

Hydrothermal Alteration Related to Cretaceous Felsic Magmatism in the Seongsan Dickite Deposits, Korea; Estimation of Ore-Forming Temperature and $a_{\text{Na}^+}/a_{\text{K}^+}$ Ratio of the Hydrothermal Fluid

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ABSTRACT: The Seongsan mine is one of the largest dickite deposits in the southwestern part of the Korean Peninsula. The main constituent minerals of the ore are dickite and quartz with accessory alunite, kaolinite and sericite. The geology around the Seongsan mine consists mainly of the late Cretaceous felsic volcanic rocks. In the studied area, these rocks make a synclinal structure with an axis of E-W direction plunging to the east.

Most of the felsic volcanic rocks have undergone extensive hydrothermal alteration. The hydrothermally altered rocks can be classified into the following zones: Dickite, Dickite-Quartz, Quartz, Sericite, Albite and Chlorite zones, from the center to the margin of the alteration mass. Such zonal arrangement of altered rocks suggests that the country rocks, most of which are upper part of the rhyolite and welded tuff, were altered by strongly acid hydrothermal solutions. It is reasonable to consider that initial gas and solution containing H_2S and other compounds were oxidized near the surface, and formed hydrothermal sulfuric acid solutions.

The mineralogical and chemical changes of the altered rocks were investigated using various methods, and chemical composition of fifty-six samples of the altered rocks were obtained by wet chemical analysis and X.R.F. methods. On the basis of these analyses, it was found that some components such as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , K_2O , Na_2O and TiO_2 were mobilized considerably from the original rocks.

The formation temperature of the deposits was estimated as higher than 200°C from fluid inclusion study of samples taken from the Quartz zone. On the basis of the chemical composition data on rocks and minerals and estimated temperatures, the hydrothermal solutions responsible for the formation of the Seongsan dickite deposits were estimated to have the composition: $m_{\text{K}^+}=0.003$, $m_{\text{Na}^+}=0.097$, $m_{\text{SiO}_2(\text{aq})}=0.008$ and $\text{pH}=5.0$, here "m" represents the molality (mole/kg H_2O).

INTRODUCTION

Dickite is an important industrial raw mineral for ceramics and refractories. Rocks composed mainly of dickite, alunite, kaolinite and pyrophyllite are collectively called "clay" in this paper. Most of clay deposits in the Korean Peninsula were found in Cretaceous volcanic rocks.

In general, clay deposits are considered to be produced by acid hydrothermal solutions at shallow levels near the surface (e.g., Iwao, 1972), but the alteration mechanisms are not simple. Some deposits have been considered to be produced by the hydrothermal alterations associated with igneous intrusive activities (e.g., Kamitani, 1974), but in most other deposits, the hydrothermal alterations seem to be

independent of the intrusive activities.

Furthermore, dickite is stable at distinctly higher temperatures than kaolinite as shown experimentally by Ross and Kerr (1930). They considered that dickite seems to have been formed by moderately heated hydrothermal solutions in some deposits. However, in other dickite deposits, the activity of hot solutions is excluded by the geologic evidences. Therefore, dickite seems to be a hypogene mineral formed in part by hot and in part by cold solutions. It is well known that the mineral results from purely weathering processes (Ross and Kerr, 1930; Meyer and Hemley, 1967).

The Seongsan mine, Haenam district, Jeonnam Prefecture, is one of the largest clay deposits in the Korean Peninsula, and many large and small clay deposits are found around this area. These clay deposits have been studied by some previous workers (Lee and Kim, 1985; Yoo, 1985; On et al., 1985

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among others). They found that the clay deposits in this area are stratiform in shape occurring in the felsic volcanic rocks. However, alteration zoning has not yet been clearly recognized, and no chemical analysis of the altered rocks has been conducted.

In this present work, the felsic volcanic rocks distributed in the southwestern part of the Korean Peninsula have been studied, with an intention to analyze their structure and petrographical characters. The purpose of this study is first to obtain detailed mineralogical and chemical data for the altered rocks, and secondarily to describe the regional rock alterations in this district, and thirdly to consider the mechanism of hydrothermal alteration.

GEOLOGICAL SETTING

The volcanic rocks widely distributed in the Haenam region have erupted during the Cretaceous time (Fig. 1). In the present work, the geology and hydrothermal alterations of the Seongsan mine have been studied in detail. Brief descriptions of these rocks will be given as follows.

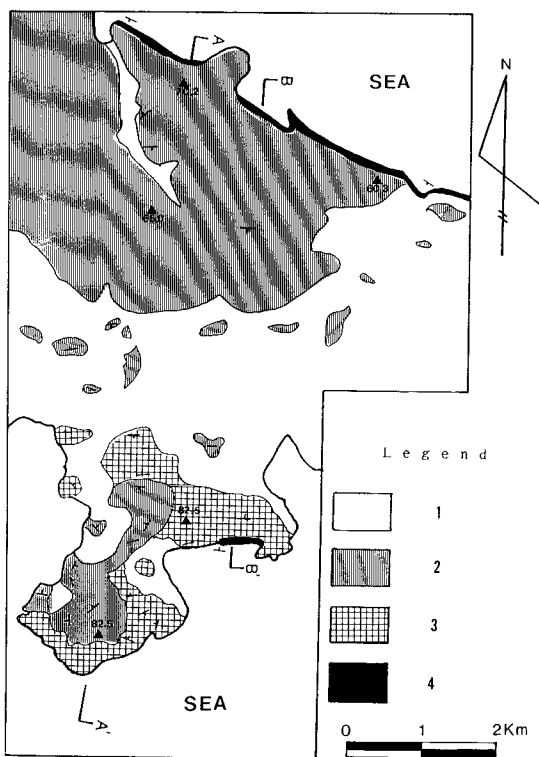


Fig. 1. Geological map of the Seongsan mine area. 1; Alluvium, 2; Tuff, 3; Rhyolite, and 4; Sedimentary rocks.

The sedimentary rocks is distributed along the northern and southern coasts of the Hwawon peninsula. The northern occurrence of the sedimentary rocks is composed mainly of oily shale and tuffaceous sandstone with small amount of chert. These rocks have suffered weak propylitization. Tuffaceous sandstone consists of quartz, feldspar and calcite. It strikes $N60\sim70^{\circ}W$ and dips $10\sim20^{\circ}SW$. The southern occurrence of the Sedimentary rocks is composed of black shale and sandstone. These rocks have undergone silicification. They strike $N70^{\circ}E$ to $N30^{\circ}W$ and dip $10^{\circ}N$. These rocks are covered by the volcanic rocks.

The volcanic rocks are distributed widely in the studied area. The rhyolite distributed in the southern part of the studied area, is commonly red in color and shows spherulitic texture. White-colored rhyolite with flow textures has been noted in some places. The rock consists mainly of angular to subangular quartz with a diameter smaller than 3mm, albite, microcline, perthite, sanidine, and small amounts of K-mica, calcite and chlorite. The rock changes to rhyolitic tuff breccia in some places, which consists of felsic ash and rock fragments. Rock fragments are composed mainly of rhyolite and small amount of shale. The size of breccias in this rock is commonly smaller than 10 cm, but reaches to 100 cm in some places. The tuff is distributed in the northern part and at the center of the southern part of the studied area. The tuff is composed mainly of welded tuff, and small amounts of ash tuff and lapilli tuff are intercalated. Most of the welded tuffs are distributed in the northern part, and are deposited unconformably above the sedimentary rocks in the northern part. They show light grey to pale green color, and have welding texture. The rocks are also propylitized. The ash tuffs are sometimes intercalated within the welded tuffs in the center of the studied area. They are light grey in color and strongly propylitized in some places. They are composed of fine-grained aggregates of quartz and feldspar. At the center of the southern part of the studied area, rocks are composed of welded tuff, bedded tuff and lapilli tuff. Most of them have suffered strong hydrothermal alteration, but the original textures of these rocks are still preserved in some places.

Three major paraplatforms are present in the Korean Peninsula, and they can be divided into several provinces by their structural features and geologic setting (e.g., Lee, 1987). According to Lee (1987), the studied area belongs to the Youngdong-Kwangju Depression Zone.

Generally speaking, in the northern part of studied area, the rocks strike E-W and dip 10~20°S, while in the southern part, the rocks strike E-W and dip 10~20°N. Therefore, as to the geological structure in the studied area these rocks make a synclinal structure with an axis of E-W direction plunging to the east.

Some of the small-scale faults which strike NW and dip 10°SW or NE, are accompanied with alteration minerals, indicating that these faults acted as passageways of hydrothermal solutions. Two sets of joints develop with N-S and E-W directions and NE-SW and NW-SE directions.

Alteration Zoning and Mineral Assemblages

The alteration zoning in the Seongsan mine area is shown in Fig.2. The relationships between the stratigraphy of the felsic volcanic rocks and the hydrothermal alteration, was studied at the point A in Fig.2, and is shown in Fig.3. Fig.4 shows the mineral assemblage of each altered zone.

The hydrothermally altered rocks can be classified

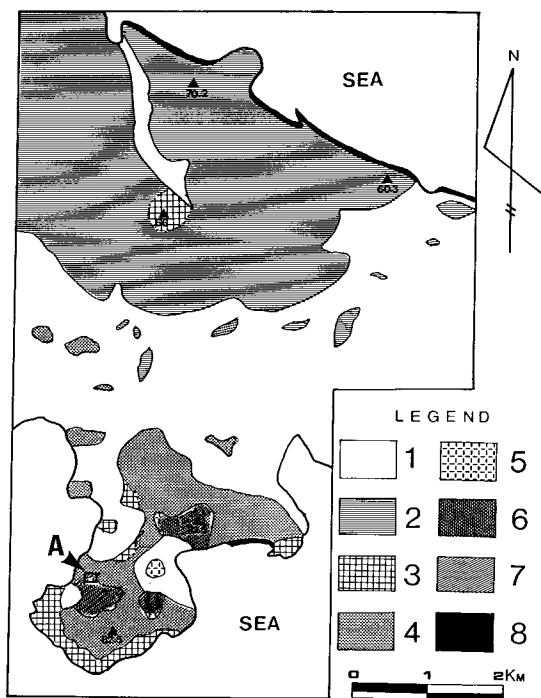


Fig. 2. Alteration zoning map of the Seongsan mine area. 1; Alluvium, 2; Chlorite zone, 3; Albite zone, 4; Sericite zone, 5; Quartz zone, 6; Dickite-Quartz zone, 7; Dickite zone, and 8; Sedimentary rocks.

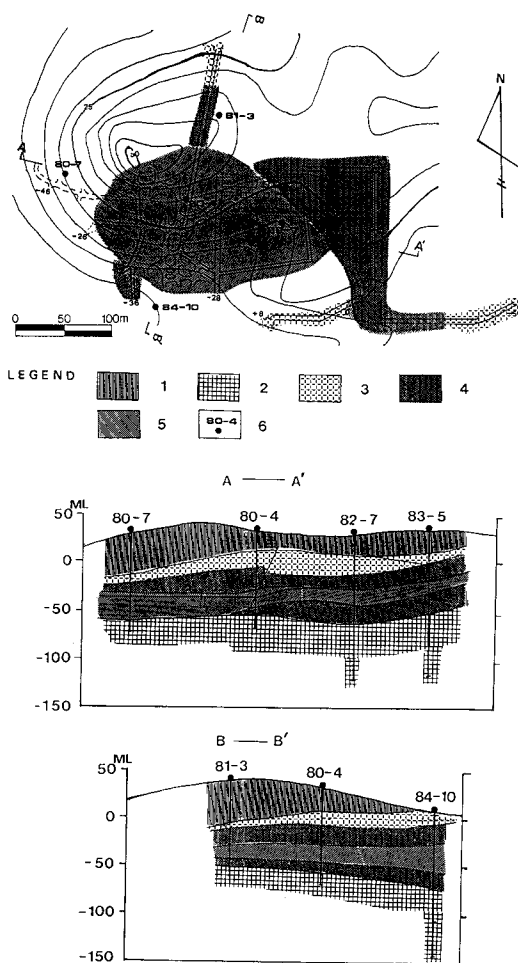


Fig. 3. Alteration zoning map of the underground and profiles in "A" part of the Fig. 2. 1; Tuff, 2; Rhyolite, 3; Quartz zone, 4; Dickite-Quartz zone, 5; Dickite zone, and 6; Drill hole.

into the following alteration zones: Dickite, Dickite-Quartz, Quartz, Sericite, Albite and Chlorite zones, going from the center to the margin of the alteration by optical and X-ray diffraction (X.R.D.) methods (Niskanen, 1964). The Dickite, Dickite-Quartz, Quartz zones and inner part of the Sericite zone, which are advanced argillic alteration type, are developed rather vertically than horizontally, and are classified as "Clay zones" in this paper, while outer part of the Sericite zone, Albite and Chlorite zones, which are propylitic alteration type, are developed rather horizontally than vertically. The characteristics of each altered zone are described as follows.

The rocks in the Dickite zone are white, gray and dark green in color, and mainly composed of dickite.

	1	2	3	4	5	6
DICKITE					■	■
ALUNITE				---	---	---
KAOLINITE					---	---
QUARTZ	■	■	■	■	■	
SERICITE			■	■		
K-FELDSPAR		■	■			
ALBITE		■	---			
CALCITE	■	---				
CHLORITE	---	---				
EPIDOTE	---					
PYRITE						

Fig. 4. Mineral assemblages in each altered zone. 1; Chlorite zone, 2; Albite zone, 3; Sericite zone, 4; Quartz zone, 5; Dickite-Quartz zone, and 6; Dickite zone.

Small amounts of quartz, alunite, kaolinite and pyrite are observed. The polymorph of dickite is determined as monoclinic one after Bailey (1963). This zone was formed through alteration of rhyolite and welded tuff. The original textures are not well preserved in strongly altered rocks, although flow textures in rhyolite are sometimes found. Vein-like aggregates of pure sericites have been found sometimes in this zone. This zone is located at the center of the hydrothermal alteration activities.

The Dickite-Quartz zone generally occurs at the margin of the Dickite zone. The rocks in this zone are white and pale-reddish white in color, and are composed mainly of dickite and quartz. The rocks in this zone are hydrothermal alteration products of the Hwangsan Formation. This zone is divided into two subzones; one subzone is characterized by the occurrence of spotted quartz, while the other subzone is characterized by compact and massive quartz, and by the absence of spotted quartz. The former is produced from welded tuff, while the latter is formed from rhyolite.

The Quartz zone generally occurs at the margin of the Dickite-Quartz zone. The rocks in this zone are white in color, and composed of quartz and small amounts of dickite and alunite. This zone is further divided into sugar Quartz zone and hard Quartz zone. The former is found in the underground of the mine. Most of rocks from this subzone are porous and white to grayish white. Very porous rocks having numerous small holes of several centimeters in diameter are developed in some places. Hydro-

thermal breccia was found in one place. The latter is also found in the underground and outcrop of the mine. The rocks from this subzone are mainly composed of fine-grained quartz and have a small amount of alunite, in which pyrite is often disseminated.

The rocks in Sericite zone are pale greenish white, yellowish white or whitish grey in color, and is composed mainly of sericite, K-feldspar and quartz. Although feldspar grains are replaced by fine-grained sericite and quartz, their original shapes can be recognized under the microscope. The albite ($\text{NaAlSi}_3\text{O}_8$) mole fraction in K-feldspar is 0.04 to 0.02, and the paragonite mole fraction in sericite is less than 0.02. The mole ratios of Fe to K in sericite vary from 0.09 to 0.37. Polytypes of sericite are determined as $2M_1$ and $1M$, and the amount of $2M_1$ is almost equal to that of $1M$. The diffraction pattern of some sericites shows a comparatively broad peaks with basal spacing of $10.2\sim 10.4 \text{ \AA}$, which changes to 10.1 \AA by ethylene glycol treatment. The fact suggests that the sericite is partly interstratified with montmorillonite layers. Montmorillonite-sericite regularly mixed layer minerals having basal spacing of 25 \AA were also recognized. But the amount of montmorillonite is smaller than that of sericite. $2M_1$ and $1M$ sericites are found in the Sericite zone and the Dickite zone. On the other hand, polytype of sericite is restricted to only $1M$ in the outer areas of the Clay zones. Here the Clay zones mean hydrothermally altered zones from the Dickite zone to Quartz zone and inner part of the Sericite zone. It has been suggested that $2M_1$ mica is more stable than $1M$ mica at high temperatures (Yoder and Eugster, 1955). The occurrence of $1M$ sericite seems to reflect the decrease of temperature from the Clay zones towards the marginal areas. Pyrite occurs all over the altered zones. Massive or vein-like aggregates of pyrite are sometimes found in the Sericite zone and Clay zones.

The southern part of the rhyolite and the Boogok tuff has suffered extensive albitization. This zone distributes surrounding the Sericite zone. The rocks in the Albite zone are pale green or reddish grey in color, and composed mainly of albite and quartz, with small amounts of K-feldspar, sericite, calcite and chlorite. Plagioclase is almost completely altered to albite and partly to calcite and sericite. Some calcites precipitated apart from feldspar grains. Albite contains small amounts of K and Ca. The albite mole fraction in the albite solid solution reaches 0.98 to 0.99. Sericite contains small amounts of Na and Fe. The mole fraction of paragonite in sericite is less

than 0.03, and the mole ratio of Fe to K ranges from 0.44 to 1.05. Sericite formed in glass and pumice in the Boogok tuff seems to have higher Fe content than that derived from plagioclase. Original texture could be recognized with the naked eye. Most of the lenses and pumices are altered to pale greenish or deep greenish sericite aggregates both in the Sericite zone and the Albite zone.

The tuff in the northern part of the study area is in general weakly propylitized, and is classified as Chlorite zone in this paper. The rocks in this zone are composed mainly of plagioclase, quartz, calcite and chlorite, with small amounts of sericite, biotite and epidote. Matrix is dark green or blackish grey in color, owing to chloritization. Alkali feldspar is altered to chlorite, and sometimes to epidote. Most of biotites are chloritized. The original shape of biotite is preserved. It can be concluded that Mg and Fe in a rock are almost fixed in chlorite, from the fact that the mole ratio of Mg/Fe+Mg in chlorite ranges from 0.21 to 0.26, and is nearly equal to that of the rock. Plagioclase has albite mole fractions of 0.51 to 0.65, corresponding to the composition of andesine. Plagioclase is commonly accompanied with calcite, and sometimes with sericite.

Chemical Composition of Altered Rocks

Fifty-six altered rock samples were analyzed to estimate the variation of chemical composition using automatic X-ray fluorescence spectrometer (X.R.F.), Rigaku IKF 3064 by glass disc method (Matsumoto and Urabe, 1980). Because Fe^{2+} was oxidized to Fe^{3+} during the analytical process, FeO was analyzed as Fe_2O_3 here. Eleven altered rock samples, five samples among them were analyzed by the X.R.F. method just mentioned, were also analyzed with wet chemical analysis method by Mr. H.Haramura.

Results of the chemical analyses are shown in Table 1. Fig.5 shows the variation of the average weight percent of each component. The chemical variations of the major components in the altered zones are summarized as follows:

SiO_2 content is 68~72 wt.% in the Chlorite zone. It increases to 73~82 wt.% in the Albite, Sericite and Dickite-Quartz zones, and goes up to 97~99% in Quartz zone. Then it decreases to 43~55 wt.% in the Dickite zone. Except for the Quartz, Dickite-Quartz and Dickite zones, Al_2O_3 content is in the range from 9 to 16 wt.%, and does not show any distinct tendency of variation. On the other hand, Al_2O_3 content of the Quartz zone is 0.3 wt.%. It increases to 10~21 wt.%

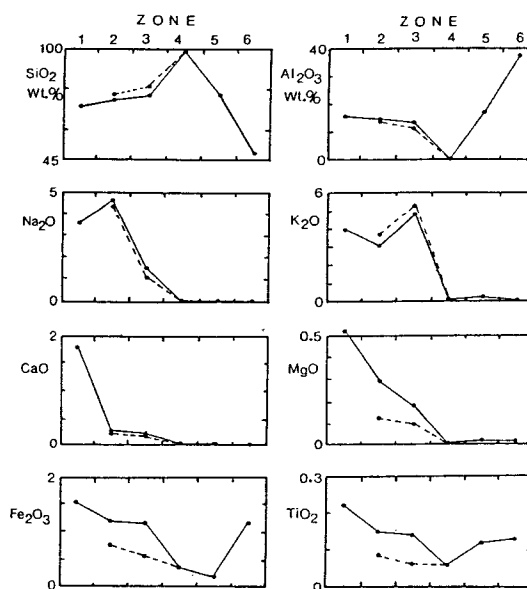


Fig. 5. Variation of average bulk chemical compositions of rocks in each zone. 1, 2, 3, 4, 5 and 6 are the same as referred in Fig. 4, straight line; Tuff, and dashed line; rhyolite.

in the Dickite-Quartz zone, and Al_2O_3 content of the Dickite zone is more than 32 wt.%. CaO content is less than 1 wt.% throughout all of the zones, except for the Chlorite zone. The Chlorite zone has CaO content more than 1%. Fe_2O_3 content, which means total iron as mentioned above, is about 1~3 wt.% in the Chlorite, Albite and Sericite zones. It decreases to less than about 1 wt.% in the Quartz, Dickite-Quartz and Dickite zones.

K_2O content is 1~4 wt.% in the Chlorite and Albite zones. It increases to 4~9 wt.% in the Sericite zone. Then it decreases to less than 0.5 wt.% in the Quartz, Dickite-Quartz and Dickite zones. Na_2O content is 1~3 wt.% in the Chlorite and Sericite zones. It increases to 3~7 wt.% in the Albite zone. Then it decreases to less than 0.2 wt.% in the Quartz, Dickite-Quartz and Dickite zones. The behavior of this element is similar to that of potassium. MgO content is less than 0.3 wt.% throughout all of the zones, except for the Chlorite zone. MgO content of the Chlorite zone is within the range of 0.3~0.6 wt.%. H_2O content is less than 3 wt.% throughout all of the zones, except for the Dickite-Quartz and Dickite zones. It increases to 4~9 wt.% in the Dickite-Quartz zone, and comes up to 10~14 wt.% in the Dickite zone. MnO, TiO_2 and P_2O_5 contents were less than about 1 wt.% throughout all of the zones, and do not

Table 1. Average chemical compositions in each altered zone and pure sericite.

Sample Name	1 (9)*	2 (7)	3 (7)	4 (6)	5 (10)	6 (6)	7 (7)	8 (4)	9 (3)
SiO ₂	47.36	76.05	98.65	75.84	80.70	74.68	76.46	70.80	46.80
TiO ₂	0.13	0.12	0.06	0.14	0.06	0.15	0.09	0.22	0.14
Al ₂ O ₃	37.51	16.18	0.34	13.32	10.89	14.20	13.49	15.14	36.61
Fe ₂ O ₃	1.29	0.21	0.39	1.28	0.70	1.29	0.82	1.69	0.61
MnO	0.00	0.00	0.00	0.04	0.05	0.06	0.04	0.10	0.08
MgO	0.02	0.02	0.01	0.18	0.10	0.29	0.13	0.52	0.54
CaO	0.01	0.01	0.02	0.20	0.16	0.27	0.24	1.77	0.00
Na ₂ O	0.03	0.03	0.02	1.50	1.03	4.56	4.35	3.62	0.30
K ₂ O	0.04	0.23	0.06	4.77	5.18	3.03	3.65	3.92	8.65
P ₂ O ₅	0.14	0.08	0.03	0.04	0.03	0.03	0.03	0.08	0.06
H ₂ O ⁺	13.37	6.29	0.83	2.31	1.10	1.22	0.82	2.35	5.67
H ₂ O ⁻	0.29	0.18	0.24	0.73	0.44	0.27	0.26	0.26	1.38
Total	100.19	99.40	100.65	100.35	100.44	100.05	100.38	100.46	100.84

Abbreviations: 1; Dickite zone, 2; Dickite-Quartz zone, 3; Quartz zone, 4; Sericite zone (Tuff), 5; Sericite zone (Rhyolite), 6; Albite zone (Tuff), 7; Albite zone (Rhyolite), 8; Chlorite zone, and 9 (Pure sericite). * Number of analysis.

show any remarkable tendency.

Transportation of Each Component through Hydrothermal Alteration Processes

Let us now consider the transportation of each component through the alteration processes on the basis of the chemical analysis data mentioned above. It can be noticed that chemical constituents of the rocks are partly removed or added by the interaction of the hydrothermal solutions with the original felsic volcanic rocks, which were subsequently involved in a series of altered zones.

The original rock and altered rock are massive and same aspect, the density of those are assumed to have the about 2.6, then a mass balance equation for each component can be written as;

$$(ai + Xi) = bi \quad (1)$$

where ai and bi represent the weights of component "i" in rock A (100g) and B ((100g + Xi)g), respectively, and Xi is the amount of component "i" added to the original rock through the alteration. Summing the weights of each component, it can be written:

$$\sum (ai + Xi) = \sum bi \quad (2)$$

If:

$$Bi = 100(bi / \sum bi) \quad (3)$$

The following equation can be obtained combining (1) with (2) as;

$$Bi = 100(ai + Xi) / (100 + \sum Xi) = Bi \quad (4)$$

It is, of course, assumed that the rocks A and B are composed of the following components: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O and TiO₂ (H₂O excluded). As has been mentioned before, it can be considered that the mobility of Al₂O₃ is much lower than those of the other components in the Sericite zone and Albite zone. Xi of other components in these zones can be decided as shown in Fig. 6, where X_{Al₂O₃} is assumed to be zero.

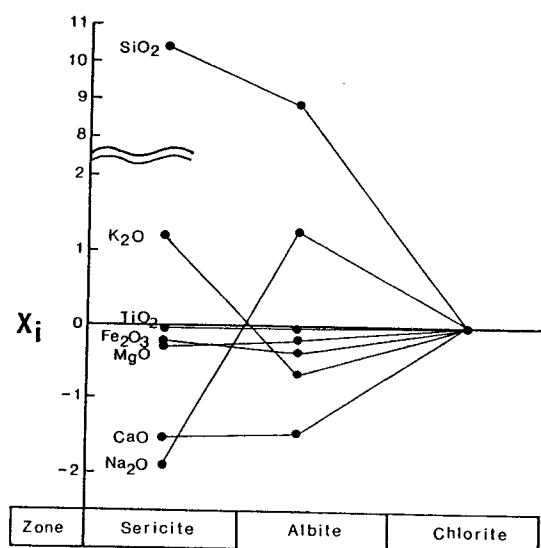
Because Al₂O₃ content is considerably variable (16~45 wt.%), its mobility can not be ignored in the Dickite and Dickite-Quartz zones. Al₂O₃ was removed from the original rocks in these zones. Therefore, it can not be assumed that X_{Al₂O₃} is zero in this case, making it difficult to deduce the Xi of each component in these zones.

Fluid Inclusion Study

Selected samples for the fluid inclusion study were sugar quartz and massive quartz in the Quartz zone. Microthermometry apparatus used in this study is Chaixmeca, Nancy-France, whose range of determination temperature is from -180°C to +600°C.

Euhedral quartz crystals are sometimes found in the porous quartzose rock. They were grown from the wall toward the center of small holes. Length of the quartz prism is 0.1 mm to 1 cm. Comparatively large crystals were separated and examined under the microscope.

They are transparent, and contain many fluid


 Fig. 6. Calculated X_i of each component.

inclusions with diameter generally not exceeding 0.02 mm and rarely reaching up to 0.05 mm. Most inclusions are composed of liquid and vapor phases. The volume occupied by the vapor phase is about less than 10 volume %, then the volume of liquid phase is generally much greater than that of vapor phase. Boiling evidence is almost lacking, if any. Inclusion types are divided into primary type and secondary type on the basis of the definition by Roedder (1984). Most of inclusions are circular and elliptic in shape.

Filling temperature was measured for inclusions in three quartz crystals on the heating stage at constant heating rate of 1°C/min. The filling temperature for each sample ranges generally from 120°C to 200°C, showing considerably large scattering (Fig. 7 and Table 2).

Freezing temperature for the same samples was also measured, and the salinity was calculated by the equation given by Potter et al. (1978). Although it was quite difficult to measure the freezing temperature due to the small size of the inclusions, some of them were estimated in the ranges of 4.0~8.0 wt.%, which is 0.07~0.13 M NaCl equivalent concentration. Table 9 shows the range of the filling temperature and salinity in each sample.

Estimation of Temperature and $a_{\text{Na}^+}/a_{\text{K}^+}$ Ratio of the Hydrothermal Fluid

On the basis of thermochemical considerations, the

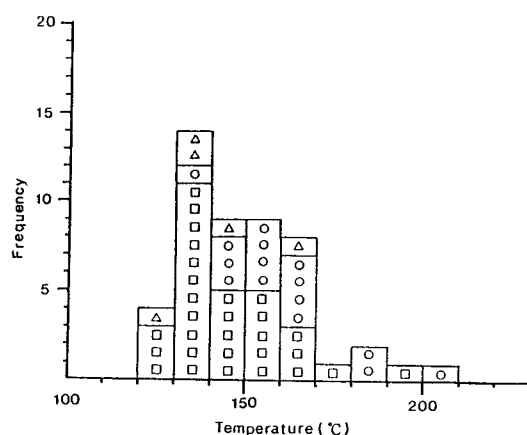


Fig. 7. Histogram for filling temperature of fluid inclusion. Quadrangle; 87051517, circle; 87051611, and triangle; 88012104.

Table 2. Fluid inclusion and salinity data for samples from the Quartz zone.

Sample Name	Mineral	Filling Temperature (°C)	NaCl Equivalent (wt.%)
87051517	Quartz	122-195	5.4-6.4
87051611	Quartz	132-208	5.1-7.9
88012104	Quartz	125-167	4.0-5.7

temperature and chemical compositions of the hydrothermal solution were estimated.

Equilibria in the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$

K_2O , Na_2O , Al_2O_3 , SiO_2 , and H_2O are the major chemical constituents transported in the process of hydrothermal alteration responsible for the formation of the rocks in the Albite, Sericite and Clay zones. Quartz is always present, suggesting that the chemical system was saturated with SiO_2 . It can be considered that H_2O is a perfectly mobile component in the alteration processes. From the above consideration, it is supposed that the relationships between mineral assemblages and chemical variations in these altered zones can be represented with the coordinates $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ as given in Fig. 8. Weakly propylitized (Chlorite zone) rocks are also plotted in this figure, where Al_2O_3 contained in plagioclase is excluded on the assumption that CaO is always fixed as an anorthite molecule.

The trend of chemical variation is shown by the arrows in Fig. 8. It could be concluded that the progress of alteration from the Albite to the Sericite

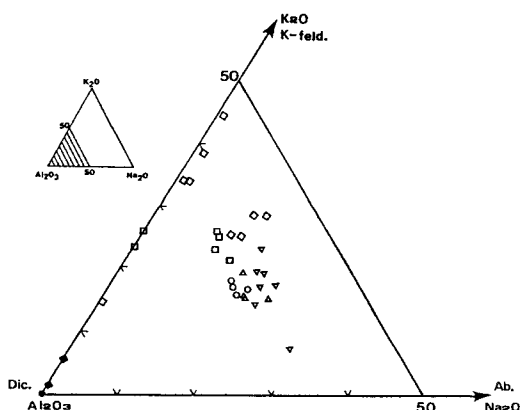
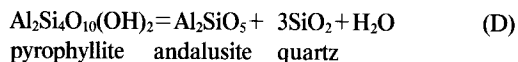
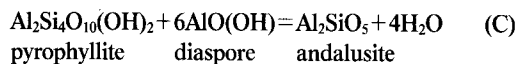
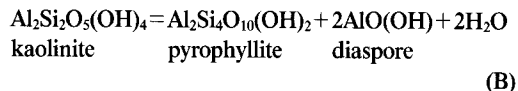
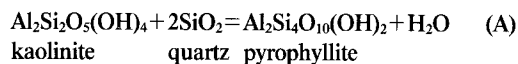


Fig. 8. Triangular diagram $\text{Al}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O}$ showing the composition of altered rocks. Open circle; Chlorite zone, Open triangle and reverse open triangle; Albite zone, Open quadrangle and open rhombus; Sericite zone, Full quadrangle; Quartz zone, Full rhombus; Dickite-Quartz zone, Full circle; Dickite zone, Open triangle and open quadrangle; Altered tuff, and reverse open triangle and open rhombus; Altered rhyolite.

zones were controlled by alteration of albite to K-feldspar and sericite. Similarly the alteration of K-feldspar to dickite through sericite controlled the process of alteration from the Sericite to the Clay zones.

In this section the temperature range of hydrothermal solution in the clay deposits will be estimated by thermochemical consideration on equilibrium among albite, K-feldspar, muscovite, paragonite, kaolinite (dickite), pyrophyllite, andalusite, diaspore, alunite, quartz and water. The reaction involving quartz are as follows:



The Gibbs free energy change for a reaction at T K and P bars, $\text{Gr}(T,P)$, can be obtained by:

$$\Delta \text{Gr}(T,P) = \Sigma \text{Gr}(T,1) + \int_1^P V_r dP \quad (5)$$

where ΔV_r represents the volume change accom-

panied with the reaction. Since $\Delta \text{Gr}(T,P)=0$ at equilibrium, and assuming that ΔV_r does not depend on P and T , we have

$$0 = \Delta \text{Gr}(T,1) + \Delta V_r(P,1) \quad (6)$$

$\Delta \text{Gr}(T,1)$ is defined as:

$$\Delta \text{Gr}^0(T,1) = \Delta H_r^0(T) - T \Delta S_r^0(T) \quad (7)$$

where $\Delta H_r^0(T)$ and $\Delta S_r^0(T)$ represent respectively the change of enthalpy and entropy for the reaction. $\Delta H_r(T)$ and $S_r(T)$ can be evaluated respectively by:

$$\Delta H_r^0(T) = \Delta H_r^0(298.15) + \int_{298.15}^T C_p dT \quad (8)$$

$$\Delta S_r^0(T) = \Delta S_r^0(298.15) + \int_{298.15}^T C_p/T dT \quad (9)$$

where C_p represents the isobaric heat capacity change for the reaction.

Thermochemical data for minerals and water were given by Helgeson et al. (1979). Here, the chemical potential for water at T and P bars, $\mu_{\text{H}_2\text{O}}^0(T,P)$ is assumed to be as:

$$\mu_{\text{H}_2\text{O}}^0(T,P) = \mu_{\text{H}_2\text{O}}^0(T,1) + RT \ln P_{\text{total}} \quad (10)$$

The P - T equilibrium curve for reactions (A)-(D) can be calculated as in Fig. 9, by using the equations (5)-(9) and the thermochemical data (Helgeson et al., 1979). It is evident that the equilibrium temperature rises with the pressure increasing in the reaction (A)-(D).

Major mineral constituents are dickite and quartz in the Clay zones. Therefore, the temperature range for the Seongsan deposit corresponds to the range in which dickite and quartz can coexist; that is, 0~290°C at 300 bars and 0~310°C at 1 Kb. This is generally in agreement with the filling temperature of fluid inclusions.

Equilibria in the system $\text{K}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-HCl}$

Although water was assumed to be pure phase in the previous section, it is reasonable to consider that the fluid phase was rich in Na^+ , K^+ , H^+ , Ca^{2+} , Cl^- , aqueous silica and others. Therefore, the factor that control the alteration processes is not only temperature and pressure but also chemical compositions of the solution (pH , a_{Na^+} , a_{K^+} , and so on; "a" represents the activity). In this section, $a_{\text{Na}^+}/a_{\text{K}^+}$ ratio of the hydrothermal solution will be estimated based on the thermochemical consideration on the system $\text{Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-HCl}$.

The chemical compositions of hydrothermal solution can be determined by the following equilibria:

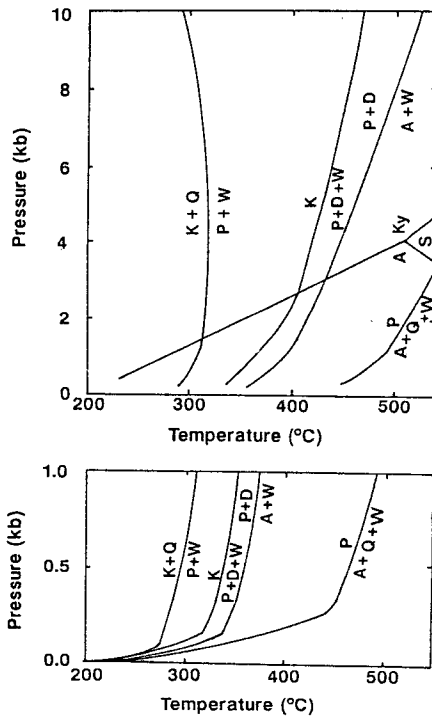
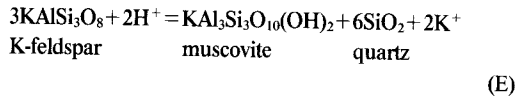
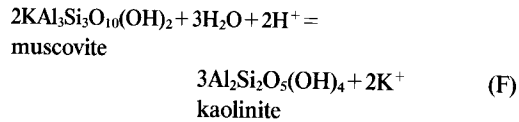


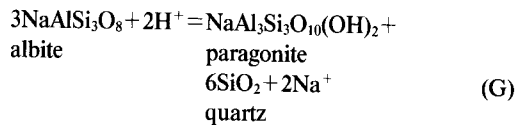
Fig. 9. Calculated pressure-temperature relation of some dehydration equilibria and the stable mineral assemblages. A; Andalusite, K; Kaolinite, P; Pyrophyllite, D; Diaspore, C; Corundom, Q; Quartz, Ky; Kyanite, S; Sillimanite, and W; Water.



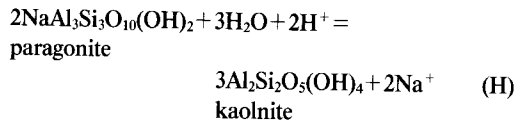
(E)



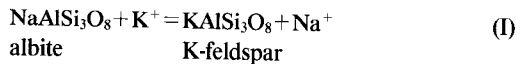
(F)



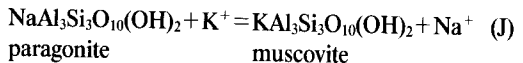
(G)



(H)



(I)



(J)

The thermochemical meaning of reaction (J) will be considered, for example. The equilibrium constant at T° K, P bars is given by:

$$K(J) = a_{\text{Mus}} \times a_{\text{Na}^+} / a_{\text{Pag}} \times a_{\text{K}^+} \quad (7)$$

If the equilibrium condition could be muscovite and paragonite are pure phases, $K(J)$ would be $a_{\text{Na}^+} / a_{\text{K}^+}$, and the equilibrium condition could be decided only by a_{Na^+} and a_{K^+} of the solution. $Gr(T,P)$ of reaction (J) can be described by:

$$\Delta Gr_{(J)}(T,P) = \mu_{\text{Mus}}(T,P) + \mu_{\text{Na}^+}(T,P) - \mu_{\text{Pag}}(T,P) - \mu_{\text{K}^+}(T,P) \quad (8)$$

where μ_{Mus} , μ_{Na^+} , μ_{Pag} and μ_{K^+} represent the chemical potentials of muscovite, Na^+ , paragonite and K^+ , respectively. Defining $\Delta G_{(J)}^\circ(T,P)$ as given by the equation (9), the equation (10) can be obtained.

$$\Delta Gr_{(J)}(T,P) = \mu_{\text{Mus}}^\circ(T,P) + \mu_{\text{Na}^+}^\circ(T,P) - \mu_{\text{Pag}}^\circ(T,P) - \mu_{\text{K}^+}^\circ(T,P) \quad (9)$$

$$\Delta Gr_{(J)}(T,P) = \Delta Gr(T,P) + RT \ln(a_{\text{Na}^+} / a_{\text{K}^+}) \quad (10)$$

where μ° represents the chemical potential of pure phase, and R the gas constant ($1.9872 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

Since $\Delta Gr(T,P) = 0$ at equilibrium, the equation can be described by:

$$\ln(a_{\text{Na}^+} / a_{\text{K}^+}) = -\Delta Gr_{(J)}(T,P) / RT \quad (11)$$

Thermochemical data for ion species were given by Robie and Waldbaum (1968), Helgeson (1969) and Ellis and Macfadden (1972). $\Delta G_{(J)}^\circ(T,P)$ can be calculated similarly at the P-T equilibrium curve. Here the partial molal volumes and heat capacity coefficients for ion species are taken as those for 200°C , assuming that each value does not change much in the range of $150\text{--}250^\circ\text{C}$. Similarly the equilibrium ratios of $a_{\text{K}^+} / a_{\text{H}^+}$ and $a_{\text{Na}^+} / a_{\text{H}^+}$ can be calculated for the other reactions. Fig. 10 shows the mineral stability relation for the system $\text{Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-HCl}$ at 300 bars and 1 Kb, and 200°C .

Although solid phases were assumed to be pure phases in the above discussion, natural albite, K-feldspar and muscovite are the solid solutions containing a small amount of K-feldspar, albite and paragonite molecules. Next, the ratio $a_{\text{Na}^+} / a_{\text{K}^+}$ of hydrothermal solution responsible for the formation of the Clay zones (pure sericite) and Sericite zone will be thermochemically estimated.

a) Muscovite-paragonite solid solution

The equilibrium between paragonite and muscovite in K(Na) mica solid solution is given by the reaction

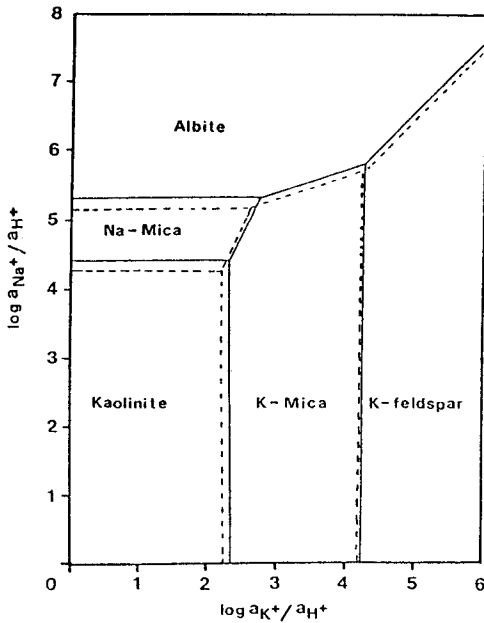


Fig. 10. Mineral stability relation as a function of $\log a_{\text{Na}^+}/a_{\text{H}^+}$ vs. $\log a_{\text{K}^+}/a_{\text{H}^+}$ in the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{HCl}$ at 300 bars (dashed line) and 1 Kb (straight line), and 200°C.

(J). $\Delta G_{r(J)}(T,P)$ is represented by:

$$\Delta G_{r(J)}(T,P) = \Delta G_r(T,P) + RT \ln(a_{\text{Mus}} \times a_{\text{Na}^+}/a_{\text{Pag}} \times a_{\text{K}^+}) \quad (12)$$

a_{Mus} and a_{Pag} are given by the mole fractions (X_{Mus} , X_{Pag}) and the activity coefficients (γ_{Mus} , γ_{Pag}).

$$a_{\text{Mus}} = X_{\text{Mus}} \times \gamma_{\text{Mus}} \quad (13a)$$

$$a_{\text{Pag}} = X_{\text{Pag}} \times \gamma_{\text{Pag}} \quad (13b)$$

$RT \ln \gamma_{\text{Mus}}$ and $RT \ln \gamma_{\text{Pag}}$ are given by:

$$RT \ln \gamma_{\text{Mus}} = (\partial G_{\text{ex}} / \partial n_{\text{Mus}}) \times n_{\text{Pag}}(P,T) \quad (14a)$$

$$RT \ln \gamma_{\text{Pag}} = (\partial G_{\text{ex}} / \partial n_{\text{Pag}}) \times n_{\text{Mus}}(P,T) \quad (14b)$$

where G_{ex} represents the excess free energy of K(Na) mica solid solution, and "n" means the mole number.

Eugster et al. (1972) gave the excess free energy of K(Na) mica solid solution for one mole (G'_{ex1}) from the solvus in the muscovite-paragonite system.

$$G'_{\text{ex1}} = (3082.1 + 0.0822P + 0.1698T) \times X_{\text{Mus}} \times X_{\text{Pag}}^2 + (4163.9 + 0.1259P + 0.3954T) \times X_{\text{Pag}} \times X_{\text{Mus}}^2 \quad (\text{cal/mole}) \quad (15)$$

where X_{Mus} and X_{Pag} represent mole fractions of muscovite and paragonite, respectively.

Sericite in the Clay zones (pure sericite) has the

Table 3. Paragonite mole fractions (X_{Pag}) in K-Na mica solid solutions.

	Sample Name	$m_{\text{Na}^+}/m_{\text{K}^+}$	X_{Pag}
	86101808	0.162	0.058
Vein-like shaped pure sericite	87051510	0.045	0.043
	87051512	0.033	0.032
	Average	0.047	0.044
	87051305	0.022	0.021
Sericite in the Sericite zone	87051902	0.031	0.030
	87052012	0.027	0.026
	Average	0.027	0.026
	87051309	0.023	0.022
Sericite in the Albite zone	87051307	0.021	0.020
	88020204B	0.022	0.021
	Average	0.022	0.021

average compositions of $X_{\text{Pag}}=0.044$ (Table 3). Assuming that the temperature and pressure of hydrothermal solution were 200 and 300 bars, the equilibrium $a_{\text{Na}^+}/a_{\text{K}^+}$ can be obtained to be 30.80 from the equations (12), (13), (14) and (15) using the thermochemical data. Furthermore, sericite in the Sericite zone and Albite zone have the average composition of $X_{\text{Pag}}=0.026$ and 0.021, and the equilibrium ratio $a_{\text{Na}^+}/a_{\text{K}^+}$ in the solutions can be estimated as 18.20 and 14.70 at 200°C and 300 bars, respectively.

b) K-feldspar-albite solid solution

K-feldspar in the Sericite zone has the composition of $X_{\text{K-feld}}=0.96\sim 0.99$ (av. 0.974). X_{Pag} of sericite is less than 0.02. Therefore, it can be said that Na is mostly fixed as K(Na)-feldspar solid solution, and that the equilibrium ratio $a_{\text{Na}^+}/a_{\text{K}^+}$ of hydrothermal solution in this zone was determined by reaction (I).

Orville (1963) experimentally determined the solves in the albite-K-feldspar binary system at 500°, 600°, 650°, 700°C and 2 Kb. Thompson and Waldbaum (1968) could obtain the excess free energy for one mole (G'_{ex2}) at T°K, 2 Kb as follows, on the assumption that K(Na)-feldspar forms the asymmetrical solid solution.

$$G'_{\text{ex2}} = (-463 + 5.052T) \times X_{\text{Or}} \times X_{\text{Ab}}^2 + (5679 - 2.954T) \times X_{\text{Ab}} \times X_{\text{Or}}^2 \quad (\text{cal/mole}) \quad (16)$$

where X_{Or} and X_{Ab} represent the mole fraction of K-feldspar and albite, respectively. Assuming the formation pressure was 300 bars and G'_{ex2} at 2 Kb = G'_{ex2} at 300 bars, the equilibrium ratios $a_{\text{Na}^+}/a_{\text{K}^+}$ of hydrothermal solution at various temperatures are estimated to be 13.18 (250°C), 16.60 (225°C), 21.88

(200°C), 31.62 (175°C), 43.65 (150°C), and 67.61 (125°C) at 300 bars.

DISCUSSION

The alteration processes responsible for the formation of a series of altered zones can be understood by the model that hydrothermal solution penetrates through the column of felsic volcanic rocks, and the processes could be summarized as follows (Fig. 11).

Solution "I" could dissolve SiO_2 from the original rock and precipitate Al_2O_3 , that is, Solution "I" was strongly acid and saturated with Al. Si, Fe, Ca, Mg, Na, K and others are dissolved from biotite, alkali-feldspar, plagioclase and glass. As a result of this reaction, the solution became richer in these components and its pH increased.

The original rock was changed, and the Sericite zone was formed by Solution "II", and the Albite zone by Solution "III". These reactions made the hydrothermal solutions richer and richer in Mg, Ca, Fe, and Ti. Solution "IV" was almost in equilibrium with the original rock.

On the above alteration processes, K dissolved in the solution would be fixed partly in sericite and K-feldspar in the Sericite zone, and Na as albite in the Albite zone. Al_2O_3 dissolved from the original rock to Solution "I" would be fixed mainly as dickite or alunite in the Clay zone (Dickite zone). Here the solution is assumed to flow only from the Clay zones to weakly altered zone. The compositions of Solution "I" and "II" will be estimated on the basis of above model.

Hemley and Jones (1964) determined the mineral stability relation in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{HCl}$ as shown in Fig. 12. Since Solution "I" had

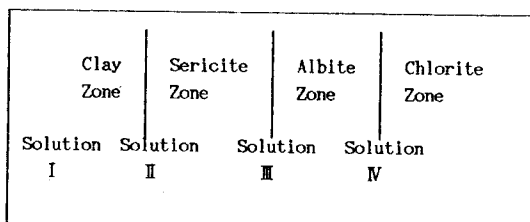


Fig. 11. Concept of alteration process. Hydrothermal solution penetrates through the column of the felsic volcanic rocks. Solution I was strongly acid and saturated with Al_2O_3 and SiO_2 . Fe, Ca, Mg, Na, K and other components are dissolved from alkali-feldspar, plagioclase, mica and glass phase. This reaction made the hydrothermal solution richer and richer in this components.

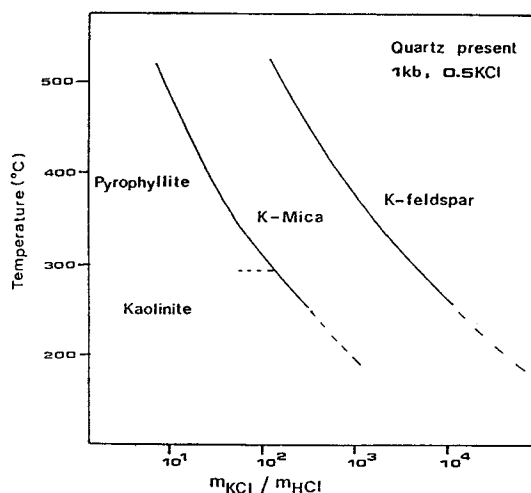


Fig. 12. Reaction curves for the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 1 Kbar and 0.5 KCl solution (Hemley and Jones, 1959 and 1964).

to be nearly in equilibrium with the Clay zone, its $m_{\text{K}^+}/m_{\text{H}^+}$ would be near the boundary between dickite and sericite in Fig. 12. If pressure difference does not give great effect on the equilibrium among dissolved ions, $m_{\text{KCl}}/m_{\text{HCl}}$ ratio in the Solution "I" could be estimated as nearly $10^{2.5}$ at 200°C. The assemblage of sericite-quartz (the Sericite zone) is stable under the condition of $m_{\text{KCl}}/m_{\text{HCl}} > 10^{2.5}$, and the assemblage of dickite-quartz (the Dickite zone) is stable under $m_{\text{KCl}}/m_{\text{HCl}} < 10^{2.5}$ at 200°C. If vein-like aggregates of sericite can be regarded as to have been in equilibrium with Solution "I", $m_{\text{Na}^+}/m_{\text{K}^+}$ of Solution "I" would be estimated to be 30.80, assuming that $a_{\text{Na}^+}/a_{\text{K}^+}$ is equal to $m_{\text{Na}^+}/m_{\text{K}^+}$.

It can be assumed that Na^+ and K^+ are dominant among metal ions in Solution "I", as well as those in geothermal waters of high temperature (Ellis, 1970) and those in fluid inclusions (Roedder, 1979). It can be considered that the data of fluid inclusions in the Quartz zone correspond to Solution "I" from their occurrence and that $m_{\text{Na}^+} + m_{\text{K}^+}$ of Solution "I" would be 0.07~0.13 (av. 0.10) from the salinity data of fluid inclusions. From the above consideration, it can be estimated that Solution "I" had the composition of $m_{\text{K}^+} = 0.002 \sim 0.004$ (av. 0.03), $m_{\text{Na}^+} = 0.068 \sim 0.126$ (ave. 0.097) and $\text{pH} = 4.9 \sim 5.2$ (av. 5.0).

Let us now assume that the composition of Solution "II" was controlled only by the reaction between the original rock and Solution "I". If the original rock (100 g) was altered into the rock of the Sericite zone by Solution "I" (X_1 liter), Solution "II" would

Table 4. Composition of solution I and II.

	Solution I	Solution II
Na(ppm)	2230	2276
K	117	119
Ca	—	80
Mg	—	14
Fe	—	11
Ti	—	1
SiO ₂ *	448	109
pH	5.0	6.8

*The concentration of SiO₂ was estimated from the quartz solubility data given by Hemley et al. (1980). The temperature of solution I and II were assumed to be 200 °C and 150 °C, respectively.

have the composition of $m_{Na^+} = 0.097 + 0.031/X_1$, $m_{K^+} = 0.003 - 0.013/X_1$ on the basis of the consideration in previous page (Table 4). a_{Na^+}/a_{K^+} of the solution in the Sericite zone has been already obtained in previous page.

If it is assumed that the formation pressure to be 300 bars, X_1 would be calculated at 200, 175, 150 and 125 °C. X_1 and m_{Na^+}/m_{K^+} at 200 °C are obtained to be 13.82 and 21.88, respectively. Therefore, m_{Na^+} and m_{K^+} can be calculated to be 0.099 and 2.1×10^{-3} , respectively. m_{K^+}/m_{H^+} of the solution in equilibrium with the assemblage of K-feldspar, sericite and quartz can be estimated to be $10^{4.5}$ from Fig. 12. pH is obtained to be 6.8 from the estimated m_{K^+}/m_{H^+} and m_{K^+} . The other components can be estimated similarly to m_{K^+} and m_{Na^+} , that is, $m_{Ca} "T" = 0.028/X_1$, $m_{Mg} "T" = 0.008/X_1$, $m_{Fe} "T" = 0.001/X_1$ and $m_{Ti} "T" = 0.0003/X_1$, where "T" represents the total substituting X_1 in the above equations by the estimated value, 13.82, the molalities can be obtained as follows: $m_{Ca} "T" = 2.0 \times 10^{-3}$, $m_{Mg} "T" = 5.8 \times 10^{-4}$, $m_{Fe} "T" = 7.2 \times 10^{-5}$ and $m_{Ti} "T" = 2.2 \times 10^{-5}$.

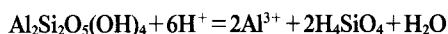
Although the compositions of Solutions "III" and "IV" can be estimated similarly to Solutions "I" and "II", they are omitted here, because there should be many supposed unknown factors such as the reverse or circular flows of solution, the mixing of the solution with ground water and so on.

And now, consideration of the hydrolytic alteration process, the minimum alkali/H⁺ values corresponding to assemblages produced in the system alumina-silica-water, with a mica present, are those of K-mica decomposition to either kaolinite, pyrophyllite, or andalusite. Low values correspond to less of K-mica from the system. The mica and montmorillonite hydrolysis curves, in general, thus define a set of end

member conditions for relations in the Al₂O₃-SiO₂-H₂O system.

The role of additional anion components in the yielding more complex assemblages is another important consideration. Alteration of sulfate to the system makes alunite a possible associated phase. With fluoride and chloride, zunyite and topaz may be produced. These more complex systems have not yet been adequately studied, but aspects of topaz chemistry have been presented by Rosenberg (1972), and alunite phase relations were discussed by Hemley et al. (1969). In terms of aqueous K₂SO₄ vs. H₂SO₄ activities, alunite, K-mica and kaolinite, in a quartz-saturated system, coexist stably at an isothermal, isobaric invariant point. At higher K₂SO₄ concentration than above this point, alunite is stable against K-mica, and at sufficiently high K₂SO₄ concentration, it is stable against K-feldspar. Under more acid conditions than the triple point value, only alunite-kaolinite or alunite is stable. In the Seongsan clay deposit, alunite is sometimes found in the Quartz zone. In general, higher temperatures and high aqueous silica activities obviously favor pyrophyllite relative to kaolinite, but high silica activities also shift the K-feldspar stability field toward that of kaolinite (Hemley et al., 1980). If solution has a high temperature and a high aqueous silica activity, the solution will produce pyrophyllite. And if not, this condition favors kaolinite. But pyrophyllite, zunyite and topaz are not found in the Seongsan clay deposit. The formation temperature of the Seongsan clay deposit is estimated as more than 200 °C from fluid inclusion study of samples taken from the Quartz zone. This condition favors formation of the K-feldspar-kaolinite association, that is fairly common in low temperature hydrothermal alteration, although the Seongsan clay deposit may be formed under highly acid condition, such as pH lower than 5.0.

Silicification, a very common feature of hydrothermal alteration, merits some further discussion relating to compositional controls in the aqueous phases. Replacement by silica, rather than simple deposition of silica in open spaces, will occur if the solution becomes undersaturated with respect to Al and other components but supersaturated with silica. Because the cooling of a hydrothermal fluid will also involve the increased ionization of its acid constituents which are largely undissociated at high temperatures, mineral dissolution and replacement by a silica phase, usually quartz, is a common occurrence. This can be seen in the case of a total mineral dissolution or hydrolysis reaction such as



in which precipitation of quartz from the released H_4SiO_4 will cause the replacement of the dissolved mineral by quartz. Note that silicification will not be favored by extreme silica supersaturation because of greater suppression of the dissolution of Al. Significant fact is that H^+ is continuously evolved and consumed as the solution migrates and cools, and no doubt most replacement occurs under only weakly acid conditions. Preservation of textures will be favored by slow reaction and a small pH gradients, whereas more aggressive replacement will be reflected in destruction of textures, where leaching exceeds precipitation, and a more porous silicified rocks will be produced.

Kaolinite (dickite), diaspore and pyrophyllite assemblages typically occur in felsic and intermediate rocks that have undergone extreme acid leaching, producing advanced argillic assemblages (Meyer and Hemley, 1967). Such environments are most commonly observed in recent volcanic terranes, and have been described in many places. Intense acid alteration is, of course, a common feature of relatively shallow hydrothermal alteration processes operating in volcanic systems because under these conditions the ionization and oxidation of magmatically derived acid constituents have reached at maximum (Hemley et al., 1980). The oxidation of H_2S is of paramount importance. Halogen acids may be generally subordinate. The form advanced argillic implies an environment of relatively intense base-leaching, as compared to ordinary argillic where kaolinite is derived from plagioclase decomposition at moderate alkali/ H^+ ratios, but a kaolinite type clay mineral is not an essential component of the assemblages formed by the magmatic hydrothermal solution. Alunite is abundant in this type deposits.

Although the shallow volcanic environment is particularly important to these associations, they are not restricted to near-surface environments. Burbank (1950) pointed out the extension of advanced argillic suites to depths, and local deep occurrences of sericite, dickite, and alunite, typically carrying sulfide assemblages of high sulfidation state (pyrite-covellite), are known from Butte and other districts (Meyer and Hemley, 1967). In fact, it is important control of H^+ on sulfidation state of the sulfides. From what has been said over, the Seongsan clay deposit may be an occurrence of shallow hydrothermal alteration processes operating in volcanic system, alunite is lower acid and lower temperature than an actual occurrence of the Seongsan clay deposit (dickite),

and alunite may be abundant than kaolinite. By the Ross and Kerr (1930) and among others, dickite deposits usually accompany metal deposits, but, until recent years, metal deposit have not been found in the Seongsan clay deposits. Therefore, metal deposit may be found through the more detailed investigation around the Seongsan clay deposit. Although some basic feature have been clarified as to the Seongsan deposits in the present, today, further discussion will be required on the detailed mechanism of the alteration.

CONCLUSIONS

1) The geology around the Seongsan clay deposits consists mainly of late Cretaceous felsic volcanic rocks.

2) Most of the felsic volcanic rocks in the studied area have undergone extensive hydrothermal alteration.

3) The hydrothermally altered rocks can be classified into the following altered zones: Dickite, Dickite-Quartz, Quartz, Sericite, Albite and Chlorite zones, from the center to the margin of the alteration.

4) On the basis of bulk chemical composition data, it was found that some components such as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO, K_2O , Na_2O and TiO_2 were mobilized considerably from the original rocks.

5) The formation temperature of the dickite deposit is estimated as more than 200°C from fluid inclusion study of a samples taken from the Quartz zone.

6) From the bulk composition data of rocks, analytical data on minerals and the estimated temperature, the hydrothermal solution formed the Clay zone estimated to have the composition: $m_{\text{K}^+} = 0.003$, $m_{\text{Na}^+} = 0.097$ and $m_{\text{SiO}_2(\text{aq})} = 0.008$ (mol/Kg H_2O) and $\text{pH} = 5.0$.

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성산딕카이트광상에서의 백악기산성마그마티즘에
관련된 열수변질작용 ; 광상형성온도의
측정 및 열수용액의 $a_{\text{Na}^+}/a_{\text{K}^+}$ 비

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요 약 : 성산광산은 한반도의 남서부에 위치하는 큰 딕카이트광상 중에 하나이다. 광석광물로는 주로 딕카이트와 석영이며, 소량의 명반석, 카올리나이트 및 견운모가 산출된다. 성산광상의 주변지질은 주로 백악기의 산성 화산암류로 구성된다. 연구지역에서 이러한 암석들은 동서방향의 축을 갖고 동쪽으로 경사지는 향사구조를 갖는다.

산성 화산암류는 심한 열수변질작용을 받고 있다. 이러한 암석들은 중심부로부터 바깥쪽으로 딕카이트, 딕카이트-석영, 석영, 견운모, 알바이트 및 녹니석대로 구분된다. 변질암의 이러한 누대배열은 주변암 (용결용회암과 유문암의 상부)이 산성 열수에 의한 변질작용으로 생성되었다. 그것은 황화수소를 함유한 용액과 초기 가스, 그리고 다른 것들이 지표 가까이에서 산화되었고, 황산열수용액에 의해 형성되어졌음을 시사한다.

변질암의 광물학적, 화학적 변화에 대하여는 여러가지 방법으로 검토하였고, 특히, 56개의 변질암에 대한 화학조성은 습식분석과 XRF로써 분석하였다. 이러한 분석자료들을 기초로 하여 고찰한 결과 거의 모든 원소가 원암으로부터 이동되었다고 사료된다.

광상의 형성온도는 석영대로부터 얻은 시료의 유체포유물 연구로부터 200 이상임이 판명되었다. 변질대의 광물조성과 암석의 화학 성분으로 보아 성산광산을 형성한 열수용액은 $m_{\text{K}^+}=0.003$, $m_{\text{Na}^+}=0.097$, $m_{\text{SiO}_2(\text{aq})}=0.008$ 및 $\text{pH}=5.0$ 으로 나타났다.