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Mineralogy and Genesis of Hydrothermal Deposits in the Southeastern Part of Korean Peninsula: (3) Miryang Napseok Doposits

우리나라 동남부지역의 열수광상에 대한 광물학적 및 광상학적 연구: (3) 밀양납석 광상

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ABSTRACT: Several "Napseok" mines are distributed in the Miryang area where the volcanic rocks are hydrothermally altered. The "Napseok" deposits are mainly developed in andesitic tuff. Main constituent minerals of "Napseok" are pyrophyllite and dickite, with a small amount of silicates such as quartz, illite, tosudite and dumortierite. Other associated minerals are oxides, hydroxides, sulfides, sulfates and phosphates.

Pyrophyllite which occurs as 2M polytype exhibits that the basal spacing increases due to dehydroxylation at 750℃. Halloysite shows tubular forms. Wavellite is precipitated in fissures during the latest stage of the hydorthermal alteration process.

Five mineral zones, that is, pyrophyllite–dickite, illite, halloysite, silica, and albite–chlorite zones, are recognized with decreasing alteration degree.

Clay minerals were formed by leaching of Si and alkali ions from the country rocks. Considering mineral assemblages, pyrophyllite polytype and thermodynamical data reported in the literature, temperatures of formation of main clay deposits are assumed to be 270 to 350℃.

요약: 경남 밀양 일대의 화산암에는 열수변질대가 상당히 넓게 발달하고 있으며, 여러 개의 점토광상이 분포한다. 납석광상은 주로 안산암질 응회암에서 배태된다. 납석광석의 주구성광물은 엽납석과 딕카이트이며, 그외에 일라이트, 토수다이트, 듀모티에라이트, 석영 등의 규산염광물들이 소량 수반되며, 다이아스포아, 황철석, 웨이브라이트 등이 산출된다.

본 지역의 엽납석은 단지 2M 다형만 산출된다. 엽납석은 약 750℃에서 OH가 빠져나감에 따라서 d_{001} 간격이 증가한다. 할로이사이트는 튜브형태로 나타난다. 웨이브라이트는 열수변질작용 말기의 낮은 온도에서 틈을 따라 침천된 것이다.

본 지역의 5개의 변질대로 구분되는데, 주광체로부터 멀어질수록 엽납석–딕카이트대, 실리카대, 일라이트대, 할로이사이트대, 녹니석–알바이트대로 대상분포를 보인다. 점토광물은 모암으로부터 Si와 알카리이온의 용탈에 의해서 형성되었다.

광물조합과 엽납석 다형 및 기존의 열역학적 자료를 고려하면 밀양광산의 형성온도는 270~350℃ 내외인 것으로 추정된다.

INTRODUCTION

Hydrothermal clay deposits are widely distributed in the Miryang area. The study area is located in Sanae−myeon, Miryang gun, Gyungsangnam–do, Korea(lat. 35° 30'N–35° 32'N, long. 128° 41'E–128° 47'E). The Miryang mine is the largest among clay deposits in this area. Mining was operated in underground mining in the past, but now is open–pit. The annual production of Napseok ore is about 1000 tons. The purpose of this work is to study the mineralogy of clay minerals from Miryang mine and their genesis.

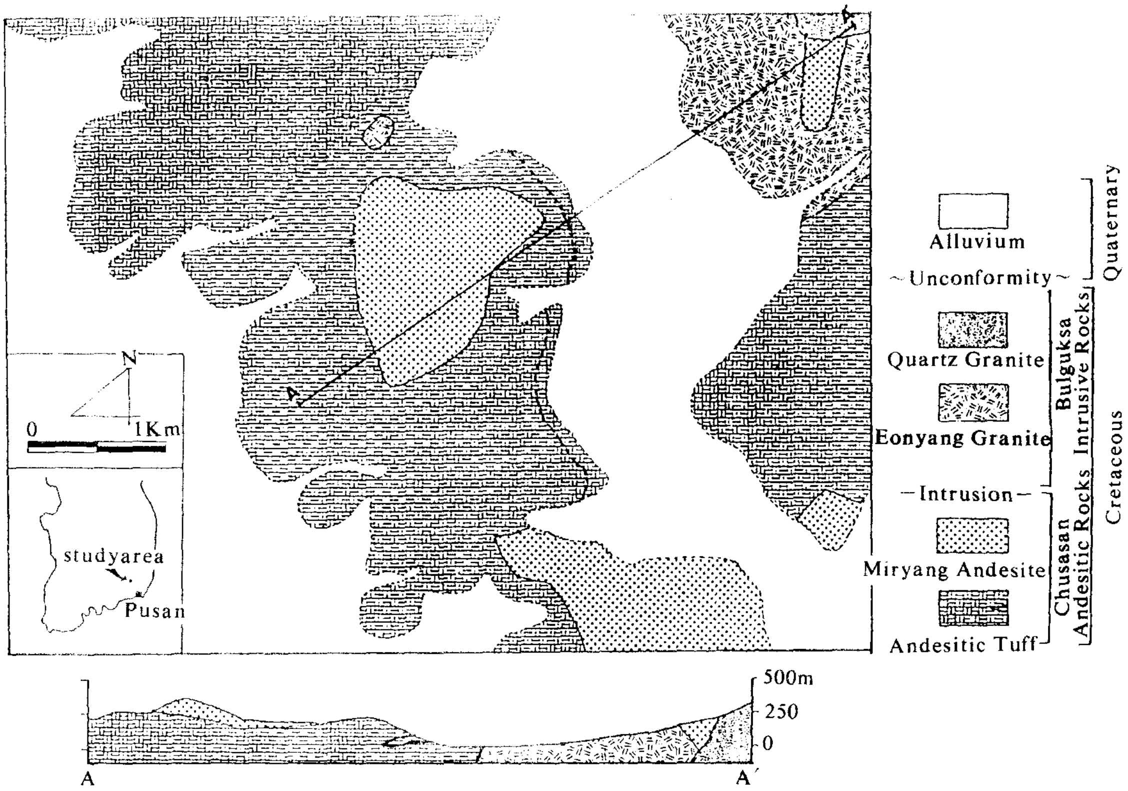

Fig. 1. Geological map of the Miryang clay deposit.

GEOLOGICAL SETTING

The geology of study area is mainly composed of volcanic rocks of the Yucheon Group and Bulguksa intrustive rocks which belong to the Late Cretaceous igneous rocks (Fig. 1). Andesitic tuff is chiefly distributed in the central part of the study area. It is greenish gray and dark brown in color. Agglomerate is intercalated in andesitic tuff from place to place. Under the optical microscope, the andesitic tuffs are mostly composed of rock fragments and plagioclase grains. Miryang andesite consists of augite, plagioclase, hornblende, chlorite and opaque minerals. It contains a lot of plagioclase phenocrysts of generally 0.5×1mm to 5×3mm in size. The groundmass is made up of plagioclase microlites. The Eonyang granite consists of quartz, orthoclase, plagioclase, biotite and hornblende. Quartz porphyry is light-yellow in color and consists of quartz, orthoclase and plagioclase.

Clay deposits are developed especially in the andestitc tuff region. In the Miryang mine, clay minerals are mainly pyrophyllite, dickite and illite, and associated minerals are quartz, dumortierite, diaspore, wavellite, etc.

EXPERIMENTAL

X-ray diffraction analysis (XRD) was carried out to identify the minerals using a Rigaku model RAD 3 C diffractometer with Ni-filtered CuKα radiation. Random and preferred orientation samples were mounted in the aluminum holder and slide glass, respectively. Infrared absorption spectra of powdered samples were recorded with a Perkin-Elmer model 283B spectrophotometer in the region of 4000−400 cm^{-1} under the condition of scanning time 12 minutes. 3mg samples were dispersed in 200mg KBr for near-infrared region and 0.5mg samples for intermediate-infrared region. Each spectrum was calibrated with polyethylene film.

Scanning electron microscopy (SEM) was carried out to study the mineral morphology using a JEOL JXA-733 scanning electron microscope. Fresh surface of samples were coated for the SEM observation.

Electron microprobe analysis was made on polished thin sections at 15 kV with a beam diameter of 10μm.

X-ray fluorescence analysis (XRF) was made for determination of major elements of bulk rock samples using a Philips model PW 1400 spectrometer.

For acid treatment experiment, finely ground samples (0.2 mg) were treated with H_2SO_4 (2ml)-HNO_3(2ml)-HF (5ml) mixture and evaporated. Then, 5ml of H_2SO_4-HNO_3 acid mixture was added. After the residue was digested with diluted HCl, it was washed several times with distilled water and dried at 60℃ in the oven.

RESULTS

Clay Mineralogy

Pyrophyllite : Pyrophyllite is the dominant mineral of the Miryang mine. Other minerals associated with pyrophyllite are dickite, quartz, dumotierite, diaspore, and pyrite. The pyrophyllite ores are green, yellow or white in color. They occur as massive mixture with the other clay minerals. Pyrophyllite shows well-crystallized flaky form (Fig. 2A). The structure is of 2M polytype. It is worth while to compare the structure of pyrophyllite from the Miryang mine with that from other areas in the Gyungsangnam-do. Choo (1990) reported 2M polytype from the Kimhae area while Kim (1989) described 1Tc and 2M polytypes from the Yangsan area.

Al/Si. ratios are 0.52−0.56 indicating the surplus of Al as compared to ideal composition (Table 1). Interalyer cations are negligible.

Wardle and Brindley (1972) studied dehydroxylation properties of pyrophyllite. The strong basal reflection of pyrophyllite occurs at 9.1−9.2 Å. This reflection is unchanged at 550℃, but shifts toward low angle at 650℃. The basal reflection is completely disappeared at 1100℃, indicating the decomposition of the structure. X-ray diffraction patterns of pyrophyllite at various temperatures are shown in Figure 3.

Table 1. Electron microprobe analyses of clay minerals. Oxygen basis used for calculation of cation numbers are 22 for pyrophyllite and 14 for dickite.

	pyrophyllite			dickite	
samples	K12-1	KJ4	K39-2	F18-2	F18-3
SiO_2	63.357	64.318	63.296	46.455	45.824
Al_2O_3	29.868	30.776	29.138	34.431	33.239
TiO_2	0.000	0.044	0.011	0.010	0.003
Cr_2O_3	0.049	0.021	0.008	0.000	0.055
FeO	0.293	0.235	0.166	0.269	0.914
MgO	0.097	0.047	0.026	0.287	1.069
MnO	0.039	0.000	0.000	0.029	0.000
CaO	0.207	0.002	0.030	0.159	0.171
Na_2O	1.003	0.192	0.258	1.382	1.491
K_2O	0.750	0.009	0.000	0.830	1.249
total	95.665	95.643	92.931	83.852	84.015
		cation numbers			
Si	7.672	7.707	7.797	4.155	4.132
Al(iv)	0.328	0.293	0.203	0.000	0.000
sum(tet)	8.000	8.000	8.000	4.155	4.132
Al(vi)	3.934	4.019	3.903	3.630	3.532
Ti	0.000	0.004	0.001	0.001	0.000
Cr	0.005	0.002	0.001	0.000	0.004
Fe^{2+}	0.003	0.024	0.017	0.020	0.069
Mg	0.018	0.008	0.005	0.038	0.144
Mn	0.004	0.000	0.000	0.002	0.000
sum(oct)	3.960	4.057	3.927	3.791	3.749
Ca	0.027	0.000	0.004	0.015	0.017
Na	0.236	0.045	0.062	0.240	0.261
K	0.116	0.001	0.000	0.095	0.144
sum(int)	0.379	0.046	0.066	0.350	0.421
Al/Si ratios	0.556	0.527	0.559	0.874	0.855

Most silicate minerals are readily decomposed by mixtures of acids. After acid mixture treatment, the residues are only pyrophyllite. The dissolution of silicates by strong acids depend essentially on adsorption of HF molecules on the surface. It is likely that the structure of pyrophyllite prevent the adsorption of HF molecules on the surface of mineral, and consequently, more resistant to acid attack.

Infrared absorption is especially sensitive to the coordination between OH groups and nearest cation neighbores. As most layer silicates, bands of the infrared vibration spectra of pyrophyllite

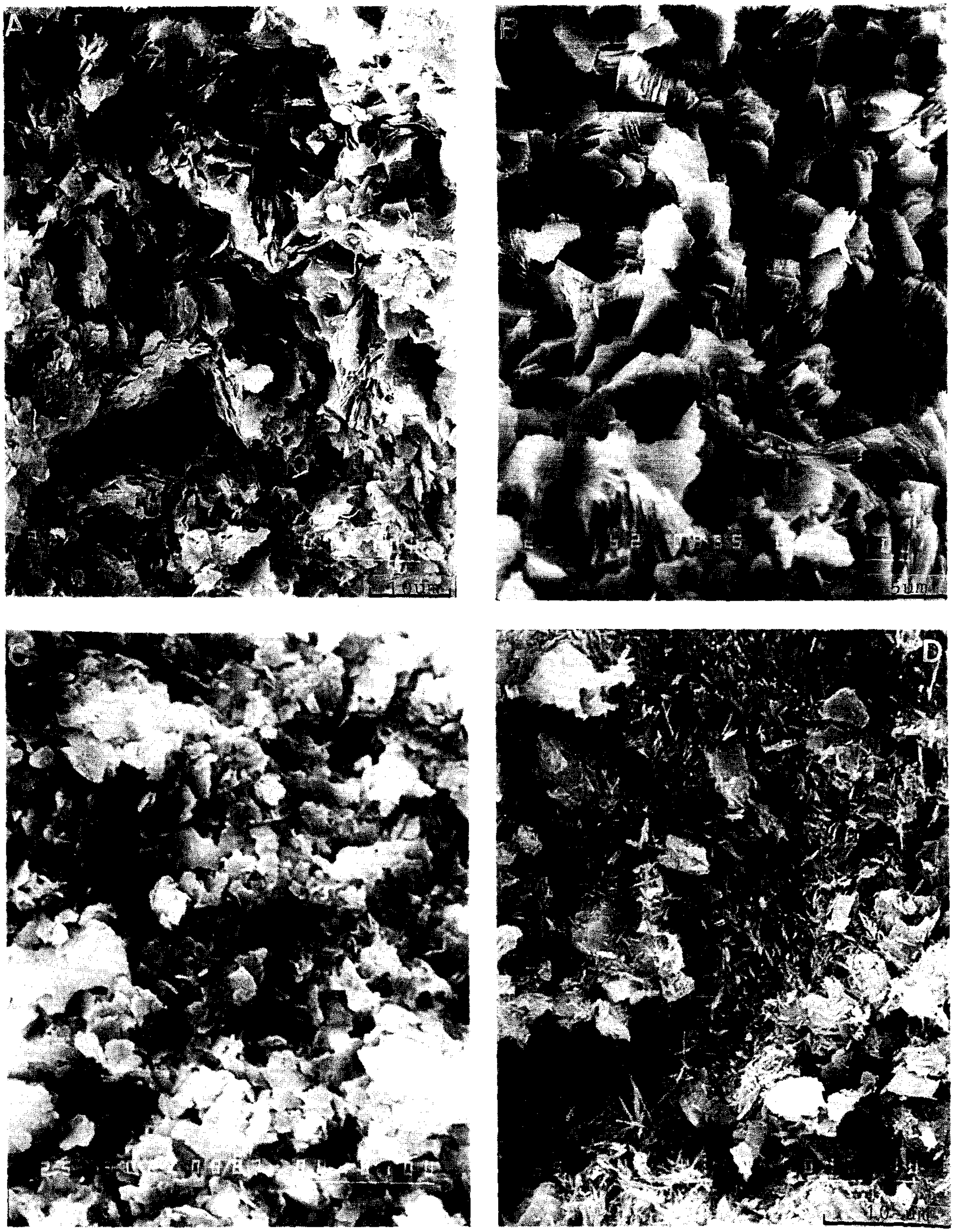

Fig. 2. SEM photographs of clay minerals from the Miryang mine area. (A) Pyrophyllite, (B) dickite showing layer-stacking, (C) illite, (D) halloysite and kaolinite showing a tubular form.

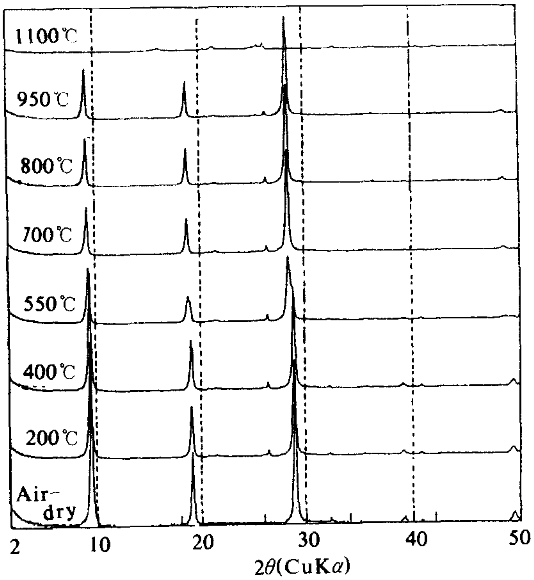

Fig. 3. XRD patterns of pyrophyllite heated for three hours at various temperatures.

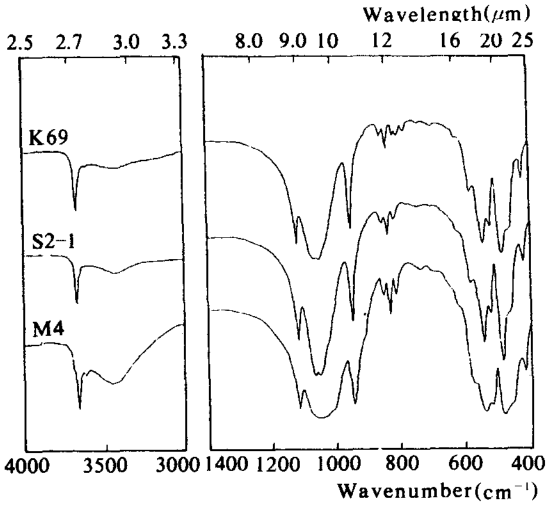

Fig. 4. Infrared absorption spectra of pyrophyllite at room temperature.

may be correlated generally with the hydroxyl, Si-O bonds and the octahedral linkage (Farmer, 1974). Farmer (1974) noted that the Si-O stretching vibrations in the 700–1200 cm^{-1} region weakely affect other vibrations, whereas the Si-O bending vibrations in the 150 to 600 cm^{-1} region are strongly coupled with the vibrations of the octahedral cation and with the vibrations of hydroxyl groups. Characteristic bands of high intensity are 3665, 1120, 1068, 1050, 950, 835, 625, 580, 540, 520, 485, 460 and 420 cm^{-1} (Fig. 4). The intensity of bands remain nearly constant at 450℃. When heated at 750℃, the bands at 3665, 1120, 950, 815, 625, 580, 540 and 420 cm^{-1} are decomposed, and new bands appear at 865, 655, 570, 440, and 410 cm^{-1}. Because Si-O bands resist to heating better than Si-OH and Al-OH groups, Si-O bands still remain when heated to 750℃.

Dickite : Dickite is one of the predominant minerals of the Napseok ores together with pyrophyllite in the Miryang mine. It is associated with pyrophyllite, diaspore, pyrite and dumortierite. Dickite in the Miryang mine occurs as a massive form, and is white or green in color. It shows book-shape with stacking of plates (Fig. 2B). Abundant silica content is charateristic of dickite from this mine (Table 1).

Halloysite : Halloysite (10Å) occurs in close association with kaolinie. It is also associated with illite and quartz. Halloysite ores are white, yellow and red in color. The structure collapsed at 550℃ for two hours. Halloysite easily transforms to halloysite (7Å) at 100℃. It shows a tubular form (Fig. 2D).

Illite : Illite is associated with pyrophyllite, dickite, and halloysite. It occurs as fine flakes (Fig. 2C) and is generally found in the outer part of main ore body. At 1100℃, the structure of illite collapses, and basal reflections completely disappear.

Tosudite : Tosudite in the Miryang mine occurs sporadically in the pyrophyllite ore body. It is commonly associated with pyrophyllite and dickite. It is blue or green in color. Ichikawa and Schimoda (1976) reported tosudite from the Hokno mine in Japan. Creach et al. (1986) described tosudite crystallization in the kaolinized granitic cupola of Montebras in France. The typical 30Å reflection shifts to 28Å at 200℃ due to dehydration of the interlayer water in double planes of water molecules. The X-ray diffraction features of the dehydration experiment on tosudite in this study can be summerized as follows. The untreated material gives rise to a reflection at 29-30Å. After treated with ethylene glycol, this reflection expands to 31–32Å, and after heated at 550-800℃ the reflection collapses to 24Å.

Kaloinite: Kaolinite occurs in association with halloysite. It is poorly crystalline (Fig. 2D).

Non-Clay Minerals

Wavellite: Wavellite is not abundantly found in the Miryang mine. It occurs as veinlets in the restricted part of the main ore body. It shows radiating aggregate of fibrous acicualr crystals (Fig. 5A). Reflection lines decrease in their intensities at 200℃ and disappear at 250℃. The fact indicates that it is especially unstable at high temperature. Wavellite has been formed by precipitation from solution in fissures during the latest stage of the hydrothermal proccess.

Dumortierite: Dumortierite, a boron-alumina-silicate, occurs as veins of aggregates of fibrous or columnar crystals. It is commonly violet and sometimes pink in color. Under the polarizing microscope, it exhibits strong pleochroism and negative elongation. SEM photographs show that it occurs as aggregate of fibrous crystals (Fig. 5B).

Diaspore: In the Miryang mine, diaspore occurs as nodules (Fig. 5C). It has a perfect cleavage in one direction similar to mica, and shows mainly tabular or platy forms under SEM (Fig. 5D).

Mineral Zoning

Five mineral zones are identified on the basis of mineral assemblage in this area (Fig. 6). They are 1) pyrophyllite-dickite. 2) illite, 3) halloysite, 4) silica and 5) albite-chlorite zones.

The pyrophyllite-dickite zone consists mainly of pyropyllite, dickite with small amounts of quartz, illite, and pyrite. The rocks in this zone are characterized by a fine-grained dense matrix with disseminated pyrites. Clay ores show various colors: gray, dark gray, yellow, white, and purple. Clay ores in this zone are highest in quality compared to those in other zones.

The silica zone consists of microcrystalline quarz. It is widely distributed in the study area. It is white to light gray in color.

The illite zone consists of illite, quartz, pyrophyllite, dickite and pyrite. The rocks of this zone are white, light-gray and dark-gray in color, This zone corresponds to the argillic alteration zone.

The halloysite zone consists of halloysite (10Å), quartz, illite and pyrite. The rocks in this zone are fine-grained and are white, gray and pink in color.

The albite-chlorite zone consists of chlorite, feldspar, quartz, illite and pyrite. The zone is developed widely in the outer part of the main ore body and corresponds to the propylitic alteration zone.

According to the chemical analyses of alteration zones, leaching of Si and enrichment of Al took place in the pyrophyllite-dickite zone. K and Na are enriched in the illite zone (Fig. 7).

GENESIS

The Miryang "Napseok" depostit is characterized by widely developed alteration zones: pyrophyllite-dickite, illite, halloysite, silica and albite-chlorite zones which are developed less systematically. With increasing alteration, Si, Ca, Na and K were leached out, whereas Al was enriched as shown in Figure. 7.

Several experiments on thermodynamic stability of pyrophyllite were reported (Brindley and Wardle, 1970; Eberl, 1979; Hass and Holdaway, 1973; Rosenberg, 1974; Rosenberg and Cliff, 1980). Temperatures of hydrothermal alteration can be estimated using mineral assemblages and pyrophyllite polytypes. Kaolinite (dickite)-quartz-pyrophyllite assemblage is stable at 273±10℃, whereas kaolinite (dickite)-pyrophyllite-diaspore is stable at 300±10℃ (Hemley, et al, 1980). Systematic experiments (Eberl. 1979) indicate that monoclinic pyrophyllite was formed at the low temperature (350℃), whereas the triclinic one was formed at above 370℃. Dickite-pyrophyllite-diaspore assemblage and 2M polytype in the Miryang mine suggest that formation temperatures of clay minerals are approximately in the range of 270 to 350℃.

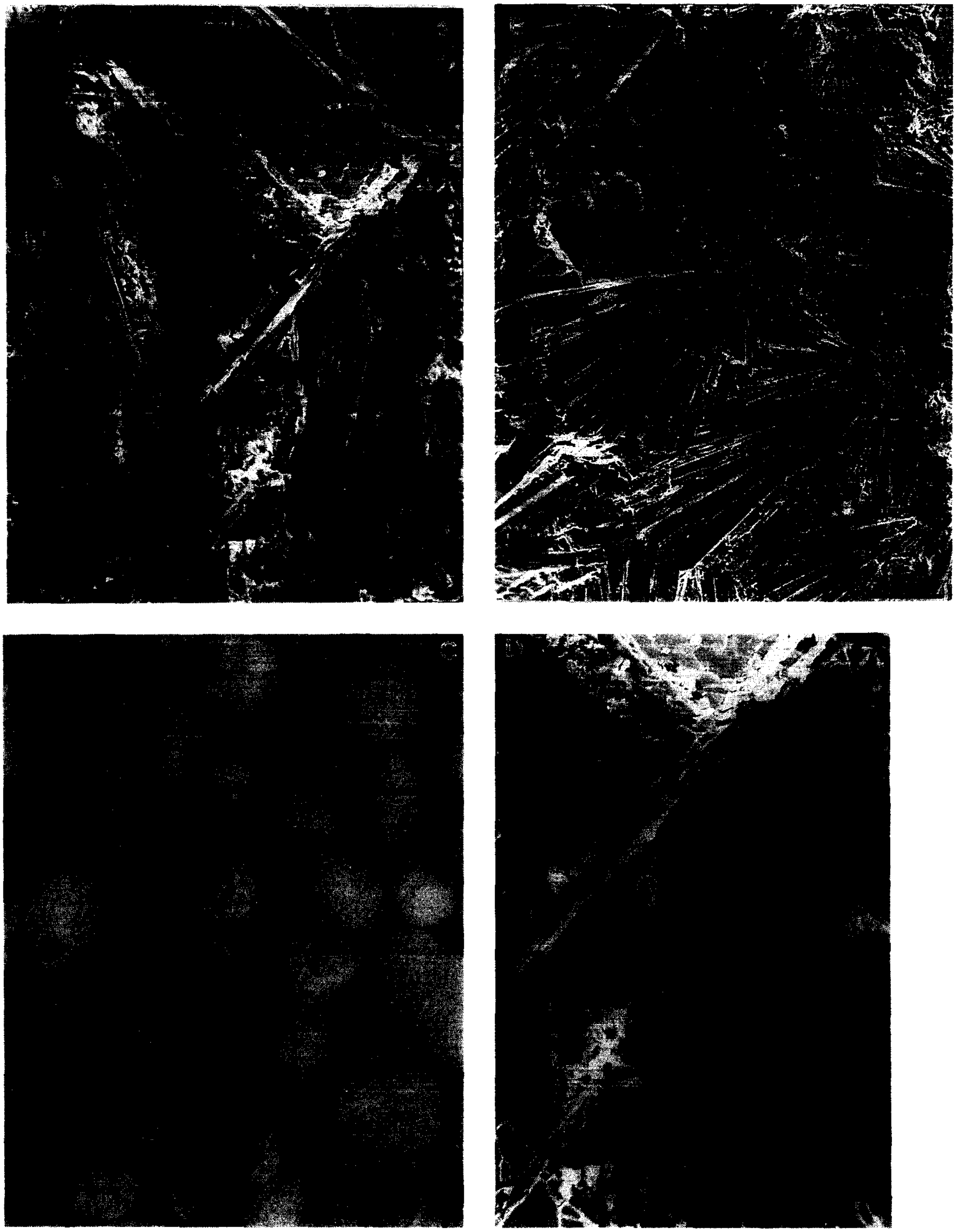

Fig. 5. SEM photographs (A, B, D) and handspecimen (C) of non-clay minerals. (A) Wavellite, (B) dumotierite (C) globular diaspore, and (D) diaspore.

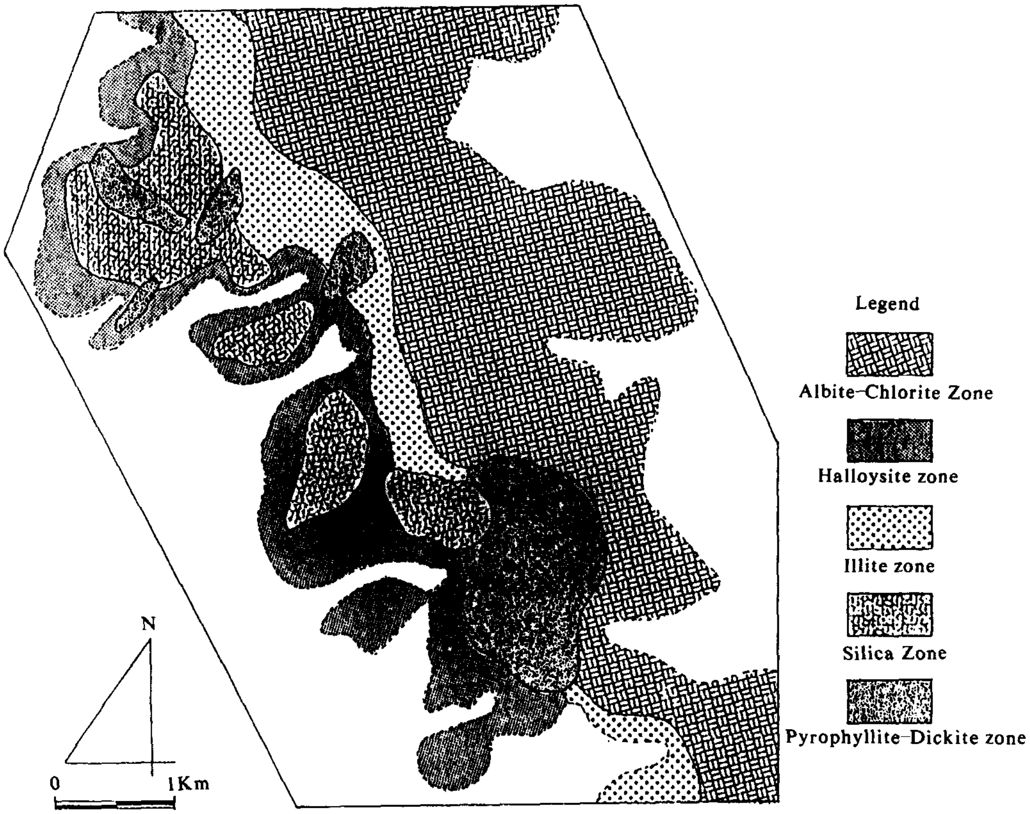

Fig. 6. Mineral zoning in the Miryang mine area.

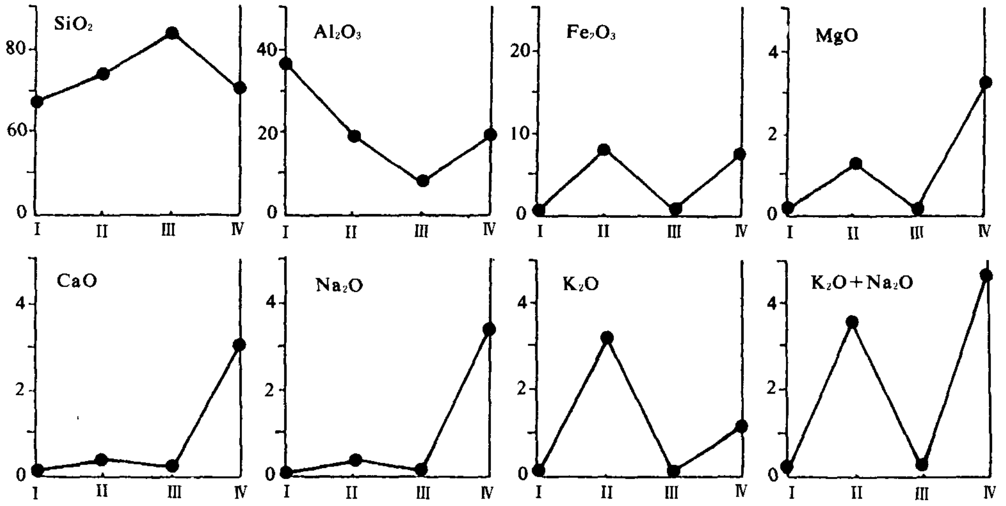

Fig. 7. Chemical compositions of mineral zoning. I. pyrophyllite-dickite zone, II. illite zone, III. silica zone and IV. albite-chlorite zone.

CONCLUSIONS

1. The Napseok (pyrophyllite ores) consist mainly of pyrophyllite, dickite, and quartz, with accessory minerals such as illite, halloysite, tosudite, dumortierite, diaspore, wavellite, and pyrite.
2. Five mineral zones are recognized. They are pyrophyllite-dickite, illite, halloysite, silica, and albite-chlorite zones from the inner to the outer part of the alteration zones.
3. Pyrophyllite occurs as only 2M polytype. Kaolin minerals are identified as dickite, halloysite (10Å) and kaolinite. Tosudite occurs in restricted part in the Miryang mine. Wavellite was precipitated in fissures in the latest stage during the hydrothermal alteration process.
4. Clay minerals were formed by leaching of Si and alkali ions by hydrothermal solutions. Formation temperature of main clay deposit is estimated as 270−350℃.

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