

Mineralogy and Genesis of Hydrothermal Deposits in the Southeastern Part of Korean Peninsula: (5) Deogbong Napseok Deposit

우리나라 동남부 지역의 열수광상에 대한 광물학적 및 광상학적 연구:
(5) 덕봉납석광상

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ABSTRACT : The Deogbong napseok clay deposit which is composed mainly of dickite and pyrophyllite has been formed by hydrothermal alteration of the Late Cretaceous volcanic rocks consisting of andesitic tuff and andesite. The mineralogy of the napseok ores and the hydrothermal alteration processes have been studied in order to know the nature of the interaction between minerals and fluids for the formation of the deposit.

Chemical distribution shows that alkali elements and silica were mobile but alumina was relatively immobile during the hydrothermal processes. It is evident that enrichment of alumina and leaching of silica from the host rock led to the formation of the napseok ore, whereas the enrichment of silica in the outer zone of the deposit gave rise to the silica zone. A large amount of microcrystalline quartz closely associated with dickite and pyrophyllite suggests the increasing activity of silica. Thus Si which was released away from the argillic zone by the increasing silica solubility moved out precipitating in the margin of the deposit to form the silica zone. Variation in dickite crystallinity implies the local change in the stability of the system.

Thermodynamic calculation shows that the invariant point of pyrophyllite-dickite (kaolinite)-diaspore-quartz assemblage at 500 bars in the system Al_2O_3 - SiO_2 - H_2O is about 300 °C. Based on the mineral assemblages and the experimental data reported, it is estimated that the main episode of hydrothermal alteration occurred at least above 270 to 300 °C and $X_{CO_2} < 0.025$. Mineral occurrence and chemical variation indicate that the activity of Al is high in the upper part of the deposit, whereas the activity of Si is high in the lower part and the margin of the deposit.

The nonequilibrium phase relations observed in the Deogbong deposit might be due to local change in intensive thermodynamic variables and fluid transport properties that resulted in the formation of nonequilibrium phases of several stages.

요약 : 김해지역의 덕봉납석광상은 모암이 안산암질용회암과 안산암으로 구성된 백악기 말기의 화산암류가 열수변질작용을 받아서 형성되었으며, 디카이트와 엽납석이 주구성광물이다. 이 연구에서는 산출하는 광물의 특성과 모암의 열수변질작용을 규명하고, 광물과 열수용액 간의 반응관계를 통하여 광상의 성인을 밝히고자 한다.

암석 내의 화학적 특성을 보면 열수변질작용동안 알칼리원소와 실리카는 유동성을 보이거나 알루미늄이나 비교적 유동성이 작다. 모암으로부터 실리카의 용탈과 알루미늄의 부화로 인하여 납석광체가 형성되고, 외곽부로 이동된 실리카의 재침전이 규화대를 생성시켰음을 볼 수 있다. 디

카이트와 엽납석과 밀접히 수반되는 다량의 미정질의 석영은 실리카의 활동도가 증가함에 따라 형성된 것으로 해석된다. Argillic 변질대에서는 열수용액의 실리카의 용해도가 증가하였고, 규화대에서는 온도와 pH가 저하되면서 그 용해도가 저하되었다. Argillic 변질대로부터 빠져나간 Si는 광상의 가장자리에 침전하여 규화대를 형성시켰다. 디카이트가 다양한 범위의 결정도를 보여주는 것은 계내의 부분적인 상안정성의 변화를 시사한다.

이 연구에서 계산된 열역학 값에 따르면, $Al_2O_3-SiO_2-H_2O$ 계에서 엽납석-디카이트 (카오리나이트)-다이아스포아-석영이 500 바에서 공존가능한 온도는 약 300 °C이다. 광물조합과 기존 실험자료를 종합하면 주요 열수변질 시기의 온도는 최소한 270-300 °C이며 X_{CO_2} 는 0.025 미만으로 추정된다. 광물의 산상과 화학적 변화양상에 따르면 Al의 활동도는 광상의 상부에, 그리고 Si의 활동도는 하부와 연변부에서 높음을 보여준다.

덕봉광상에서 흔히 관찰되는 비평형 상관계는 열역학적 변수와 용액운반특성의 국부적인 변화로 인하여 화학적으로 비평형인 상들이 여러 단계에 걸쳐 형성되었음을 지시한다.

INTRODUCTION

The napseok, a commercial name for the soapy clay which is mainly composed of pyrophyllite and/or kaolin minerals, occurs widely in volcanic rocks in the southeastern part of the Korean peninsula. It has been well known that the napseok ore has been formed by hydrothermal alteration of volcanic rocks such as andesite, rhyodacite, or tuffs (Kim et al., 1992; Kim et al., 1993). The mineral assemblages of the napseok ore vary depending mainly on the chemistry of host rocks and hydrothermal fluids, formation conditions (T, P, pH), permeability of the host rocks, and alteration processes.

The Deogbong napseok deposit is located in Saenglim-myeon, Kimhae-gun, Kyungsangnam-do. The deposit lies about 15 km northwest of Kimhae city (Long. $128^{\circ}49'10.4''$ - $128^{\circ}50'10.4''$, Lat. $35^{\circ}18'$ - $35^{\circ}19'$). The deposit is characterized by the mineral assemblage of dickite, pyrophyllite and quartz, with subordinate diaspore, alunite, calcite, and epidote. The deposit is found in the hydrothermal alteration zone of volcanic rocks, as in many other napseok deposits in the southeastern part of Korea. However, so far any mineralogical and genetic study has not been made yet for this deposit. The present study aims to characterize the mineralogy and hydrothermal alteration process of the wall rock, and to study the interaction process between minerals and hydrothermal fluids for the formation of the

napseok deposit.

GEOLOGY AND ORE DEPOSIT

The geology of the area consists of the Cretaceous andesite and andesitic tuff which belong to the Yucheon Group, the upper group of the Kyungsang Supergroup (Fig. 1). Andesite is distributed in the northwestern side of the area. It is usually greenish grey in color and slightly altered by hydrothermal alteration. Andesitic tuff is widely distributed in the central part of study area. It is mainly composed of grey or greenish grey tuff. However, breccias are found in the mid-

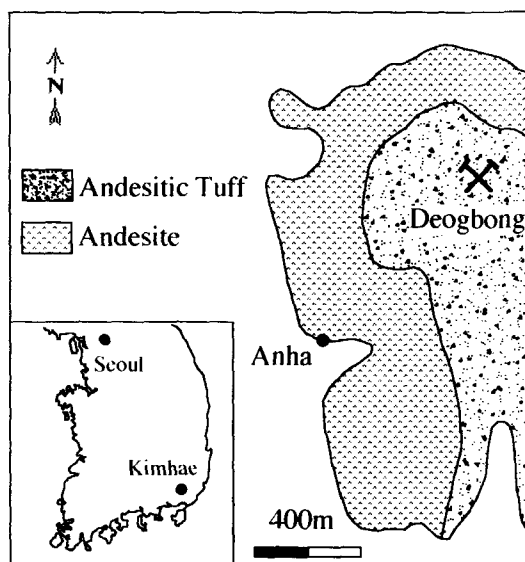


Fig. 1. Geological map of the study area.

dle to lower parts of the andesitic tuff. The fragments in breccia in andesitic tuff are generally 5 to 30 mm in size and angular to subangular in shape. They consist of andesite, andesite porphyry and felsic rock fragments. Lamination is well developed in andesitic tuff which contains quartz and feldspar crystals of 0.5-1 mm in size. The fragments of breccia in the andesitic tuff are generally green color, whereas its matrix shows greyish or whitish grey colors. The weakly altered country rocks exhibit grey or light green colors. It is locally observed that breccia remains fresh compared to fine-grained matrix.

The napeok occurs mainly as a massive body in andesitic tuff. It consists predominantly of dickite with minor pyrophyllite, diaspore, illite, alunite, illite, sulfide minerals and quartz. The color of ores is different from place to place, but grey and white colors are predominant.

EXPERIMENTAL

Field work was carried out to know the occurrence of the ore deposit and its genesis. Samples for laboratory studies were systematically taken from the alteration zones and borehole cores of 100m in depth. Identification and structural characterization of minerals were made using X-ray powder diffractometer (XRD). The chemistry of bulk samples were analyzed using X-ray fluorescence spectrometer (XRF) to know the variations of chemical compositions of alteration zones. Automated X-ray diffractometer, Rigaku model Rad-3C with Cu target and $K\alpha$ radiation was operated at 40 kV/30 mA. Structural analyses of clay minerals were carried out on pure monomineral samples which were prepared by a centrifuge technique after crushing the ore samples in a mortar with deionized water in order to prevent possible structural damage resulting from grinding effect. Grinding may change the diffraction patterns of kaolin minerals through a decrease in crystallinity, which means an increase

in the number of stacking faults. For dickite, intensities of 020, 110, and 111 reflections were used for the study of the defect structures.

Chemical compositions of minerals were analyzed using a JEOL JAX-733 Superprobe electron microprobe fitted with automated wavelength-dispersive spectrometers, at a beam diameter of 5 μm , a beam current of 10 nA and an accelerating voltage of 15 kV, with 20-seconds counts at the Department of Geological Sciences, Seoul National University. Both Na and K were counted first so as to avoid alkali loss.

Quantitative analyses were performed using a ZAF X-ray intensity reduction routine. Optical microscopy and scanning electron microscopy (SEM) were used for the mineral identification and textural study. A Philips SEM model 505 equipped with energy-dispersive spectrometer (EDS) at Korea Institute of Geology, Mining and Materials (KIGAM) was used.

RESULTS

Wall Rock Alteration and Chemical Variation

Vertical and lateral variations in mineralogy are observed in Deogbong napeok deposit, but the variations are somewhat gradational. Based on the mineral assemblages, the Deogbong deposit is subdivided into three alteration zones, that is, the argillic, propylitic, and silica zones.

The argillic zone whose constituent minerals are dickite, diaspore, pyrophyllite, and illite, corresponds to the main ore body. The propylitic zone consists of albite, epidote, and carbonate. The silica zone which consists mainly of quartz is developed in the outer part of the deposit. In this zone, quartz occurs as euhedral to anhedral fine- to coarse-grained aggregates, with some iron oxide minerals filling the fractures or boundaries of quartz grains.

Fig. 2 shows chemical variation in the altered

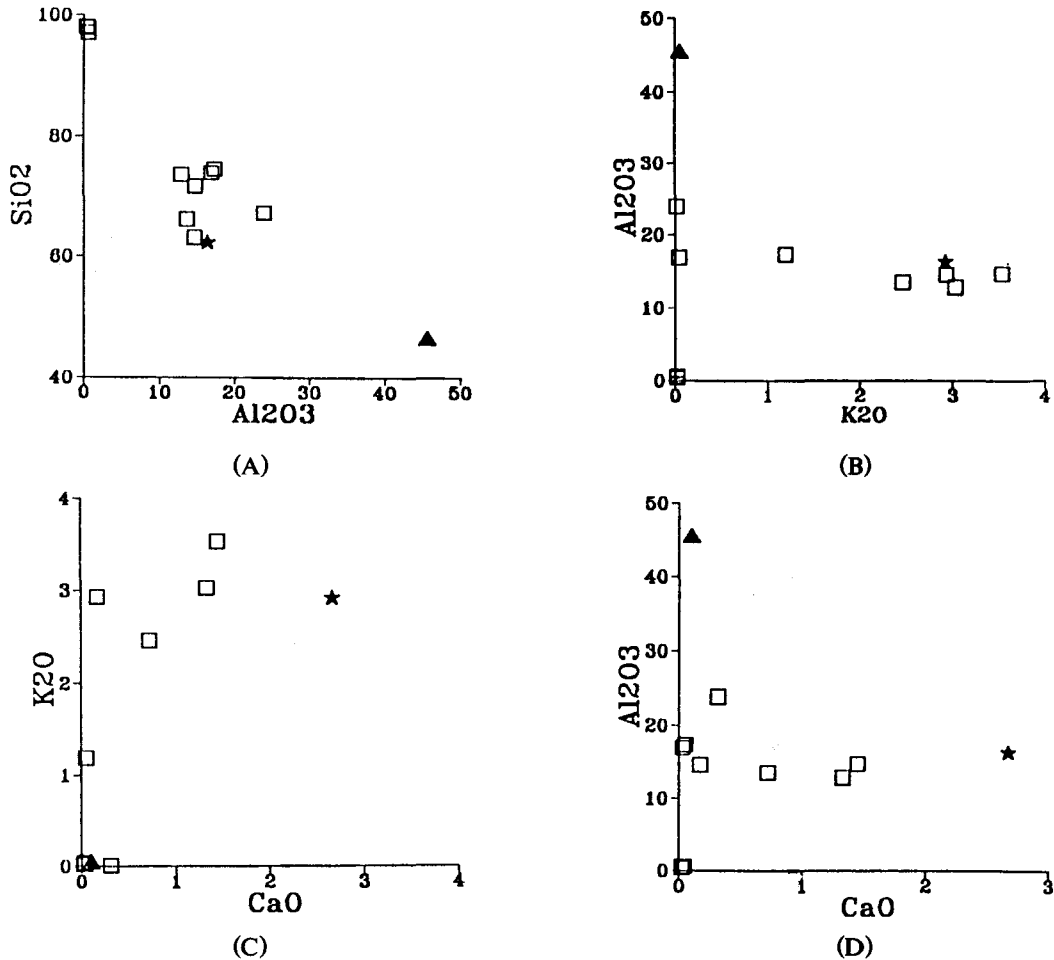


Fig. 2. Chemical variations of altered andesitic tuffs and ore. (A) Plot of SiO₂ to Al₂O₃. (B) Plot of Al₂O₃ to K₂O. (C) Plot of K₂O to CaO. (D) Plot of Al₂O₃ to CaO. Symbols ; triangle = high-quality napseok ore, star = fresh rock, and squares = altered bulk rock samples.

andesitic tuff and ores. Their chemistry vary with the relative abundance of each mineral in the sample. The plot of SiO₂ to Al₂O₃ shows a negative linear relationship (Fig. 2A). It suggests that the separation of SiO₂ and Al₂O₃ is not of gradational but abrupt nature. Abnormally high values of SiO₂ are recorded in samples from the silica zone. Enrichment of Al₂O₃ and depletion of SiO₂ are encountered in the high grade napseok which is composed chiefly of dickite and quartz. SiO₂ is most enriched in the silica zone. The content of Al₂O₃ is nearly constant, regardless of the content

of K₂O except in the napseok ore. The plot of K₂O to CaO displays a positive relationship, suggesting the distinct leaching of CaO and K₂O out of the fresh rock. The plot of Al₂O₃ to CaO shows a distinct negative relationship. The argillic zone zone is characterized by enrichment of Al₂O₃, whereas the silica zone by high enrichment of SiO₂. Na₂O is recorded only in the fresh rock (not presented here). It is clear that enrichment of alumina and leaching of silica from the host rock led to the formation of the napseok ore and the enrichment of silica gave rise to the silica zone.

Chemical comparison of alteration zones shows that alkali elements such as K, Ca and silica were mobile but alumina was relatively immobile during the hydrothermal process.

Occurrences of Minerals

Dickite, the most ubiquitous mineral in the deposit, is closely associated with diaspore and quartz, and enriched in the upper part of the deposit. Dickite occurs not only as well-crystallized grains of a platy habit, but also as poorly crystallized grains (Fig. 3A). It is very interesting that well-crystallized dickite grows between quartz phenocrysts, with a consistent habit (Fig. 3B). The crystal sizes of dickite vary from less than 1 μm to 0.5 mm depending on crystallinity. In some cases dickite shows well-crystallized hexagonal shape and stacking structure. In rare cases, dickite is closely associated with pyrite (Fig. 4A, B, C). Dickite grows in fractures of pyrite crystals. It is generally observed that dickite grows from diaspore (Fig. 5A).

Pyrophyllite is less abundant than dickite. It, however, is enriched in the middle part of the deposit. Illite occurs near the lower part of the deposit. It is associated with dickite, pyrite, calcite and quartz. It is subordinate to dickite and py-

rophyllite. Diaspore occurs as large single grains or aggregates. It is replaced by dickite along its margin or cracks (Fig. 5).

Quartz occurs frequently in association with dickite. Primary quartz shows corroded texture (Fig. 6A). Fine-grained quartz is commonly sub-micron-sized and equigranular, making up the matrix or replacing dickite (Fig. 5B and Fig. 6B). It is an interesting subject whether quartz was formed by direct precipitation from fluids that was supersaturated with respect to silica, or by dissolution of precursor minerals such as dickite and glass materials. Its origin should be differentiated based on the mineral paragenesis.

Calcite occurs in tuff breccias as veinlets or replacement of quartz, pyrite, feldspar or glassy matrix. It is microcrystalline to coarse-grained. Epidote is characterized by aggregates of fine-grained acicular or lath crystals within carbonate cement. It certainly replaces calcite cement. Trace alunite occurs in the upper part of the deposit, always in association with dickite. Pyrite occurs as aggregates and dissemination in the matrix throughout the deposit. It shows generally euhedral forms. Pyrite is closely associated with dickite, pyrophyllite, calcite and quartz. Hematite occurs as veinlets in association with pyrite or quartz.

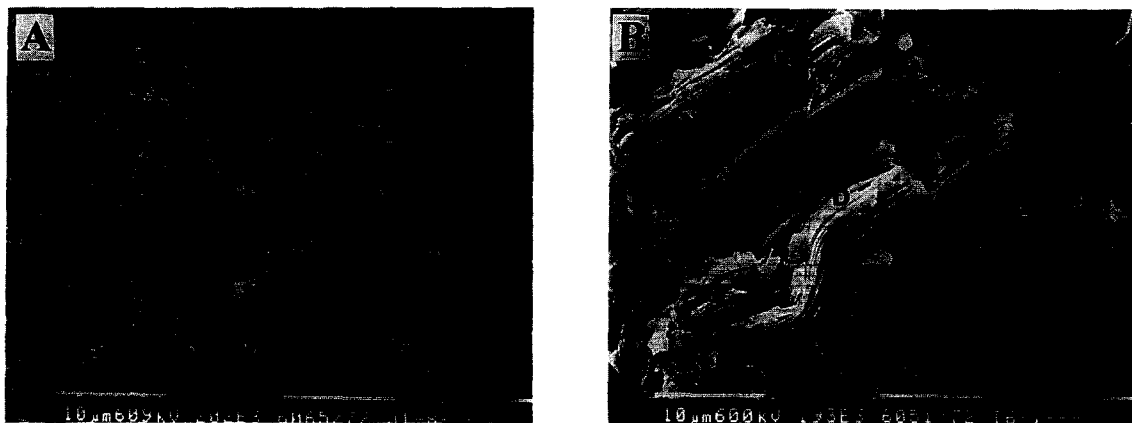


Fig. 3. Scanning electron micrographs of the Deogbong napseok. (A) Poorly crystallized dickite (sample No. J1-8). (B) Stacking of dickite flakes associated with quartz (sample No. T6-1). D=dickite, Q=quartz. Scale is 10 μm .

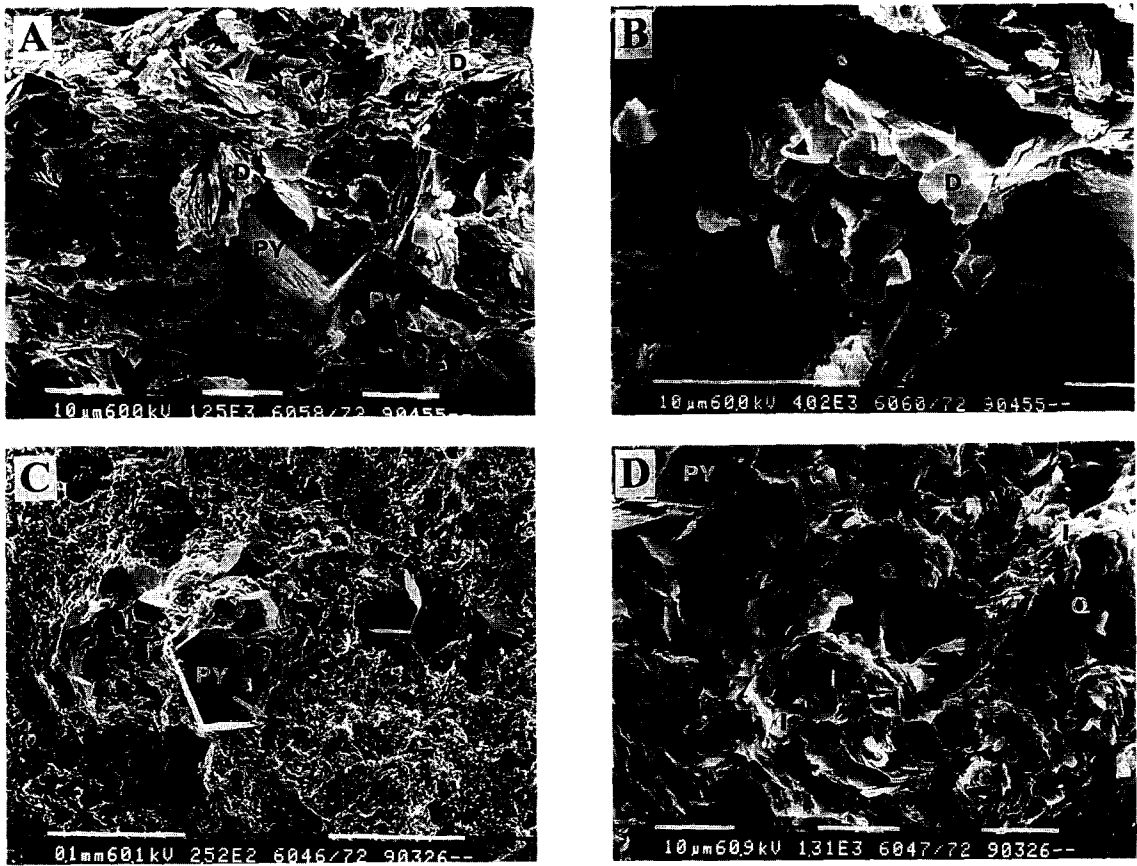


Fig. 4. Scanning electron micrographs of the Deogbong napseok and sulfides. (A) Dickite flakes associated with pyrite (sample No. 90455). (B) High magnification of the area shown by an arrow in (A) (bottom right). (C) Aggregate of euhedral pyrite, illite, and quartz (sample No. 90326). (D) High magnification of the area shown by an arrow in (C) (central part). D=dickite, I=illite, PY=pyrite, Q=quartz. Scale bars are 10 μm in (A), (B), and (D) and 0.1 mm in (C).

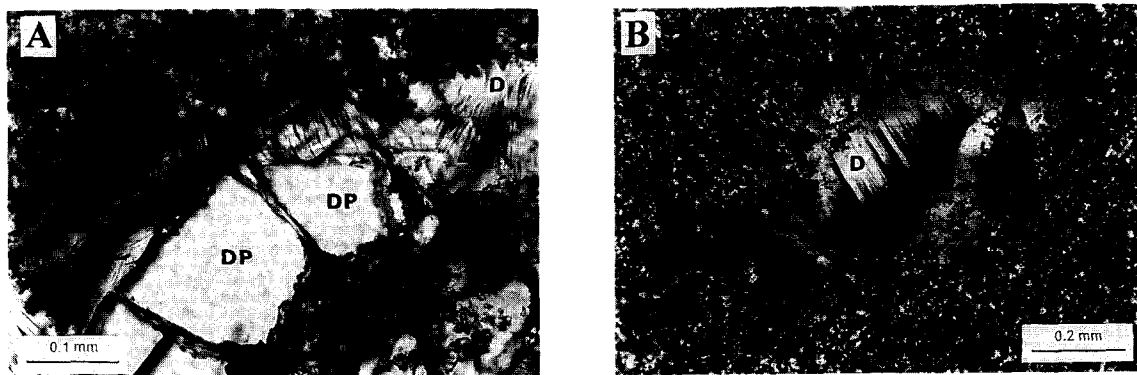


Fig. 5. Microphotographs showing dissolution textures in dickite and diaspore. (A) Diaspore has been dissolved along its margin and fractures (sample No. T8-4). (B) Microcrystalline quartz in the margin of well-crystallized dickite (sample No. TK5). D=dickite and DP=diaspore.

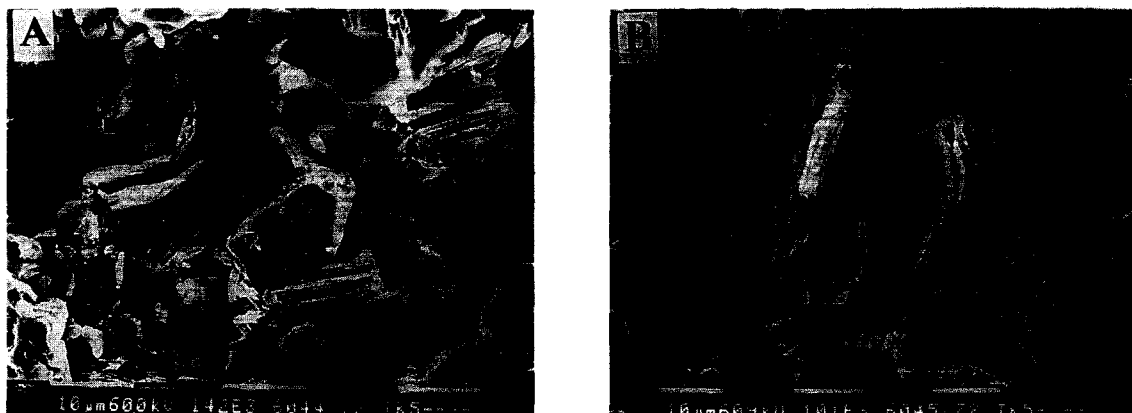


Fig. 6. Scanning electron micrographs of dickite (sample No. TK5). (A) Dickite stacks in association with quartz. (B) Microcrystalline quartz around well-crystallized dickite book. D=dickite and Q=quartz. Scale bars are 10 μm .

Table 1. Chemical analyses of dickite from the Deogbong deposit.

Sample No.	90570	90445	90559	9554	T6-1	T8-4	T2	TK3	TK5
SiO ₂	45.711	45.701	44.778	44.650	45.132	44.177	45.379	42.374	43.604
Al ₂ O ₃	36.529	39.401	38.921	36.644	38.967	38.928	38.827	38.438	38.761
TiO ₂	0.001	0.005	0.006	0.034	0.006	0.011	0.004	0.006	0.008
Cr ₂ O ₃	0.006	0.006	0.008	0.019	0.001	0.023	0.000	0.027	0.013
FeO*	0.037	0.013	0.025	0.033	0.001	0.009	0.014	0.004	0.012
MgO	0.015	0.002	0.007	0.006	0.000	0.002	0.000	0.005	0.006
MnO	0.001	0.004	0.002	0.006	0.006	0.003	0.000	0.017	0.020
CaO	0.008	0.021	0.000	0.000	0.019	0.003	0.012	0.000	0.001
Na ₂ O	0.005	0.000	0.000	0.034	0.002	0.004	0.004	0.008	0.015
K ₂ O	0.006	0.001	0.003	0.000	0.010	0.002	0.001	0.005	0.001
Total	82.317	85.152	83.749	81.425	84.145	83.162	84.240	80.883	82.441
Based on 14 Oxygens									
Si	4.100	3.971	3.957	4.053	3.969	3.933	3.985	3.883	3.918
Al	0.000	0.029	0.043	0.000	0.031	0.067	0.015	0.117	0.082
Sum(T)	4.100	4.000	4.000	4.053	4.000	4.000	4.000	4.000	4.000
Al	3.862	4.006	4.011	3.920	4.008	4.018	4.003	4.034	4.023
Ti	0.000	0.000	0.000	0.002	0.000	0.001	0.000	0.000	0.001
Cr	0.000	0.000	0.001	0.001	0.000	0.002	0.000	0.002	0.001
Fe ²⁺	0.003	0.001	0.002	0.003	0.000	0.001	0.001	0.000	0.001
Mg	0.002	0.000	0.001	0.001	0.000	0.000	0.000	0.001	0.001
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Sum(O)	3.867	4.009	4.015	3.928	4.009	4.022	4.004	4.039	4.027
Ca	0.001	0.002	0.000	0.000	0.002	0.000	0.001	0.000	0.000
Na	0.001	0.000	0.000	0.006	0.000	0.001	0.001	0.001	0.003
K	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.000
Sum(I)	0.002	0.002	0.000	0.006	0.003	0.001	0.002	0.002	0.003

* Total Fe as ferrous

Table 2. Chemical analyses of pyrophyllite from the Deogbong deposit.

Sample No.	90554	90570	90445	TK4
SiO ₂	63.710	63.792	65.192	62.864
Al ₂ O ₃	28.816	28.058	29.191	29.792
TiO ₂	0.016	0.009	0.076	0.020
Cr ₂ O ₃	0.000	0.000	0.011	0.014
FeO*	0.028	0.048	0.034	0.071
MgO	0.027	0.020	0.001	0.011
MnO	0.018	0.009	0.005	0.023
CaO	0.000	0.025	0.032	0.003
Na ₂ O	0.111	0.095	0.184	0.120
K ₂ O	0.011	0.019	0.028	0.004
Total	92.736	92.073	94.679	92.919
Based on 22 Oxygens				
Si	7.849	7.911	7.864	7.741
Al	0.151	0.089	0.136	0.259
Sum(T)	8.000	8.000	8.000	8.000
Al	4.033	4.011	4.014	4.065
Ti	0.001	0.001	0.007	0.002
Cr	0.000	0.000	0.001	0.001
Fe ²⁺	0.003	0.005	0.003	0.007
Mg	0.005	0.004	0.000	0.002
Mn	0.002	0.001	0.000	0.002
Sum(O)	4.044	4.022	4.026	4.080
Ca	0.000	0.003	0.004	0.000
Na	0.026	0.023	0.043	0.029
K	0.002	0.003	0.004	0.001
Sum(I)	0.028	0.029	0.052	0.030

* Total Fe as ferrous

Crystal Chemistry of Minerals

Dickite. Dickite occurs in association with diaspore, pyrophyllite, and quartz. It shows a book structure in which the stacks of well-crystallized crystals are developed. The Hinckley index of Deogbong dickite measured varies from 0.56 to 1.2, indicating a wide variation in crystallinity. Plançon et al. (1988) reported that in most kaolin minerals the Hinckley index varies between 0.2 and 1.5. The kaolinite in the Georgia sample falls in HC=4 in all size fractions above 8–5 μm (Lombardi et al., 1987). Ruiz Cruz and Moreno Real (1993) described that the Hinckley index varies depending on particle sizes and that

for the size 2–20 μm it is 0.56–2.71, whereas for the size below 2 μm it ranges 0.28–0.62.

Table 1 represents chemical analyses of dickite. The content of Si varies from 3.88 to 4.10, whereas octahedral Al shows a variation ranging from 3.86 to 4.03. The content of FeO is negligible ranging from 0.001 to 0.037 wt.%. High Fe content is correlated with low degree of order (Brindley et al., 1986). Dickite composition shows little cation substitutions in the structure, corresponding to its stoichiometry.

Pyrophyllite. Pyrophyllite is a subordinate constituent mineral in the napseok. Its structure corresponds to 2M type. It is a low temperature form relative to 1Tc polytype (Eberl, 1979). As given in Table 2, cation substitution is scarcely observed in tetrahedral and octahedral sites. Based on 22 oxygens, Si ranges from 7.741 to 7.911, while octahedral Al varies from 4.011 to 4.065. The content of total cations in octahedral sites ranges from 4.022 to 4.080 showing slight excess of cations in the sites.

Illite. Illite occurs in the lower part of the deposit. The crystallinity of illite is low giving the Kubler index of 0.85. Based on 22 oxygens, the Si content is 6.677 and the tetrahedral Al is 1.323. The octahedral Al is 3.863. Fe is 0.043 and Mg content is 0.125. K content in the interlayer is 1.301. The cation content in the interlayer is very low. Despite its low crystallinity and low cation content in the interlayer, illite does not exhibit mixed layering such as illite/smectite. It implies that illite might grow directly by precipitation from fluids, not by transformation of precursor minerals such as illite/smectite that is a possible phase in most cases.

Diaspore. Diaspore is an aluminum oxide mineral found in the argillic zone, with a close association with dickite. The content of Al₂O₃ ranges from 82.07 to 84.42 wt.%.

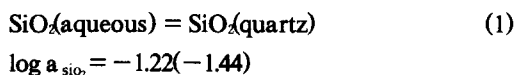
Epidote. In epidote the content of SiO_2 ranges 33.118 to 34.152 wt.%, and the Al_2O_3 content varies from 22.922 to 23.158 wt.%, and the content of Fe_2O_3 ranges 8.257 to 8.951 wt.% and the CaO content ranges 21.134 to 21.250 wt.%. $\text{Fe}/(\text{Fe}+\text{Al})$ averages 0.185 to 0.203. Epidote is depleted in SiO_2 and Al_2O_3 contents.

Carbonates. In carbonates CaCO_3 predominates over other components in the solid solution. The mol % of CaCO_3 averages 96.095 with a standard deviation of 2.403 % and the mol % of MnCO_3 averages 2.865 with a standard deviation of 1.943 %. The mol % of FeCO_3 averages 0.59 and the mol % of MgCO_3 averages 0.45.

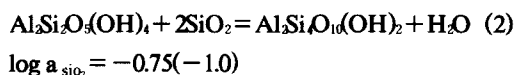
Phase Equilibrium in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ System

Phase stability of each mineral actually observed can be predicted by calculating phase equilibrium based on mineral assemblages actually observed. It is assumed that temperature and pressure are 250 °C and 300 °C at 500 bar because most hydrothermal systems do not exceed these conditions (Fournier, 1986). Using thermodynamic data of SUPCRT92 (Johnson et. al., 1992), equilibrium constants at 250 °C and 300 °C are calculated. The values in parenthesis that follows refer to the equilibrium constants at 250 °C.

For the reaction between aqueous silica and quartz,



For the reaction between dickite and pyrophyllite,

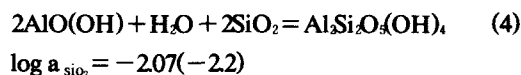


For the reaction between diasporite and pyrophyllite,

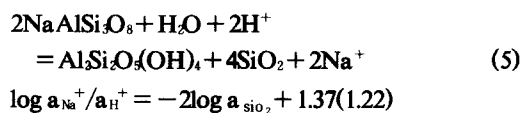


$$\log a_{\text{SiO}_2} = -1.405(-1.603)$$

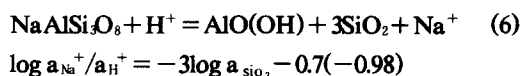
For the reaction between diasporite and dickite.



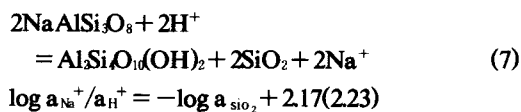
For the reaction between albite and dickite.



For the reaction between albite and diasporite,



For the reaction between albite and pyrophyllite,



Phase stability diagrams constructed are shown in Fig. 7. Equilibrium temperature can be estimated using TWEEQ program (Berman, 1991). The temperature at which kaolinite, diasporite, pyrophyllite, and quartz are in an equilibrium state under 500 bars is about 297 °C whereas under 300 bars the temperature is 295 °C so that contribution of changes in pressure to mineral stability coexisting with quartz is negligible in the pressure conditions assumed above. In the reaction (4) that is observed in Fig. 5A, dickite is stable with respect to diasporite with increasing the activity of α -quartz and with increasing temperature. Since the difference of the free energy between dickite and kaolinite is negligible though thermodynamic data in TWEEQ do not include dickite, the calculation for the equilibrium state represents a very good result in understanding the phase stability of minerals. Phase diagram with respect to α -quartz at 500 bars shows an invariant point of about 297 °C where dickite (kaolinite), pyrophyllite, diasporite and quartz are in

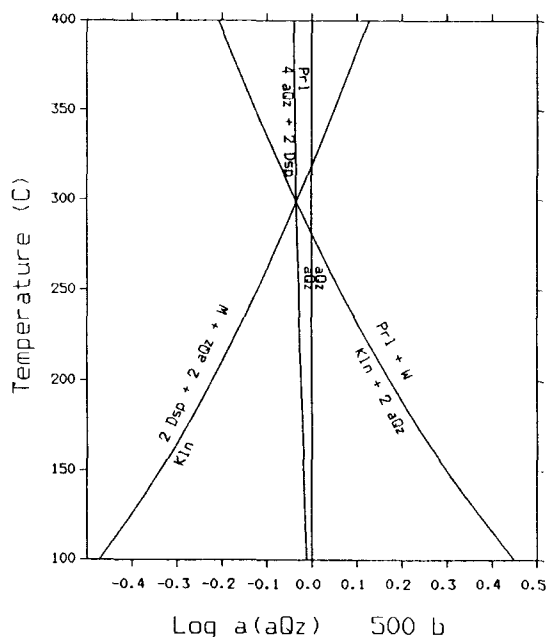


Fig. 7. α -quartz activity-temperature phase diagram at a constant pressure of 500 bars. It shows an invariant point at about 297 °C where dickite (kaolinite), pyrophyllite, diaspore and quartz are in equilibrium. The temperature for the reaction of diaspore and quartz to form dickite increases as the activity of quartz increases. Temperature for the reaction of dickite and quartz to form pyrophyllite decreases as the activity of quartz increase.

equilibrium (Fig. 8). The temperature for the reaction of diaspore with quartz to form dickite increases as the activity of quartz increases. Temperature for the reaction of dickite and quartz to form pyrophyllite decreases as the activity of quartz increases. The stability field of dickite is slightly widen from 250 to 300 °C, whereas that of pyrophyllite is narrow at the same conditions. Dickite and quartz coexist between $\log a_{\text{SiO}_2(\text{aq})} = -1.45$ to -1.0 at 250 °C and 500 bars, whereas they coexist between $\log a_{\text{SiO}_2(\text{aq})} = -1.25$ to -0.75 at the same conditions. Pyrophyllite cannot coexist with quartz, while diaspore cannot coexist with pyrophyllite, which is well consistent with mineral assemblage observed. An invariant point where dic-

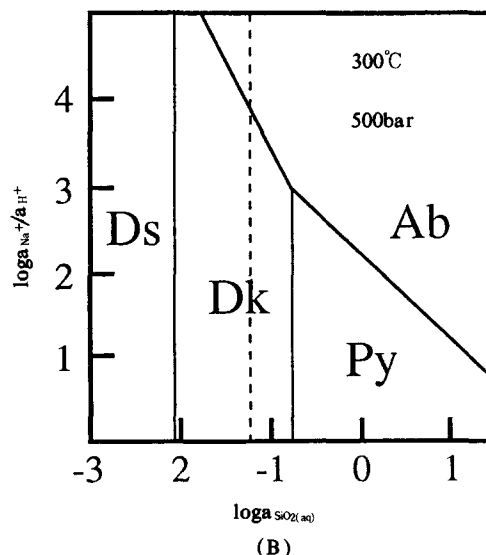
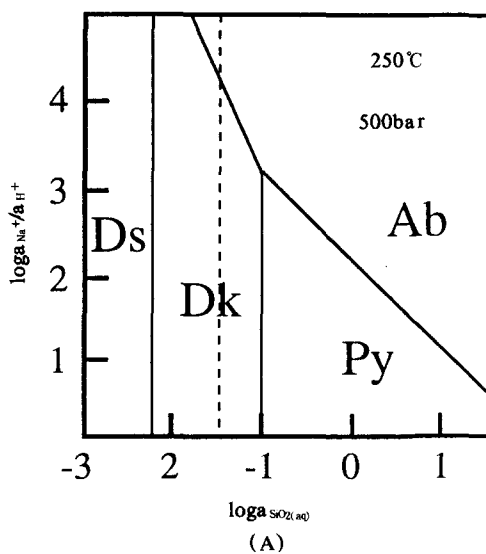


Fig. 8. Logarithmic activity-activity diagram constructed at 500 bars. (A) At 250 °C. (B) At 300 °C. The dashed line denotes a line of saturation of quartz. With increasing silica activity pyrophyllite becomes stable with respect to dickite. Ab=albite, Ds=diaspore, Dk=dickite, and Py=pyrophyllite.

kite, pyrophyllite and albite coexist lowers with decreasing the activity of Na and increasing the activity of silica, as temperature increases. Ac-

According to thermodynamical calculation for assemblages including epidote, plagioclase and calcite, it is estimated that the X_{CO_2} in fluids is very low to be less than 0.025.

DISCUSSIONS

Chemical Mobility of Elements

Chemical mobility of elements is mainly dependent of the ionic potential of elements. The activity of dissolved species is controlled by the solubility of the minerals which is concerned with the mineral decomposition. Many workers show that the decomposition processes of minerals proceed through the dissolution or hydrolysis. Dissolution of most minerals involves incongruent processes in which the reaction consists essentially of a ligand exchange reaction (Stumm and Morgan, 1970). Mineral hydrolysis occurs through surface composition of protons or ligands from solution and destruction of framework bonds in aluminosilicates occurs through decomposition of these surface complexes (Blum and Lasaga, 1988; Carroll-Webb and Walther, 1988; Oxburgh et al., 1994). The rates of hydrolysis show a strong dependence on pH and temperature (Hellmann, R. 1994). But the chemical mobility of elements at high temperature is less known due to experimental constraints.

The potassium content is variable depending on bulk rocks. The plot of K_2O to CaO displays a distinct leaching of CaO and K_2O out of the fresh rock. The relation of Al_2O_3 and CaO shows a decrease in the CaO content from the fresh rock to ores. Alumina might be preserved in the average napseok with a constant content. However, the extreme enrichment of alumina results in the formation of napseok of high quality, whereas leaching of it develops a silica zone. Chemical variation in whole rocks shows that alkali elements and silica were mobile but alumina was relatively immobile during the hydrothermal process.

It is clear that enrichment of alumina and leaching of silica from the host rock led to the formation of the napseok ore and that enrichment of silica gave rise to the silica zone. Aluminum is relatively immobile relative to silica. Al solubility is higher in low pH (acidic) than Si, so that Al leaching may occur. The fact that dickite is more stable than diaspore indicates that silica activity increases with increasing alteration processes. Increasing activity of silica results in the production of a large amount of microcrystalline quartz closely associated with dickite and pyrophyllite. It is observed that dickite forms with breakdown of diaspore, indicating that the activity of silica increases with decreasing activity of aluminum. A wide variation in dickite crystallinity implies changes in the stabilities of local phases in the system.

Silica content in alteration zones is controlled by the solubility of quartz. Vigorous acid attack on silicate rocks tends to derive silica rapidly and metastably into solution to the values of quartz saturation. High concentrations of aqueous silica do not readily crystallize to quartz at low temperatures, especially in acid solutions (Hemely et al., 1980). The solubility and dissolution rate of quartz are regarded very important in the silica-water reaction under the hydrothermal alteration processes and have been studied in detail (Walther and Helgeson, 1977; Rimstidt and Barnes, 1980; Fournier and Potter, 1982; Knauss and Wolery, 1988). High pH favors increased dissociation of silica so that amounts of dissolved silica in solution increase. Leaching of quartz suggests that increasing in the solubility of silica in fluids took place in the argillic zone and the decreasing in the solubility proceeded in the silica zone with decreasing temperatures and pH. It is generally accepted that the solubility of Si is low and constant in acidic to neutral conditions, so that preferential precipitation of Si may occur under these conditions. Because of lowering in pH caused by sulfide decomposition in the deposit, it is inter-

puted that Si released away from argillic zone moved out precipitating in its margin to form the silica zone under acidic condition. Faceted quartz crystals generally grow in solutions that are not greatly supersaturated with silica, indicating changing conditions (Fournier, 1986).

The solubility of quartz controls dissolved silica in all geothermal reservoir waters at temperatures greater than 180 °C. In active hydrothermal systems, little silica appears to precipitate underground where water rises relatively quickly from reservoirs where temperature are less than 230–250 °C (Fournier, 1986). Microcrystalline quartz is in association with the formation of dickite and the breakdown of diaspore, suggesting that the activity of silica increases with decreasing activity of aluminum.

It is also supported by experimental results of Walther and Helgeson (1977) in which diaspore is decomposed with increasing activity of silica to form pyrophyllite at least above about 140 to 320 °C at 1 kb, with quartz saturation. Replacement by silica will occur if the solution is becoming undersaturated with respect to Al, and deposition of silica from a supersaturated state is taking place.

Deogbong epidote is characterized by aggregates of fine-grained acicular crystals within carbonate cement. The earlier formed carbonate cement is gradually replaced by epidote. The mole% of pistacite in epidote ranges from 18.5 to 20.3. Epidote compositions from most geothermal systems show no obvious correlation of pistacite content with depth or temperature (Bird et al., 1984). In the Cerro Prieto geothermal field, epidote occurs as veins and interstitial cement at temperature above 230 °C (Bird, et al., 1984). Since epidote occurs with calcite in the later stage of the weakly altered zone, it is likely that formation temperature of epidote was relatively low.

Fe-oxide that consists mainly of hematite is also commonly associated with pyrite in the deposit. It is likely that a decrease in pressure or temperature in the system results in supersa-

turation of sulfides in the solution and sulfide precipitation occurs. It is clear that the precipitation of sulfides from metal complexes takes place as a result of the change in pH and S^{2-} activity. Thereafter FeS_2 is dissolved and oxidized under hydrothermal alteration.

Properties of Hydrothermal Fluids

The association of microcrystalline quartz with pyrophyllite and dickite indicates that SiO_2 concentration of hydrothermal fluids was high enough to precipitate quartz though some subangular quartz with corroded texture are locally observed only in the propylitic zone. Because of low pH caused by sulfide decomposition, preferential precipitation of Si occurred. There is no other certain systematic correlation between observed compositional trends of calc-silicates and either depth or temperature in most geothermal systems (Bird, et al., 1984). Calcite occurs as replacements of plagioclase and quartz, or the veinlet. In the latter case, it commonly displays a dissolution texture indicative of fluctuations in fluid composition. According to thermodynamical calculation for assemblages of epidote, plagioclase and calcite, it is estimated that the X_{CO_2} in fluids is very low enough to be less than 0.025. It is nearly constant with respect to the temperature under the hydrothermal condition.

Temperature and pH Effects

It is well known that ore deposits which consist of pyrophyllite, dickite, diaspore and alunite-bearing assemblage are originated by acid leaching of the andesitic host rocks. Intense acid alteration is common in the relatively shallow hydrothermal alteration processes operating in volcanic systems because under these conditions the ionization and oxidation of magmatically derived acidic components have reached a maximum (Hemley et al., 1980). Acidity presumably

results from oxidation of H₂S, partly from oxidation of sulfides in the rock. Silicification accompanying acid attack is due to strong leaching of alkalis. If initial temperature is between 200–340 °C, slow cooling of a hydro-thermal solution causes precipitation of quartz (Fournier, 1986). On the other hand, at temperature below 180 °C slight silica supersaturation with respect to quartz results in precipitation of chalcedony directly from solution (Fournier, 1986).

The pH decreases from argillic zone to silica zone with increasing degree of hydrothermal alteration. The lowering of pH is associated with decomposition of sulfides, thus forming alunite and diaspore in the argillic zone. In argillic zone where pH is high, silica is dissolved, but it recrystallized under the low pH in the silica zone.

Silica saturation can be predicted from the data of mineral association and the phase equilibrium calculation. When the dissolved SiO₂ concentration of hydrothermal fluids is buffered by quartz solubility, kaolinite forms at lower temperatures with respect to pyrophyllite (Hemley et al., 1980).

Hemley et al. (1980) reported from experiments performed under the system Al₂O₃-SiO₂-H₂O at 1 kb that stability relationships of kaolinite-pyrophyllite-diaspore assemblage and kaolinite-pyrophyllite-quartz assemblage are 300 ± 10 °C and 273 ± 10 °C, respectively and the upper stability limit of pyrophyllite relative to andalusite plus quartz is 366 ± 10 °C. Pyrophyllite polytype is a lower temperature 2M form. Eberl (1979) synthesized pyrophyllite 2M at 355 °C at 2 kb H₂O. If diaspore is in equilibrium with pyrophyllite, it forms between 270 to 360 °C according to the thermodynamic study by Knight (1977). But diaspore and pyrophyllite do not coexist in Deogbong napseok. According to experiments by Walther and Helgeson (1977), maximum temperature at which diaspore decomposes into pyrophyllite is 320 °C at 1 kb. At 350–355 °C and 15000 psi. muscovite decomposes to pyrophyllite and diaspore

instead of dickite because of the instability of dickite above this temperature (Hemley, 1959). It is reasonable to accept 270 °C as the lower limit of formation temperature of mineral assemblages containing diaspore.

According to thermodynamic calculation for the present study, the invariant point of pyrophyllite-dickite(kaolinite)-diaspore-quartz assemblage at 500 bars in the system Al₂O₃-SiO₂-H₂O is about 300 °C. Based on the mineral assemblages and the experimental data reported in the literature, it is estimated that the main episode of hydrothermal alteration occurred at least above 270 to 300 °C and X_{CO₂} < 0.025.

Mineral occurrences and chemical variations indicate that the activity of Al is high in the upper part of the deposit, whereas the activity of Si is high in the lower part and the margin of the deposit.

The fact that the Deogbong dickite shows various crystallinity and size suggests the extensive change in the formation condition. Lombardi et al. (1987) reported that the complex assemblages of the size fractions of the Sasso hydrothermal kaolin appear to be the product of a multiphase hydrothermal process ranging over a broad spectrum of temperatures and fluid chemistries. They also found that the well-crystallized dominant dickite is the result of the main stage of hydrothermal alteration of the host rock. Chemical compositions of bulk rocks and fluids are important factors controlling the observed compositional characters of minerals. The nonequilibrium phase relations in the assemblage of sulfide and dickite of the Deogbong deposit might be due to local change in intensive thermodynamic variables and fluid transport properties that resulted in the nonequilibrium phases of several stages.

CONCLUSIONS

Chemical study of the alteration zones in the Deogbong napseok deposit shows that alkali ele-

ments and silica were mobile but alumina was relatively immobile during the hydrothermal process. It is evident that the enrichment of alumina and the leaching of silica from the host rock led to the formation of the napseok ore and that the enrichment of silica to the outer zone of the deposit gave rise to the silica zone. Increasing activity of silica resulted in the production of a large amount of microcrystalline quartz closely associated with dickite and pyrophyllite. Wide variation in dickite crystallinity implies changes in the stabilities of local phases in the system.

The increasing silica solubility of fluids took place in the argillic zone and the decreasing silica resulted in the silica zone in the outermost part of the deposit. Si released from the argillic zone moved out and to in the margin of the deposit to form the silica zone.

According to thermodynamic calculation for the present study, the invariant point of pyrophyllite-dickite (kaolinite)-diaspore-quartz assemblage at 500 bars in the system Al_2O_3 - SiO_2 - H_2O is about 300 °C. Based on the mineral assemblages and the experimental data reported, it is estimated that the main episode of hydrothermal alteration occurred at least above 270 to 300 °C and $X_{CO_2} < 0.025$. Mineral occurrence and chemical variation reveal that the activity of Al is high in the upper part of the deposit, whereas the activity of Si is high in the lower part and the margin of the deposit.

The nonequilibrium phase relations observed in the Deogbong deposit might be due to local change in intensive thermodynamic variables and fluid transport properties that resulted in the formation of non-equilibrium phases of several stages.

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