)

**Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질학과)

ABSTRACT : The Sungsan clay deposits have been formed by the hydrothermal alteration of volcanic and volcanoclastic rocks of the Hwangsan Formation of Cretaceous age. Claystones are mainly composed of dickite, quartz, alunite, illitic minerals and tosudite. The mineralogical properties of clay minerals have been studied using X-ray diffraction analysis, electron microscopy, electron microprobe analysis, and infrared absorption analysis. The physicochemical condition for the clay deposits also have been studied by the activity diagrams and mineral assemblages.

Dickite, the dominant mineral in clay deposits, occurs generally as massive aggregates. It shows book-structure of well-defined hexagonal plates. Chemistry of dickite agrees with its ideal formula.

Peak depth ratios in infrared absorption spectra were used for discrimination between pure and mixture of kaolin minerals.

Five hydrothermal alteration zones are divided according to the mineral assemblages. From center to margin, alunite, dickite, illite and albite zones are discernible. Quartz zone occurs as small lenticular form in dickite zone. The formation of dickite and illite zones are promoted by decreasing a_{K^+} . An increase in $a_{H_2SO_4}$ or $a_{K_2SO_4}$ is required for the formation of alunite zone. Estimated temperature of formation ranges 110-270 °C

요약 : 성산납석광상은 백악기의 황산층 내 화산암과 화산쇄설암이 열수변질을 받아 형성된 광상이다. 납석을 구성하는 주성분광물은 디카이트, 석영, 명반석, 일라이트 및 토수다이트이다. 점토광물의 광물학적 특성을 X선회절분석, 전자현미경관찰, 전자현미분석과 적외선흡수분광분석법에 의하여 연구하였으며, 이온의 활동도 다이어그램과 광물조합으로부터 광상 형성에 대한 물리화학적 조건을 규명하였다.

납석을 구성하는 가장 중요한 광물인 디카이트는 대체로 괴상으로 산출된다. 이 광물은 육각 판상의 입자들로 구성된 book-structure를 보여주며, 화학조성은 이상적인 화학식과 잘 일치된다. 적외선흡수 스펙트럼에서의 peak depth ratio 역시 카올린광물 사이의 구별에 이용되었다.

열수변질대 내의 광물조합에 의하여 다섯 개의 열수변질대로 나누어졌다. 열수변질대의 중심으로부터 바깥쪽으로 갈수록 명반석대, 디카이트대, 일라이트대 및 엘바이트대가 분포하며, 석영대는 디카이트대 내에 작은 렌즈상으로 분포한다. a_{K^+} 의 감소에 의하여 디카이트대와 일라이트대의 형성이 촉진되었으며, 명반석대의 형성에는 $a_{H_2SO_4}$ 또는 $a_{K_2SO_4}$ 의 증가가 필요한 것으로 추정된다. 열수변질 작용은 100-270 °C의 범위에서 일어난 것으로 추정된다.

INTRODUCTION

The Sungsan mine is located in Hwangsan-myeon, Haenam-gun, Jeonra-namdo (Lat. 34° 33'

N, Long. 126° 24' E), Korea. A number of clay deposits are distributed around the mine. These are Okmaesan, Gusi, Ipyoung, Haenam, Juckjeon, Okchul, Yaksan, Nohwa, and Wando mines. The

Sungsan mine produced mainly alunite ore in the past. But it now produces clays (Napseok and porcelain clay) about 5,000 tons per month from both the open-pit and the underground adits. The mine is also called the Hwangsan, Baekam or Bugok mine.

The clays in the Sungsan mine usually occur as hard claystones. They are embedded in rhyolitic Tuffs of the Hwangsan Formation. They have been formed by hydrothermal alteration (Moon, 1975; Shin, 1990). The claystone of the Sungsan mine consists mainly of dickite with minor other minerals. The purpose of this study is to investigate the mineralogy and genesis of clay minerals from the mine.

Geology of the study area consists of volcanic or volcanoclastic rocks of the Haenam Group, Kyeongsang System (Fig. 1). The Haenam Group can be correlated with the Yucheon Group of Late Cretaceous (Lee and Lee, 1976; Chang, 1977). The Haenam Group is divided into the Uhangri Formation, Hwangsan Formation, and Jindo Rhyolite in ascending order. A fault trending N70°E is inferred in the area.

The Uhangri Formation is the lowest sequences in this area and consists of alternation of laminated black shale and gray sandstone. The Hwangsan Formation conformably overlies the Uhangri Formation, and is mainly composed of tuff. The Hwangsan Formation is subdivided into three units; the Baekam, Jokbaksan, and Bugok tuffs. The Baekam Tuff consists mainly of light

GEOLOGIC SETTING

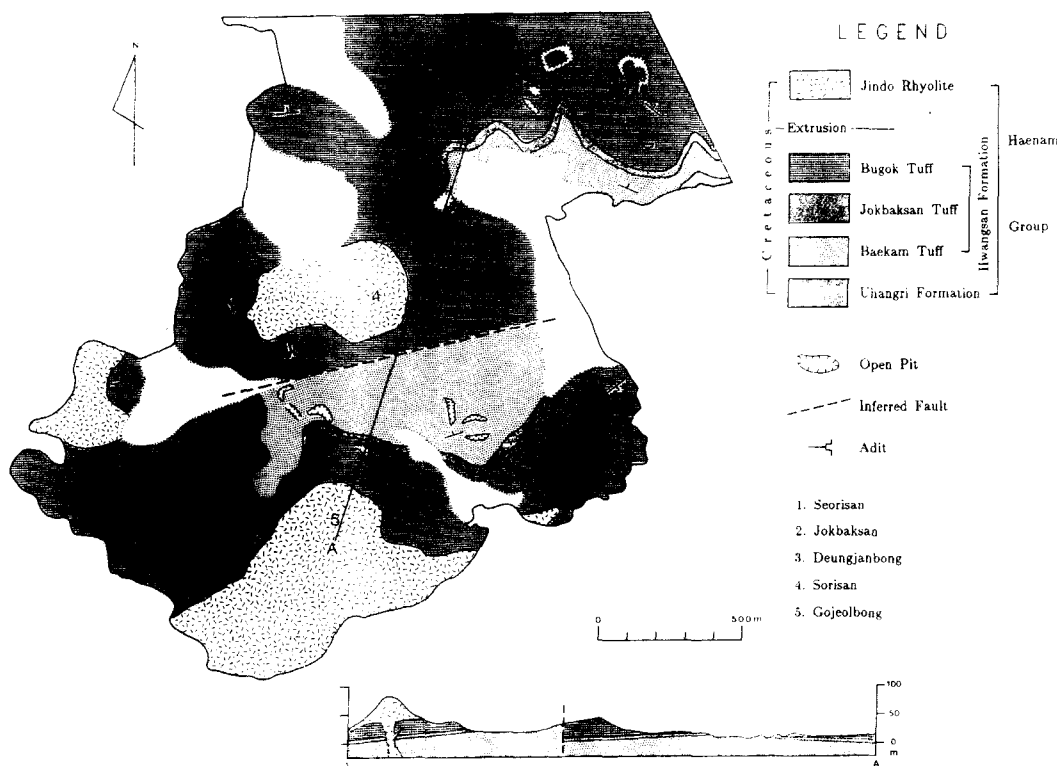


Fig. 1. Geologic map of the Sungsan mine.

gray fine-to medium-grained rhyolitic tuff which are weakly welded. Generally it shows flow banding. Cross-bedding and fiammes are occasionally observed. The lower part of the Baekam Tuff contains accretionally lapilli. The Jokbaksan Tuff consists of greenish gray, medium-to coarse-grained rhyolitic tuff with cognated lapilli. It is more or less fissile. The Buguk Tuff overlies conformably the Jokbaksan Tuff, and is composed of white to light gray fine-grained rhyolitic tuff with lapillistone. It usually shows massive structure, but sometimes bedding in places. The Jindo Rhyolite usually overlies the Hwangsan Formation but the former intrudes the latter in a small scale at some places. It consists of deep red rhyolite with numerous spherulites, and shows flow structure. Spherulites are composed of very finely intergrown needles of quartz, plagioclase, and K-feldspar.

EXPERIMENTAL METHODS

The morphology and texture of the clay minerals were studied using polarizing microscope, JEOL JXA-733 scanning electron microscope (SEM), and JEOL JEM 200CX transmission electron microscope (TEM). X-ray powder diffraction (XRD) analysis with a Rigaku RAD 3-C and Ni-filtered $\text{CuK}\alpha$ radiation was used for the analysis of mineral compositions of the various rocks and ores. The energy dispersive X-ray (EDS) and the wavelength dispersive X-ray (WDX) spectrometer were used for analysis of the chemical composition and elemental distribution in minerals. EDX and WDX analyses were conducted with a JEOL JXA-733 electron probe microanalyzer (EPMA). Infrared (IR) absorption spectra were recorded with Perkin-Elmer 283B Spectrophotometer. KBr pellet method was used over the range of $4,000\text{--}200\text{ cm}^{-1}$.

RESULTS

Mineralogy

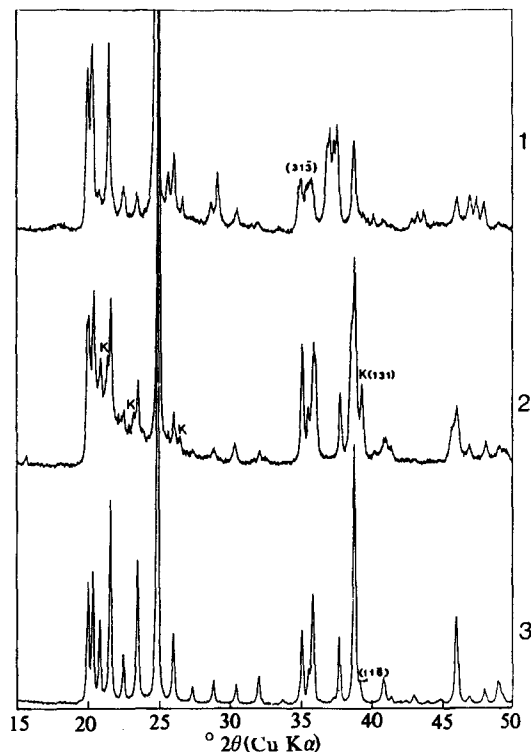


Fig. 2. X-ray powder diffraction patterns of kaolin minerals from the Sungsan mine. (K: kaolinite) 1. nacrite (#P6B), 2. dickite+kaolinite (#P15), 3. dickite (#M100).

Kaolin minerals. Kaolin minerals are important constituents of the claystone in this mine. Three kinds of kaolin minerals occur in the Sungsan mine. Among them dickite is the predominant kaolin mineral. Kaolinite does not occur as separate phase but as mixture with dickite. Nacrite is found rarely in the claystone, but commonly intergrown with dickite.

XRD patterns of kaolin minerals are shown in Fig. 2. Although XRD patterns of kaolinite and dickite are similar to each other, there are somewhat difference between two. The most prominent difference is that $(11\bar{6})$ peak of dickite is shoulder of (132) peak, but (131) peak of kaolinite is separate and distinct one.

Dickite generally occurs as massive aggregate. Occasionally it occurs as veinlet cutting quartz

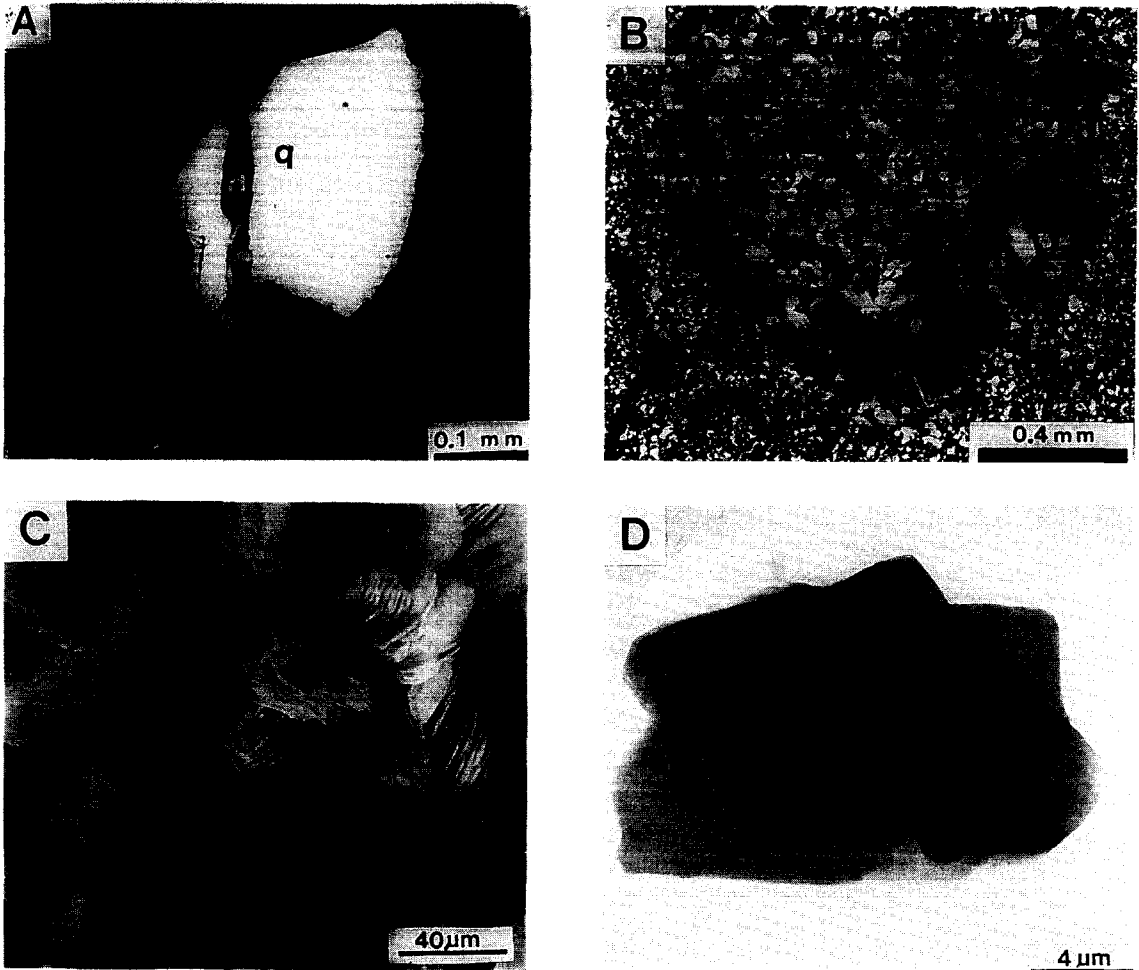


Fig. 3. Occurrence and morphology of dickite. A. Dickite veinlet (d) cutting quartz grain (q). Crossed nicols. B. Dickites (d) in cavity. Crossed nicols. C. SEM photograph showing book-structure of dickite composed of well-crystallized hexagonal plates. D. TEM photograph of dickite showing well-defined hexagonal plate.

grains (Fig. 3A), or in cavities (Fig. 3B). Dickite also replaces quartz. It shows hexagonal plates less than 10 μm in size and book-structure due to the stacking of platy grains (Fig. 3C). Dickite shows well-defined hexagonal plates about 10 μm in size under the transmission electron microscope (Fig. 3D).

More than 200 counts were analyzed for dickite using EPMA. Table 1 lists the selected and averaged chemical compositions of dickite. Dickite shows little or no change in main chemis-

try. The Al/Si ratios of dickite is 0.977–1.015. There is little or no substitution of Al for Si in the tetrahedral site. PbO contents of dickite range from 0.12–0.93 wt.% and BaO contents from 0.05–1.04 wt.%. These two values show positive relationship.

Fig. 4 shows IR absorption spectra of kaolin minerals from this mine. The peaks at 3700cm^{-1} (A) and 3635cm^{-1} (B) are common in all three kaolin minerals, and the peak depth ratio A/B of kaolinite is 1.2–1.5 whereas that of dickite is 0.59–

Table 1. Electron-microprobe analyses of dickite from the Sungsan mine.

#	A2 (10)	A7 (9)	A8 (32)	C2 (18)	C3 (9)	C5 (11)	E4 (11)	M100 (9)	R52 (8)
SiO ₂	44.93	44.97	44.69	45.08	45.90	45.51	45.04	45.38	45.21
Al ₂ O ₃	37.89	37.93	38.47	38.06	38.07	37.92	38.22	37.64	37.85
TiO ₂	0.01	0.13	0.04		0.08	0.04		0.01	0.01
Fe ₂ O ₃ *	0.04	0.05	0.04	0.01	0.05	0.05	0.01	0.12	0.09
MgO	0.00	0.02	0.01	0.00	0.01	0.02	0.00	0.01	0.01
MnO	0.03	0.06	0.01	0.01	0.02	0.06	0.01	0.01	0.05
PbO	0.21	0.75	0.93		0.82	0.52		0.12	0.12
SrO	0.08	0.15	0.23	0.06	0.02	0.00	0.07	0.08	0.11
BaO	0.24	1.04	0.15	0.08	0.48	0.51	0.05	0.11	0.15
CaO	0.01	0.03	0.01	0.02	0.02	0.04	0.00	0.02	0.05
Na ₂ O	0.01	0.03	0.02	0.02	0.02	0.04	0.02	0.02	0.01
K ₂ O	0.00	0.04	0.02	0.01	0.01	0.00	0.01	0.01	0.02
Total	83.50	85.23	84.68	83.34	85.48	84.74	83.44	83.53	83.70

Numbers of cations on the basis of 14 oxygens

Si	4.002	3.981	3.958	4.005	4.022	4.015	3.997	4.030	4.012
Al ^{IV}		0.019	0.042				0.003		
ΣTet.	4.002	4.000	4.000	4.005	4.022	4.015	4.000	4.030	4.012

Al ^{IV}	3.977	3.938	3.974	3.985	3.931	3.942	3.974	3.940	3.959
Ti	0.001	0.009	0.003		0.005	0.002		0.000	0.001
Fe	0.003	0.003	0.003	0.000	0.003	0.003	0.001	0.003	0.006
Mg	0.000	0.003	0.001	0.000	0.002	0.003	0.000	0.001	0.001
Mn	0.003	0.005	0.001	0.001	0.002	0.004	0.001	0.001	0.004
Pb	0.005	0.018	0.022		0.019	0.012		0.003	0.003
Sr	0.004	0.008	0.012	0.003	0.001	0.000	0.004	0.004	0.006
Ba	0.008	0.036	0.005	0.003	0.016	0.018	0.002	0.004	0.005
ΣOct.	4.001	3.963	4.019	3.992	3.980	3.984	4.002	3.961	3.985

Ca	0.001	0.003	0.001	0.001	0.002	0.004	0.000	0.002	0.005
Na	0.001	0.005	0.003	0.004	0.003	0.006	0.003	0.002	0.002
K	0.000	0.004	0.002	0.001	0.001	0.000	0.001	0.001	0.002
Si/Al	0.994	0.994	1.015	0.995	0.977	0.982	1.000	0.978	0.987

* Total Fe as Fe₂O₃. Numbers in the parentheses are points for average.

0.67 (Table 2). The peak ratios A/B of dickite mixed with kaolinite are 0.90–1.03, corresponding to the value between those of kaolinite and dickite. A useful spectral region to recognize disorder in kaolin minerals is between 795 and 758 cm⁻¹ (Russell, 1987). The two weak bands are of about equal intensity for well-ordered kaolin minerals, whereas 795 cm⁻¹ band is reduced to a

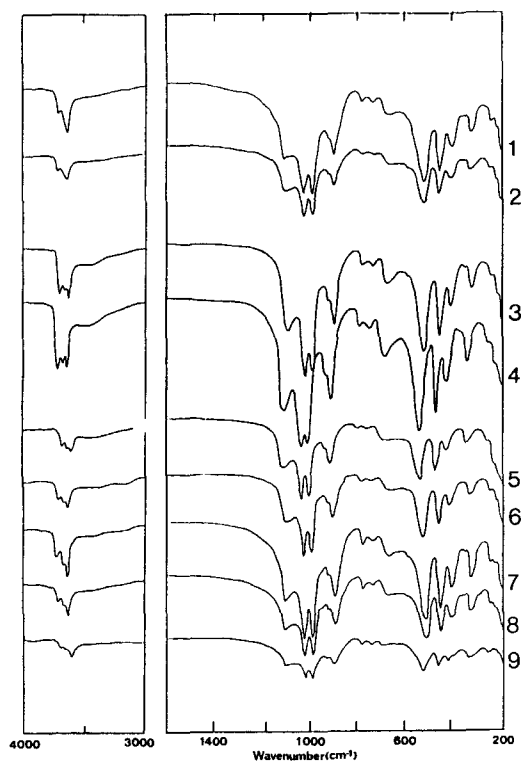


Fig. 4. Infrared absorption spectra of kaolin minerals from the Sungsan mine. 1. dickite+kaolinite (# P3-2), 2. dickite+kaolinite (# P15), 3. nacrite (# P6B), 4. nacrite (# P10), 5. dickite (# M6-2), 6. dickite (# C5), 7. dickite (# M100), 8. dickite (# A2), 9. dickite (# V5).

Table 2. Peak depth ratio (R) of kaolin minerals from the Sungsan mine.

#	Nacrite		Dickite+Kaolinite		Dickite				
	P6B	P10	P3-2	P15	M6-2	C5	M100	A2	V5
R	0.58	0.63	0.90	1.03	0.90	0.65	0.59	0.58	0.67

R=(peak depth at 3700 cm⁻¹)/(peak depth at 3635 cm⁻¹)

very weak reflection for disordered kaolin minerals. Two bands of kaolin minerals from this study are of about equal in intensity, therefore disorder in kaolin minerals is not recognized. It agrees with the results of XRD analysis.

Illitic minerals. The term “illitic mineral” is

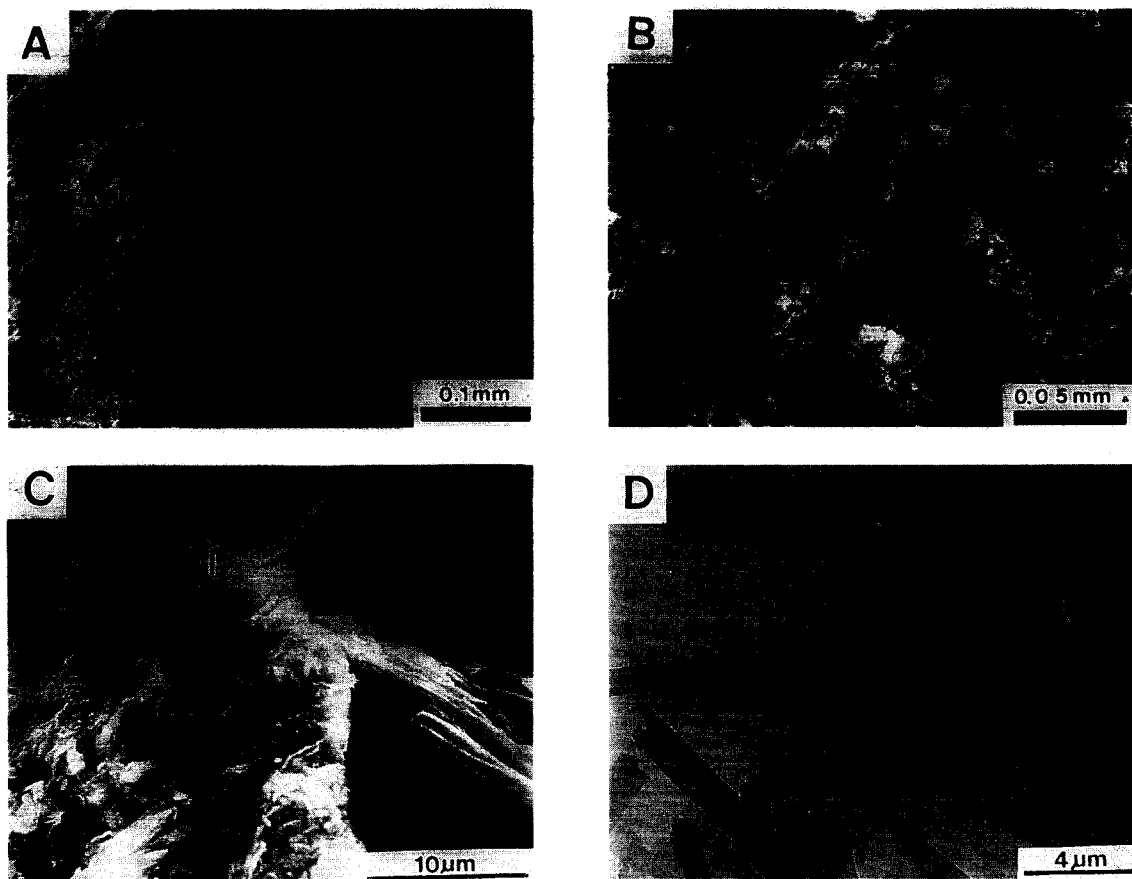


Fig. 5. Occurrence and morphology of illitic minerals. A. Illitic minerals (I) replacing muscovite (M). Crossed nicols. B. Radiating spherules of illitic minerals. Crossed nicols. C. SEM photograph of illitic minerals (I) developed from muscovite flakes (M). Illitic minerals consist of small plates with ragged margin. D. TEM photograph of illitic minerals showing well-developed long laths.

used as a group name implying a material which mainly comprises illite and possible some expanded layers (Srodon, 1984). Illitic minerals are one of the subordinate minerals in this Sungsan mine. They occur as alteration products of pre-existing minerals such as feldspar, muscovite or quartz (Fig. 5A) or cavity-filling (Fig. 5B). Illitic minerals generally occur as small flakes or plates (Fig. 5C). Illitic minerals in the cavities show radiating laths or flakes (Fig. 5D).

In this study, XRD identification of illitic minerals was made using the Srodon's (1984) and Srodon and Eberl's (1984) procedure. Table 3

gives the result of XRD identification for illitic minerals. It indicates that only three samples belong to illite/smectite and all others to illite. Most of illitic minerals belong to I+IS type and only one to I+ISII type. They contain >15-40 % smectite layer. Polytypes of illitic minerals are dominantly 1M or 1M₀ and rarely 2M₁, which suggests that illitic minerals in this mine might have been formed at relatively low temperature (Yoder and Eugester, 1955; Yoder, 1959; Velde, 1965).

Tosudite. Tosudite is mineral name for an 1:1

Table 3. X-ray diffraction data for illitic minerals from the Sungsan mine.

#	Reflections from glycolated preparations (2θ CuK α)						BB1 (2θ)	BB2 (2θ)	Reflections from air-dry prepara- tions (2θ CuK α)		Ir	%S	Type of illitic minerals
	7.71	8.96	17.22	26.61	34.49	44.96			8.33	17.08			
U17	7.71	8.96	17.22	26.61	34.49	44.96	5.1	5.2	8.33	17.08	5.36	15	IS/ISII
U21	7.86	9.08	17.25	26.57	34.52	44.86	4.8	5.2	8.36	17.09	4.23	14	ISII
A11	—	8.98	17.52	26.67	sh	45.18	4.2	4.1	8.62	17.49	2.56	5	IS
V11	—	8.83	17.65	26.66	33.43	45.41	4.6	4.3	8.51	17.72	4.42	37	I+IS
U13	7.72	8.81	17.67	26.60	33.47	45.34	4.9	4.7	8.32	17.69	4.23	35	I+IS
R10	7.42	8.89	17.71	26.63	33.64	45.31	5.4	5.5	8.35	17.73	4.15	31	I+IS
S10	—	8.83	17.71	26.69	33.36	45.25	5.0	4.1	8.74	17.69	4.00	39	I+IS
G11	—	8.81	17.64	26.62	diff	45.12	4.4	4.4	8.51	17.49	3.60	>15	I+IS
M186	5.31	8.93	17.66	26.72	33.54	45.34	3.5	4.0	8.68	17.69	3.02	33	I+ISII
M40	6.35	8.86	17.61	26.67	33.65	45.28	5.6	5.1	8.48	17.25	2.95	31	I+IS
M65	5.24	8.89	17.65	26.68	33.51	45.30	4.0	4.2	8.62	17.74	2.43	34	I+IS
U22	—	8.81	17.66	26.67	34.59	45.36	3.5	2.1	8.55	17.69	2.07	13	I+IS
U23	—	8.84	17.77	26.71	—	45.47	4.6	4.3	8.70	17.76	1.96	>15	I+IS
M80	sh	8.85	17.60	26.64	—	45.07	4.7	—	8.51	17.64	1.76	>15	I+IS
U25	sh	8.81	17.69	26.65	sh	45.22	5.8	4.0	8.71	17.65	1.54	>15	I+IS
M180	sh	8.83	17.61	26.63	diff	45.16	4.2	4.2	8.71	17.70	1.24	>15	I+IS

sh; shoulder. diff; diffuse reflection

Table 4. X-ray diffraction data of tosudite from the Sungsan mine after various treatments (unit; Å).

00l	A	B	C	D	E	F	G
001	29.3	31.3	32.0	28.9	27.2 ^a	23.4	23.3
002	14.2	15.4	15.2	13.8	13.2	11.9	11.9
003	9.5		9.5	9.2	8.4 ^b		
004		7.8	8.0			5.8	5.8
005	5.70	5.70	5.70	5.69	4.79	4.68	4.69
006	4.78	5.16	5.29	4.67		4.49	4.48
	4.44		4.74	4.46	4.47		
007		4.47	4.55				
008				3.49	3.45	2.93	2.91
009		3.46	3.51		2.88		
00.10	2.85			2.76			
00.11		2.83	2.87				
060	1.492						

A, air dry; B, ethylene glycol saturation; C, glycerol saturation; D, heated at 110 °C for 3 hrs, E, heated at 300 °C for 3 hrs, F, heated at 500 °C for 3hrs, shoulder; b, broad.

regular interstratification of chlorite and smectite (C/S) that is octahedral on average (Bailey et al., 1982). Tosudite is an important constituent mineral of the massive claystone in this mine. It also occurs as cavity-filling together with nacrite and/

or quartz. It shows thin flakes with curled margins.

XRD data of tosudite are given in Table 4. The characteristic (001) reflection appears at 29.3 Å. The (060) reflection at 1.492 Å indicates that it is dioctahedral. The systematic appearance of high order reflections suggests that it is a regularly interstratified mineral. The experimental XRD data of tosudite correspond to the theoretically calculated XRD data of tosudite (a regular interstratification of donbassite and dioctahedral smectite) using NEWMOD program (Reynolds, 1985).

Alunite. Alunite occurs in three different modes, that is 1) massive, 2) cavity-filling, and 3) veinlets. Massive alunite consists of anhedral, short prismatic or tabular crystals of 20–50 μm in length. Cavity-filling alunite is long prismatic or tabular in habit and 50–100 μm in size. It is associated with dickite and barite. In alunite-dickite veinlets, alunite grows on the walls of veinlets whereas dickite is present in the central part (Cho, 1990). Alunite often shows color zoning due

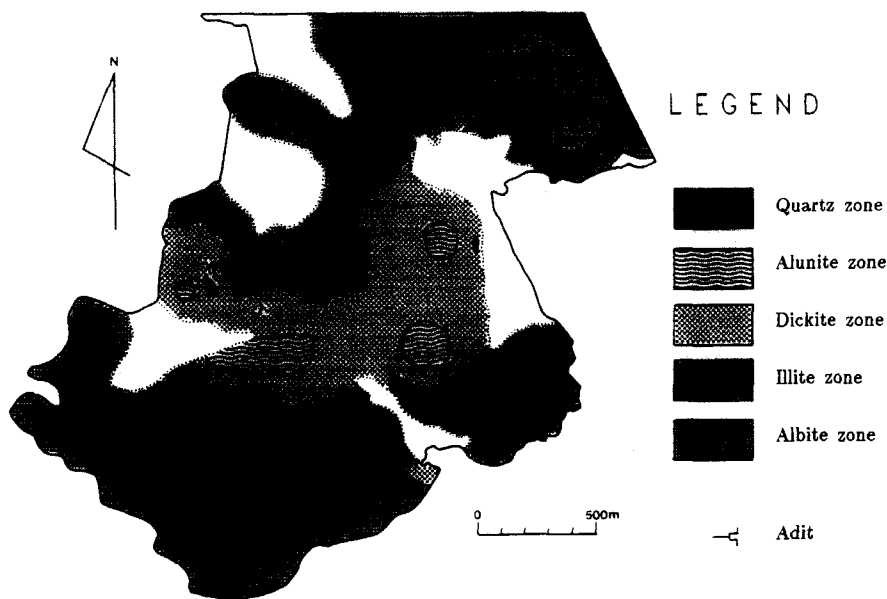


Fig. 6. Hydrothermal alteration zones in the Sungsan mine area.

to the variation of Na and K contents (Cho and Kim, 1993).

Mineral Zoning

Five mineral zones recognized by major mineral species of samples over the whole area (Fig. 6). They are 1) quartz, 2) alunite, 3) dickite, 4) illite, and 5) albite zones. The alunite zone-dickite zone-illite zone-albite zone are the general order of zone distribution from the central part to outside. The zonal mineral distribution pattern in this mine is similar to that of replacement type alunite deposits (Hall, 1970).

The quartz zone consists only of microcrystal. line quartz. It shows white to light gray in color and porous in texture. It is found as small lenticular-shape in the dickite zone in the Bugok Tuff. The alunite zone is composed mainly of alunite and quartz with minor dickite and pyrite. It shows white or pink color. This zone occurs as circular or lenticular shape in a few place. Original texture is blurred but still recognized in thin section. The dickite zone consists of dickite and quartz with minor kaolinite, nacrite, alunite, illitic min-

erals, tosudite etc. Claystones in this zone show various color; white, gray, pink, green, yellow or purple. This zone is widely distributed in the Hwangsan Formation. The illite zone consists mainly of illitic minerals and quartz with minor dickite, tosudite, and pyrite. This zone is developed mainly in the Jokbaksan Tuff. It is distributed around the dickite zone. The albite zone consists mainly of albite, quartz, sanidine with minor illitic minerals. This zone is developed widely in the weakly altered outer fringe in the Jindo Rhyolite and Hwangsan Formation.

GENESIS

The volcanic and volcanoclastic rocks of the Sungsan mine area have been subjected to hydrothermal alteration, thus resulting in the formation of clay minerals and alunite. According to the mineral assemblages, five alteration zones are recognized. The alteration zones are arranged in order of the alunite, dickite, illite and albite zones from center to outside. These zones correspond to the advanced argillic, argillic and

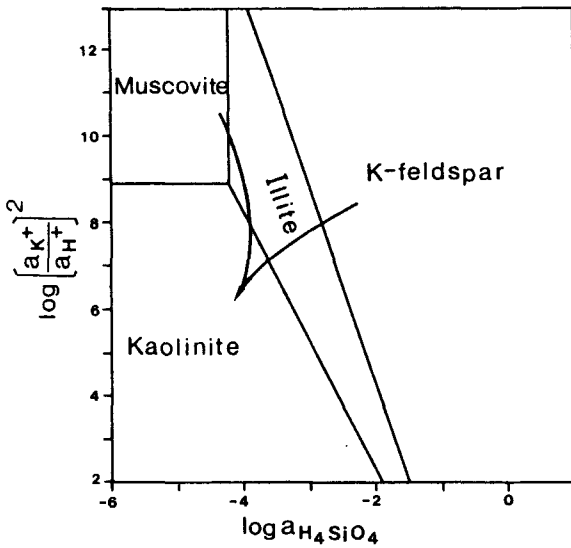


Fig. 7. Ion activity diagram illustrating the stability of kaolinite and illite(modified from Garrels, 1980).

propylitic zones of common porphyry copper deposits (Lowell and Guilbert, 1970).

In order to understand the condition of hydrothermal alteration, thermochemistry of the alteration minerals has been studied for the alteration mineral assemblages using the data from the literatures (Garrels and Christ, 1965; Hemley et al., 1969; Knight, 1977; Garrels, 1984). Because the alteration minerals are almost potassium-containing the activity diagrams of potassium has chiefly used for this work. The hydrothermal alteration has been studied in two different system. For the alunite-involving system, activity diagrams of $a_{K_2SO_4}$ and $a_{H_2SO_4}$ have been applied. For the alunite-absent system, as in the albite, illite or dickite zones, activity diagram of $a^2_{[K^+/H^+]}$ has been applied.

The equilibrium relations excluding alunite are illustrated by the activity diagram in Fig. 7. The main alteration feature in the albite zone is the alteration of feldspars to illitic minerals, albitization of plagioclase, and formation of cal-

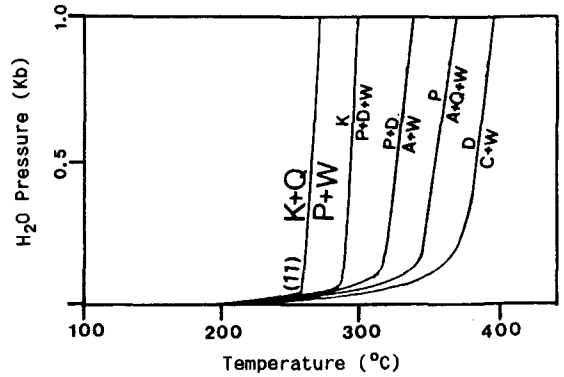


Fig. 8. Calculated pressure-temperature curves in the system $Al_2O_3-SiO_2-H_2O$ based on 1 kb stability relationship and thermodynamic data (after Hemley et al., 1980). A, andalusite, C, corundum; D, diaspore; K, kaolinite; Ky, kyanite; P, pyrophyllite; Q, quartz; Si, sillimanite; W, water.

cite. The formation of albite is promoted by increasing a_{Na^+} or $a_{H_2SiO_4}$. Illitic minerals in the illite zone replace K-feldspar, muscovite or quartz. As shown in Fig. 7, illitization of K-feldspar occurs by decreasing a_{K^+} or increasing $a_{H_2SiO_4}$. Therefore decrease of $a^2_{[K^+/H^+]}$ is essential factor in the formation of illite. The dickite zone comprises mainly dickite and quartz. Dickite occurs as replacement of quartz and precipitation in the cavities. Many investigators reported that kaolin minerals are formed from feldspar, muscovite or illite (Grim, 1968; Murray, 1987). On the basis of activity diagram, the stability region of kaolinite lies in the area of low a_{K^+} and low $a_{H_2SiO_4}$. Decrease of a_{H^+} or $a_{H_2SiO_4}$ promotes the formation of kaolin minerals. The stability relations among the kaolin minerals are not established. But many researchers reported that dickite and nacrite are the high temperature form of kaolinite (Ross and Kerr, 1931, Hanson et al., 1981; Lombardi et al., 1987).

The alunite zone consists of alunite and quartz. Alunite in the alunite zone replaces dickite. According to Knight (1977), alunite replaces feld-

spars and muscovite. Alunite is characteristic mineral produced under the condition of acid-sulfate alteration of silicate rocks (Hemley et al., 1969). Hemley et al. (1969) made alunite stability diagram using experimental data. According to them, a fairly high H_2SiO_4 concentration is required before alunite can be produced in equilibrium with muscovite, K-feldspar or kaolinite. If alunite repacles kaolinite, increase of a H_2SiO_4 or a K_2SO_4 is required. When a H_2SiO_4 increases, larger value of a H_2SiO_4 is required to stabilize alunite.

Maximum and minimum temperatures of hydrothermal alteration are estimated using mineral assemblages and thermodynamic calculation (Cho, 1990). As shown in the zonal arrangement of alteration zones, temperature of hydrothermal solution decreases from dickite zone through illite zone to albite zone. Hemley et al. (1980) made a P-T diagram in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ based on 1 kb stability relationships and thermodynamic data (Fig. 8). The mineral assemblage in the dickite zone (dickite and quartz) only lies along reaction curve (11) in Fig. 8. In this zone, dickite coexists with quartz but pyrophyllite does not occur in the Sungsan mine. Therefore temperature of formation for the dickite zone is below than that of reaction curve (11). For 1 kb H_2O , temperature of formation for dickite zone is less than 270 °C. Boles (1982) studied the albitization of plagioclase in Oligocene Gulf Coast sandstone and suggested that active albitization occurs at temperature of 110-120 °C. According to above consideration, it is estimated that the hydrothermal alteration in the Sungsan mine occurred in the range from 110-270 °C.

CONCLUSIONS

Claystones in the Sungsan mine are mainly composed of dickite, quartz, alunite, illitic minerals, and tosudite with accessory minerals such as kaolinite, nacrite, pyrite and barite.

Volcanic and volcanoclastic rocks around the Sungsan mine are intensively altered. Five hydrothermal alteration zones are discernible according to the main constituent minerals. The dickite and alunite zones are considered as the center of hydrothermal alteration. The albite zone is the outermost fringe of alteration. The illite zone lies between dickite zone and albite zone. The quartz zone distributed as small lenticular in the dickite zone.

With increasing distance from the center of hydrothermal alteration, activity of potassium increases and temperature of formation decreases. Estimated temperature of formation for hydrothermal alteration ranges from 110-270 °C.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Mr. Hunsoo Choi for his assistance in EPMA and SEM experiments. We also thank Mr. K. H. Maeng for his skilled technical assistance in TEM study.

REFERENCES

- Bailey, S. W. Brindley, G. W., Kodama, H. and Martin, R. T. (1982) Report of the clay minerals society nomenclature committee for 1980-1981, nomenclature for regular interstratification. *Clays Clay Miner.*, 30, 76-78.
- Boles, R. J. (1982) Active albitization of plagioclase, Gulf Coast Tertiary. *Amer. J. Sci.*, 282, 165-180.
- Chang, K. H. (1977) Late Mesozoic stratigraphy, sedimentation and tectonics of southern Korea. *Jour. Geol. Soc. Korea*, 13, 76-90. (in Korean)
- Cho, H. G. (1990) Mineralogy of clays and their associated minerals in the Sungsan mine, Korea. Seoul Nat. Univ., Ph. D. Thesis, 202p.
- Cho, H. G. and Kim, S. J. (1993) Oscillatory zoning in alunite from the Sungsan mine, Korea. N.

- Jb. Miner. Mh., 1993, 185-192.
- Garrels, R. M. (1984) Montmorillonite/illite stability diagrams. *Clays Clay Miner.*, 32, 161-166.
- Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria*. Harper and Row, New York, 450p.
- Grim, R. E. (1968) *Clay Mineralogy* (2nd ed.). McGraw-Hill, New York, 596 p.
- Hall, R. B. (1978) World nonbauxite aluminum resources-Alunite. U.S. Geol. Surv. Prof. Paper, 1076-A, A1-A35.
- Hanson, R. M., Zamora, R. and Keller, W. D. (1981) Nacritite, dickite and kaolinite in one deposit in Nayarite, Mexico. *Clays Clay Miner.*, 29, 451-453.
- Hemley, J. J., Hostetler, P. B., Gude, A. J. and Mountjoy, W. T. (1969) Some stability relations of alunite. *Econ. Geol.*, 64, 599-612.
- Hemley, J. J., Montoya, J. W., Marinenko, J. W. and Luce, R. W. (1980) Equilibria in the system $Al_2O_3-SiO_2-H_2O$ and some general implications for alteration/mineralization processes. *Econ. Geol.*, 75, 210-228.
- Knight, J. E. (1977) A thermochemical study of alunite, enargite, luzonite and tennantite deposits. *Econ. Geol.*, 72, 1321-1336.
- Lee, D. S. and Lee, H. Y. (1976) Geological and geochemical study on the rock sequences containing oily materials in southwestern coast area of Korea. *J. Korean Inst. Mining Geol.*, 9, 45-74.
- Lombardi, G., Russell, J. D. and Keller, W. D. (1987) Compositional and structural variations in the size fractions of a sedimentary and a hydrothermal kaolin. *Clays Clay Miner.*, 35, 321-335.
- Lowell, J. V. and Guibert, J. M. (1970) Lateral and vertical alteration-mineralization zoning in porphyry ore deposits. *Econ. Geol.*, 65, 373-408.
- Lyen, R. J. P. and Tuddenham, W. M. (1960) Infra-red determination of the kaolin group minerals. *Nature*, 185, 835-836.
- Moon, H. S. (1975) A study on genesis of alunite deposits of Jeonnam area. *J. Korean. Inst. Mining Geol.*, 8, 183-202. (in Korean)
- Murray, H. H. (1987) Kaolin mineral: their genesis and occurrences. In: Bailey, S. W. (ed.) *Hydrous Phyllosilicates. Reviews in Mineralogy*, vol. 19, Miner. Soc. Amer., 67-89.
- Ross, S. D. and Kerr, P. F. (1931) The kaolin minerals. U. S. Geol. Surv. Prof. Paper, 165, 151-180.
- Russell, J. D. (1987) Infrared methods. In: Wilson, M. J. (ed.) *A Handbook of Determinative Methods in Clay Mineralogy*, Blackie, Glasgow and London, 133-173.
- Reynolds, R. C. (1985) Newmode, Computer Program for the Calculation of One-dimensional Diffraction Patterns of Mixed-Layered Clays. Publ. by author 8 Brook Road, Hanover, New Hampshire.
- Shin, S. U. (1990) Geochemistry and mineralogy of the pyrophyllite, kaolinite and alunite deposits associated with Cretaceous volcanic activity in southwestern area of Cheonnam. cheonnam Nat. Univ., Ph. D. Thesis, 165 p. (in Korean)
- Srodon, J. (1984) X-ray powder identification of illitic minerals. *Clays Clay Miner.*, 32, 337-349.
- Sordon, J. and Eberl, D. D. (1984) Illite. In: Bailey, S. W. (ed.) *Micas. Reviews in Mineralogy*, vol. 13, Miner. Soc. Amer., 495-544.
- Velde, B. (1965) Experimental determination of muscovite polymorph stabilities. *Amer. Miner.*, 50, 436-449.
- Yoder, H. S. (1959) Experimental studies on micas: a synthesis. *Clays Clay Miner.*, 6, 42-60.
- Yoder, H. S. and Eugester, H. P. (1955) Synthetic and natural muscovites *Geochim. Cosmochim. Acta*, 8, 225-280.