

Alteration Zoning, Mineral Assemblage and Geochemistry of the Hydrothermal Clay Deposits Related to Cretaceous Felsic Magmatism in the Haenam Area, Southwest Korea

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ABSTRACT: In the present study, three clay deposits, named the Seongsan, Ogmaesan and Haenam deposits, were investigated. The altered zones are recognized in the hydrothermally altered rocks of the clay deposits from the center of the alteration to the margin: Kaolin, Kaolin-Quartz, Quartz, Sericite and Chlorite zones in the Seongsan deposits; Quartz zone, Alunite zone, Kaolin zone, Sericite zone and Chlorite zone in the Ogmaesan deposits; Quartz zone, Pyrophyllite zone, Sericite zone and Chlorite zone in the Haenam deposits. These zones can be grouped into two types of alteration: Acidic alteration such as Pyrophyllite zone, Alunite zone, Quartz zone, Kaolin zone, Kaolin-Quartz zone and a part of Sericite zone; Propylitic alteration such as Chlorite zone and a part of Sericite zone. All clay deposits belong to high-sulfidation (acid-sulfate) system. The rocks of the acidic alterations are composed of pyrophyllite, alunite, kaolin minerals, sericite, quartz and pyrite.

On the basis of bulk chemical compositions, it was found that some components such as SiO_2 , TiO_2 , Fe_2O_3 , FeO , MgO , CaO , K_2O and Na_2O were mobilized considerably from the original rocks. The mobility of these major elements is related to, and controls, mineral assemblages in each altered zone.

Polytypes of sericite are determined as $2M_1$ and $1M$ by X-ray diffraction method. The amount of $2M_1$ is nearly equal to that of $1M$ in the Seongsan deposits whereas $2M_1$ is less and higher than that of $1M$ in the Ogmaesan and the Haenam deposits. These facts indicate that formation temperature of sericite is relatively high in the Haenam deposits, moderate in the Seongsan deposits, and low in the Ogmaesan deposits. The ratios of $\text{Na}/(\text{K}+\text{Na})$ for alunite in the Ogmaesan deposits determined by electron microprobe analyzer (EPMA) are higher than those in the Seongsan deposits. Thus, the alunite of the Ogmaesan deposits must have been formed from the solutions with relatively high aqueous $\text{Na}/(\text{K}+\text{Na})$ ratios and low pH at a high temperature rather than that of the Seongsan deposits.

From all data, it is clarified that alunite is hypogene in origin, and has been formed by oxidation of hydrogen sulfide in the steam-heated environment, and that alunite has been produced by the spectacular solfataric alteration observed at the surface of some present-day hydrothermal systems.

INTRODUCTION

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.

Recently, hydrothermal systems are classified into high sulfidation and low sulfidation systems (also termed acid-sulfate and adularia-sericite, respectively, by Heald et al., 1987) by Hedenquist (1987). The

high sulfidation type is characterized by the extreme conditions of very low pH and relatively oxidizing environments (Hemley et al., 1969; Hemley et al., 1980; Rye et al., 1989).

Alunite is unique among common alteration minerals, and contains hydrogen, sulfur, and both hydroxyl and sulfate oxygen. Aoki (1990) suggested that sulfur in alunite is exchanged by phosphorus ion in some cases. Alunite is recently used for stable isotope study (Rye, 1989) and K-Ar age determination (Tingley and Berger, 1985).

Most of the clay deposits, which are included in Cretaceous volcanic rocks, are distributed in the southwestern and the southeastern parts of the Korean Peninsula. The study area is located in the Haenam area, southwestern part of Korean Peninsula. A large number of the hydrothermal clay deposits including the Seongsan, Ogmaesan and

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Haenam deposits in the area are generally considered to be genetically related to Cretaceous felsic magmatism. Since the clay deposits of the area were first described by Kinoshita (1935), many revisions on geology and genesis of the clay deposits in the area, have been made by numerous geologists. Recently, there are many workers who have been studied to the hydrothermal clay deposits. For example, mineralogical (Cho and Kim, 1989; Kim, 1989 and 1991) and geochemical (Cheong and Chon, 1989 and 1990; Kim, 1989 and 1991) studies were reported. Kim (1989, 1990a, 1990b and 1991) has described alteration zoning and fluid inclusion study. Cheong and Chon (1990), Kim et al. (1990) and Kim (1991) discussed oxygen isotope study. Sulfur isotope study of the clay deposits were reported by Kim et al. (1990), Chon et al. (1991) and Kim (1992b). In the present work, the author studied alteration zoning, mineral assemblages, and chemical compositions of alunite and altered rocks of the clay deposits from three mines. The regional variation of those of the clay deposits is of great interest from the viewpoint of formation mechanism of the hydrothermal clay deposits.

The purposes of the present investigation are to obtain detailed mineralogical and chemical data for the altered rocks and to describe alterations of each rock type in these deposits.

OUTLINE OF GEOLOGY AND ORE DEPOSITS

Geology

The Haenam area consists of Precambrian metamorphic rocks, Jurassic and Cretaceous granitic rocks and Cretaceous volcanic rocks. The geological map and cross sections of the area are shown in Fig. 1. The study area belongs to the southwestern part of the Youngdong-Kwangju Depression Zone (Lee, 1987). The geology was detailed studied by Kim (1991, 1992a and b). The geology of the area is briefly described as follows.

Precambrian Metamorphic Rocks

These rocks are distributed in the western and eastern parts of the area. In the western part of the area, they occur in fault contact with Cretaceous volcanic rocks such as Hwawon Formation. They are intruded by Jurassic and Cretaceous granitic rocks, and are unconformably covered by Cretaceous volcanic rocks in the eastern part of the area. They

are composed mainly of biotite gneiss and mica schist.

Jurassic Granitic Rocks

These rocks are distributed in the central and eastern part of the area. They intruded Precambrian metamorphic rocks, and are unconformably covered by Cretaceous volcanic rocks, and are intruded by Cretaceous granitic rocks. The rocks are called Weolgagsan granite. K-Ar ages of 140.9 and 144.8 Ma on biotite separated from the Weolgagsan granite were reported by Kim (1991). They composed of hornblende-biotite, biotite and two mica granites.

Cretaceous Volcanic Rocks

These rocks are widely distributed in the area, and have suffered extensive propylitization, and in some places have undergone strong hydrothermal alterations producing clay deposits. The rocks are divided into three formations in the present study: Hwawon, Hwangsan and Jindo Formations. Hwawon Formation is distributed in the western part of the area and covers Precambrian rocks with unconformity. The name of the Formation is derived from its distribution mostly at the Hwawon peninsula. The Formation is divided into the Hwawon basalt and Inji andesite. According to the classification of the stage on volcanic activity by Moon et al. (1990), the Inji andesite belongs to the first stage, and K-Ar age of andesite gives 94.1 Ma. But, Kim (1991) reported the ages of Hwawon Formation as follows: Hwawon basalt gives 101.9 and 103.4 Ma, and Inji andesite 92.7 and 95.4 Ma. The Formation is about 500 meters in maximum thickness. Hwangsan Formation is the most widely distributed Cretaceous volcanic rocks in the area. According to the classification of the stage on volcanic activity by Moon et al. (1990), the Formation belongs to the second stage, and the age of the Formation gives 79.4 and 82.8 Ma. But, Kim (1991) reported the ages of Hwangsan Formation as follows: Hwangsan dacite gives 84.5 to 86.4 Ma and Weolho rhyolite Jindo Formation is distributed in the northwestern and southwestern parts of the area, and conformably overlies Hwangsan Formation. The Formation is divided into the Samji tuff, Jindo rhyolite and Gaji tuff with ascending order. Kim (1991) reported the ages of Jindo Formation as follows: Samji tuff gives 73.9 to 76.3 Ma, Jindo rhyolite 72.5 to 75.4 Ma and Gaji tuff 66.2 to 70.9 Ma. The total thickness of the

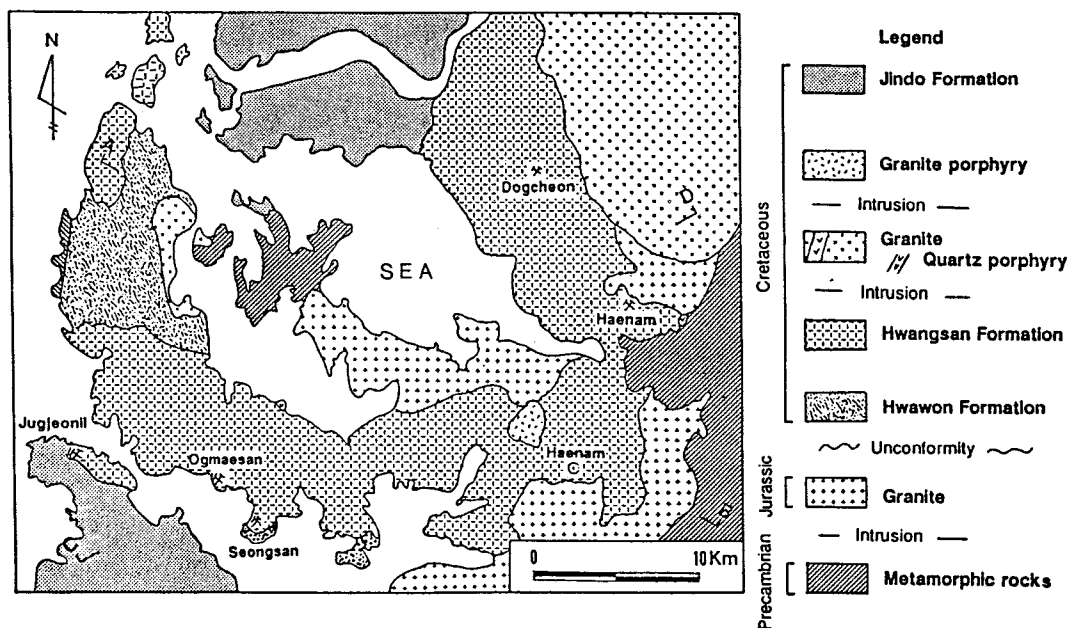


Fig. 1. Geological map of the Haenam area.

Formation is about 600 m.

Cretaceous Granitic Rocks

These rocks are mainly distributed in the eastern and western parts of the area. The rocks are divided into Jiyoungsan granite, Weolchulsan granite, Weolgangdu quartz porphyry and Jangseong granite porphyry. Jiyoungsan Granite is distributed in the western part of the area, and intrudes Hwawon Formation. Jiyoungsan granite at Mt. Ilseong retains K-Ar ages of 67 Ma (Lee and Lee, 1976) and 81.5 Ma (Kim, 1991). It is composed of hornblende-biotite and granites. Weolchulsan Granite is distributed in the eastern part of the area, and intrudes Precambrian basements, Weolgagsan Jurassic granite and Hwangsan Formation. Kim (1991) reported that K-Ar ages of K-feldspar and whole rock of Weolchulsan granite show 77.0 and 81.2 Ma. Weolgangdu Quartz Porphyry is distributed widely in the area, and intrude Hwangsan Formation as small stocks. Weolgangdu quartz porphyries at locality retain the ages of 63 Ma (Lee and Lee), 79.6 Ma (Moon et al., 1990) and 75.0 to 77.9 Ma (Kim, 1991). The rock shows typical porphyritic texture. Jangseong Granite Porphyry occurs in the central part of the area. Kim (1991) reported that Jangseong granite porphyry gives 71.8 Ma. It intrudes Weolgagsan Jurassic granite and Hwangsan Formation.

Ore Deposits

Representative clay deposits in the southwestern part of Korea include Seongsan, Ogmaesan, Haenam and Dogcheon mines in the Haenam area, Gushi mine in the Hyounsansan area, Jugjeonil mine in the Jindo island, Nohwa, Wando and Gwangmyoung mines in the Nohwa island, Jangsan mine in the Jangsan island, and Gasa mine in the Gasa island. These deposits can be classified into two types as Pyrophyllite and Kaolin types. Pyrophyllite type includes Haenam, Dogcheon, Gushi, Nohwa, Wando and Gwangmyoung mines, and Kaolin type includes Seongsan, Ogmaesan, Jugjeonil, Jindo, Jangsan and Gasa mines. Most of these deposits are considered to be genetically related to Cretaceous felsic magmatism and are distributed in the Cretaceous volcanic rocks.

These clay deposits were studied by numerous geologists. These deposits have different mineral assemblages, zoning patterns and zonal structures. In the present study, four representative deposits, such as the Seongsan, Ogmaesan, Haenam and Dogcheon mines, were investigated. These clay deposits retain the ages of 71.8 to 76.6 Ma (Moon et al., 1990) and 78.1 to 81.4 Ma (Kim, 1991). They can be grouped into two types based on the mineral assemblages: Kaolinite type deposits includes Seongsan and Ogmaesan mines, and pyrophyllite type deposits is

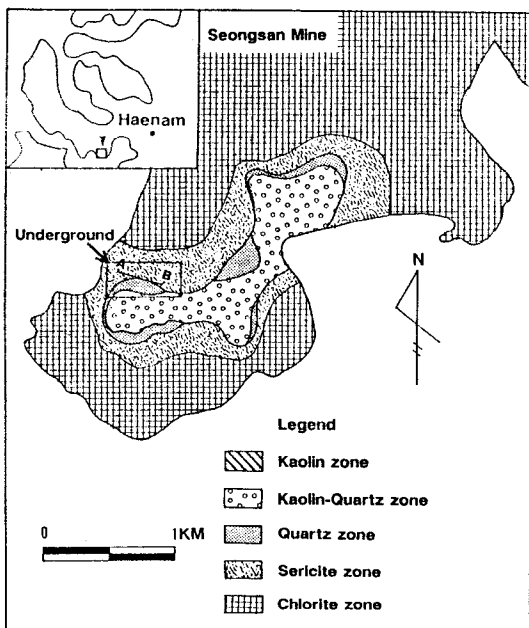


Fig. 2. Alteration zoning map of the Seongsan mine area.

Haenam and Dogcheon mines. Center of zone in the Seongsan clay deposits is Kaolin zone, whereas that in the Ogmæsan clay deposits is Quartz zone. This fact indicates that two deposits were formed by different conditions. Therefore, though two deposits are included in a same Kaolinite type, each deposit can be classified into different subgroup.

MODE OF OCCURRENCE OF CLAY DEPOSITS

Seongsan Mine

The Seongsan mine, which is producing about 5,000 tons/month of dickite ore, is one of the largest dickite deposits in Korea, and is located in the southwestern part of the area. Most parts of the Hwangsans Dacite, host rocks of the deposits, have suffered strong hydrothermal alteration. A fault trending N70°W is developed in the Seongsan mine area. A number of minor faults less than several meters in length showing NW-SE trend develop around the large fault.

The main constituent minerals of the ore are dickite and quartz, while the accessory minerals are alunite, kaolinite and sericite. The alteration zoning in the Seongsan mine area is shown in Fig. 2. The relationship between the stratigraphy of the felsic volcanic rocks and the hydrothermal alteration, was

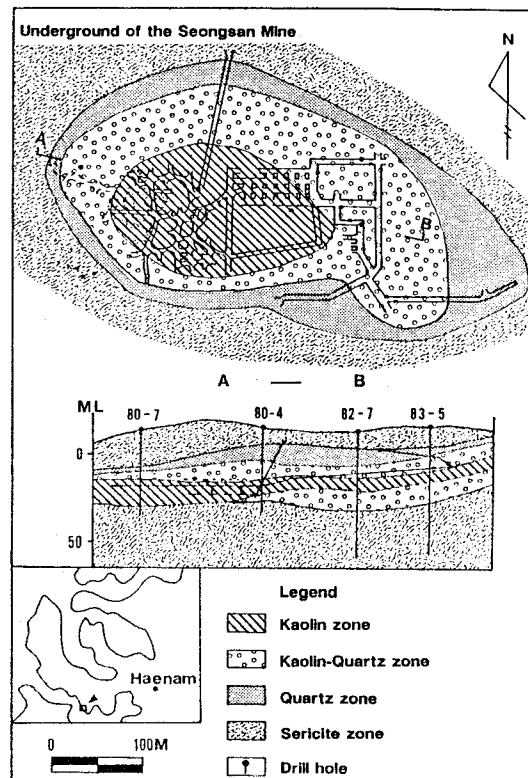


Fig. 3. Alteration zoning map of the underground in Fig. 2.

studied at the point A in Fig. 2, and is shown in Fig. 3. Table 1 shows the mineral assemblage of each altered zone.

The hydrothermally altered rocks can be classified into the following zones by optical and X-ray diffraction (XRD) methods (Nikane, 1964): Kaolin, Kaolin-Quartz, Quartz, Sericite and Chlorite zones, from the center to the margin of the alteration zone. Dickite ore is from Kaolin and Kaolin-Quartz zones. Kaolin zone, Kaolin-Quartz zone, Quartz zone and a part of Sericite zone are developed vertically rather than horizontally, and are classified as Acidic zone in this paper, while Chlorite zone and a part of Sericite zone are developed horizontally rather than vertically, and are classified as Propylitic zone in this paper. This zonal arrangement is well explained in the description by Utada (1980). Two different Sericite zones are very difficult to be distinguished at the outcrop. The characteristics of each altered zone are described as follows.

Acidic zone

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

Table 1. Mineral assemblages in each altered zone from the Seongsan mine.

	CZ	SZ	QZ	KQZ	KZ
Quartz	+	+	++	+	
Pyrite	+	+	+	+	+
Kaolin				+	++
Alunite			-	-	-
Sericite	+	++			
Albite	++	-			
K-feldspar	+	+			
Chlorite	+				
Calcite	++				
Epidote	-				

Abbreviations: CZ; Chlorite zone, SZ; Sericite zone, QZ; Quartz zone, KQZ; Kaolin-Quartz zone, KZ; Kaolin zone, -; Rare, +; Moderate or a little, and ++; Abundant.

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 dacite, welded tuff and small amounts of rhyolite in Hwangsan Formation. The original textures are not well preserved in strongly altered rocks, although flow textures in dacite are sometimes found. Vein-like shaped pure sericites have been found sometimes in this zone. This zone is the center of the hydrothermal alteration activities based on the concentric distribution of the alteration zones.

The Kaolin-Quartz zone generally occurs at the margin of the Kaolin zone. The rocks in this zone are white and pale-reddish white in color, and are mainly composed of dickite, kaolinite and quartz. Small amounts of alunite and pyrite are observed. This zone is divided into two subzones. One is characterized by the occurrence of spotted quartz, while the other is characterized by compact and massive quartz. The former is produced from welded tuff, whereas the latter is formed from dacite of Hwangsan Formation.

The Quartz zone generally occurs at the margin of the Kaolin-Quartz zone. The rocks in this zone are white in color, and are composed of quartz and small amounts of dickite and alunite. This zone is further divided into sugar Quartz zone and hard Quartz zone. The sugar Quartz zone is found in the underground of the mine. Most rocks from this zone are porous and white to grayish white. Very porous rocks having numerous small holes of several millimeters in diameter are developed in some parts. Hydrothermal breccia was found in one part. The

hard Quartz zone is also found in the underground and at outcrop of the surface. The rocks from this zone are mainly composed of fine-grained quartz, in which pyrite is often disseminated. Alunite is also found in this zone. This kind of hydrothermally altered siliceous rock is called occasionally secondary quartzite (Kashkai, 1961; Toan, 1981).

The rocks in the Sericite zone are pale greenish white, yellowish white or whitish grey in color, and are mainly composed of sericite and quartz, and small amounts of pyrite. Crystalline pyrite is often found. Although feldspar grains are replaced by fine-grained sericite and quartz, their original shapes can be recognized under the microscope. Polytypes of sericite are determined as $2M_1$ and the amount of $2M_1$ is almost equal to that of $1M$. Sometimes, the diffraction pattern of sericite shows a comparatively broad peak with basal spacing of $10.2\sim 10.4\text{\AA}$ which shifts to 10.1\AA by ethylene glycol treatment. This fact indicates that sericite is partly interstratified with smectite layers. Sericite-smectite regularly mixed layer minerals having basal spacing of 25\AA were also recognized. The amount of smectite is smaller than that of sericite.

Propylitic zone

The Sericite zone is distributed in the surrounding of the Acidic zone. The southern part of the Jindo Rhyolite and the Hwangsan Dacite have suffered extensive albitization. The rocks in the zone are pale green or reddish grey in color, and are mainly composed of albite, quartz and sericite, with small amounts of K-feldspar, calcite and chlorite. Polytypes of sericite are also determined as $2M_1$ and $1M$, and the amount of $1M$ is less than that of $2M_1$. Sericite is partly interstratified with smectite and chlorite. Plagioclase is almost completely altered to albite and partly to calcite and sericite. Some calcites are precipitated apart from feldspar grains.

The Hwangsan Dacite occurring in the northern part of the Seongsan deposits is generally weakly propylitized, and is classified as Chlorite zone in this paper. The rocks in this zone are mainly composed 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.

Ogmaesan Mine

The Ogmaesan mine, which is producing about 1,

Table 2. Mineral assemblages in each altered zone from the Ogmaesan mine.

	CZ	SZ	KZ	AZ	QZ
Quartz	+	+	+	+	++
Enargite					-
Pyrite	+	+	+	+	+
Alunite				++	-
Kaolin			++	-	
Sericite	+	++			
Albite	++	-			
K-feldspar	+	-			
Chlorite	+				
Calcite	+				
Epidote	-				

Abbreviations: CZ; Chlorite zone, SZ; Sericite zone, KZ; Kaolin zone, AZ; Alunite zone, QZ; Quartz zone, -; Rare, +Moderate or a little, and ++; Abundant.

000 tons/year of kaolin ore, is one of the alunite-producing deposits in Korea, and is located in the southwestern part of the area. Most parts of the Hwangsan Dacite, host rock of the deposits, have suffered strong hydrothermal alteration. A fault trending N40°W is developed in the Ogmaesan mine area. The main constituent minerals of the ore are alunite, kaolinite and quartz, while the accessory minerals are dickite and sericite. The alteration zoning in the Ogmaesan mine area is shown in Fig. 4. Table 2 shows the mineral assemblage of each altered zone.

Five hydrothermal alteration zones are recognized by the naked eye: they are Quartz, Alunite, Kaolin, Sericite and Chlorite zones, going from the center to outward. They are also divided into Acidic (Quartz, Alunite, Kaolin and a part of Sericite zones) and Propylitic (a part of Sericite and Chlorite zones) zones. The characteristics of each altered zone are described as follows.

Acidic zone

The Quartz zone generally occurs at the center of the deposits. The rocks in this zone are white in color, and are composed of quartz and small amounts of alunite and disseminated pyrite. Most of rocks from this zone are characterized by compact and massive quartz, but sometimes porous quartz is found in this zone. Enargite is found near the porous quartz aggregate in one part. This zone is the center of the hydrothermal alteration activities.

The Alunite zone generally surrounds the Quartz zone. The rocks in this zone are white or pink in color, and are mainly composed of alunite and

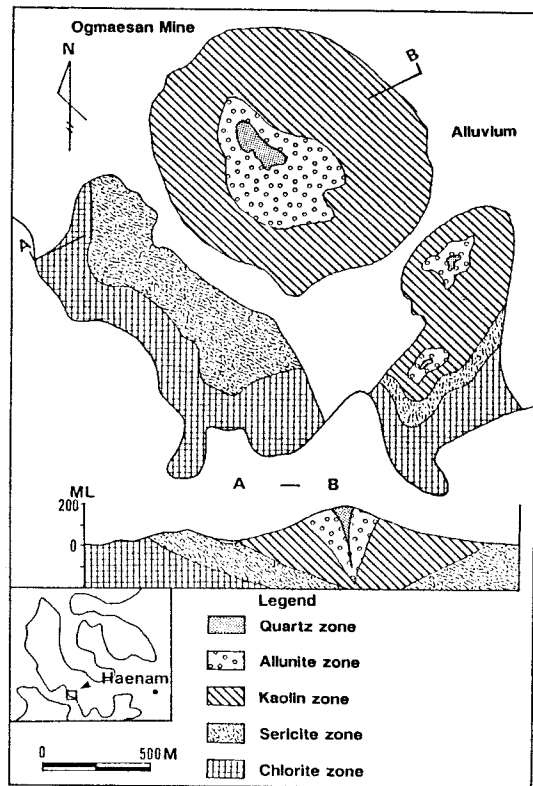


Fig. 4. Alteration zoning map of the Ogmaesan mine area.

quartz with small amounts of dickite, kaolinite and pyrite. Quartz occurs as recrystallized microcrystals. Circular shaped alunite was found in a few places. This zone was formed through alteration of dacite and welded tuff in Hwangsan Formation. The original textures are scarcely preserved.

The rocks in Kaolin zone are white or pink in color, and are mainly composed of kaolinite and quartz. Minor amounts of dickite and pyrite are also observed. This zone was also formed through alteration of dacite and welded tuff in Hwangsan Formation. The original textures are not well preserved in strongly altered rocks, although flow textures in dacite and bubble wall textures in welded tuff are sometimes found.

The rocks in the Sericite zone are pale greenish white, yellowish white or whitish grey in color, and is mainly composed of sericite and quartz, and small amounts of pyrite and K-feldspar. Pyrite is mostly disseminated with sericite. Although feldspar grains are replaced by fine-grained sericite and quartz, their original shapes can be recognized under the microscope. Polytypes of sericite are determined as

Table 3. Mineral assemblages in each altered zone from the Haenam mine.

	CZ	SZ	PZ	QZ
Quartz	+	+	+	++
Pyrite	+	+	+	+
Pyrophyllite			++	+
Diaspore			-	-
Sericite	+	++	-	-
Albite	++	-		
K-feldspar	+	-		
Chlorite	+			
Calcite	+			
Epidote	+			

Abbreviations: CZ; Chlorite zone, SZ; Sericite zone, QZ; Quartz zone, PZ; Pyrophyllite zone, -; Rare, +; Moderate or a little, and ++; Abundant.

2M₁ and 1M, and the amount of 1M is more than that of 2M₁. Sericite is illitic minerals, and is interstratified with smectite.

Propylitic zone

Propylitic zone of Ogmæsan deposits is almost same as that of Seongsan deposits. Samji Tuff in the southern part of this deposits, however, is weakly propylitized.

Haenam Mine

The Haenam mine, which is producing about 1,500 tons/month of pyrophyllite and sericite ores, is one of the large pyrophyllite-producing deposits in Korea, and is located in the northeastern part of the area. Most parts of the Hwangsan Dacite have suffered strong hydrothermal alteration around the deposits. A fault trending N45°W is developed in this area. The main constituent minerals of the ore are pyrophyllite, sericite and quartz, while the accessory minerals are diaspore and pyrite. The alteration zoning in the Haenam mine area is shown in Fig. 5. Table 3 shows the mineral assemblage of each altered zone.

The hydrothermally altered rocks can be classified into the following zones: Quartz, Pyrophyllite, Sericite and Chlorite zones from the center to the margin of the alteration. They are also divided into Acidic (Quartz, Pyrophyllite and a part of Sericite zones) and Propylitic (a part of Sericite and Chlorite zones) zones. The characteristics of each altered zone are described as follows.

Acidic zone

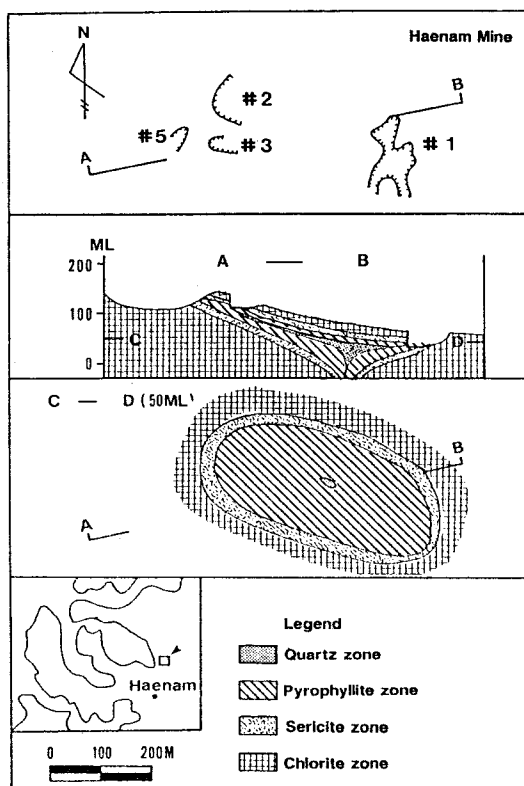


Fig. 5. Alteration zoning map of the Haenam mine area.

The Quartz zone occurs at the center of the Acidic zone. The rocks in this zone are white in color, and are composed of quartz, and small amounts of pyrophyllite, diaspore and pyrite. Quartz in this zone is fine-grained, and makes compact and massive rocks. Pyrite is often disseminated in them with diaspore.

The rocks in the Pyrophyllite zone are grayish white, pale green and dark green in color, and are mainly composed of pyrophyllite. Small amounts of quartz, diaspore, sericite and pyrite are observed. This zone was formed through alteration of dacite and welded tuff in Hwangsan Formation. Although feldspar grains are replaced by very fine grained pyrophyllite in this zone, their original shapes can be often recognized under the microscope. When matrix is replaced strongly by pyrophyllite, however, the original shapes of feldspar grains are not well preserved.

The rocks in the Sericite zone are pale greenish white, yellowish white or whitish grey in color, and are mainly composed of sericite and quartz, and small amounts of albite. Although feldspar grains are

replaced by fine-grained sericite and quartz, their original shapes can be recognized under the microscope. Polytypes of sericite are determined as $2M_1$ and $1M$, and the amount of $2M_1$ is more than that of $1M$. Sometimes, sericite is partly interstratified with smectite layers.

Propylitic zone

Propylitic zone of Haenam deposits is almost the same as that of other deposits.

The Sericite zone is distributed in the surrounding of the Acidic zone. Hwangsan Dacite and Weolho Rhyolite around the deposits have suffered extensive albitization. The rocks in the zone are pale green or reddish grey in color, and are mainly composed of quartz and sericite, with small amounts of K-feldspar, albite and calcite. Polytypes of sericite are also determined as $2M_1$ and $1M$, and the amount of $2M_1$ is almost equal to that of $1M$. Sericite is partly interstratified with smectite. Plagioclase is almost completely altered to albite and partly to calcite and sericite. Some calcites precipitated apart from feldspar grains.

The Hwangsan Dacite and Weolho Rhyolite around the Haenam deposits are in general propylitized. The rocks in the Chlorite zone are mainly composed 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 biotites are chloritized, but the original shape of biotite is preserved.

CHEMICAL COMPOSITION OF ALUNITE AND ALTERED ROCKS

Analytical Procedure

Electron microprobe analyzer (EPMA): The chemical compositions of minerals were analyzed by an EPMA (JEOL JCMS 733 markII) of the Geological Institute, Faculty of Science, University of Tokyo, following the procedure outlined by Nakamura and Kushiro (1970). Operating conditions were 15 kV accelerating voltage and 1.2×10^{-8} Å beam current. The analysis of alunite broad electron beams (about 5 to 40 mm in diameter) were used with background deduced from mean atomic number, with calibration procedure by following the correction procedure after Bence and Albee (1968) using alpha factors given in Nakamura and Kushiro (1970).

X-ray fluorescence spectrometer (XRF): Analytical procedure of altered rocks by XRF is almost the same as those of whole-rock geochemistry.

Variations of chemical composition of fifty-six altered rock samples from the Seongsan deposits, of twenty-eight altered rock samples from the Ogmaesan deposits and of thirty-three samples from the Haenam deposits were determined by X-ray fluorescence spectrometer (XRF) analysis using Rigaku IKF 3064KF, Geological Institute, Faculty of Science, University of Tokyo. For analyses, 1 g of dried rock-powder was mixed with flux. Rock powder-flux ratio was 1:5 in weight. Other procedures are the same as those of whole-rock geochemistry. 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 XRF method just mentioned, were also analyzed with wet chemical analysis method with the instruction by Mr. Haramura.

Chemical Composition of Alunite

Alunite is unique among common alteration minerals because it contains both hydroxyl and sulfate. Alunite group minerals show a wide range substitution of components. They have general chemical formula, $KAl_3(SO_4)_2(OH)_6$. K ion is exchanged by Na, Ca or ammonium ions (Ossaka et al., 1982; Aoki, 1984; Stephen et al., 1988; Stoffregen and Cygan, 1989). Al ion is replaced by Fe ion (Ripmeester et al., 1986). Aoki (1990) suggested that sulfur is exchanged by phosphorus ion in some case. Recently, alunite can be used for stable isotope study and K-Ar dating.

The composition and structural formula of alunites based on 11 oxygens from the Seongsan and Ogmaesan deposits are shown in Tables 4 and 5. The exchange values of $Na/(K+Na)$ ratios range from 0.005 to 0.101 in the Seongsan deposits, and from 0.035 to 0.317 in the Ogmaesan deposits. Substitution of Fe for Al is negligible. The exchange values of $Na/(K+Na)$ ratios in the Ogmaesan deposits are higher than those in the Seongsan deposits.

Hemley et al. (1969) pointed out that the difficulty of synthesis, and the rarity in nature, of natroalunite, indicate considerably lower stability of Na phase relative to K phase. Therefore, the Ogmaesan alunite must have been formed by solutions with higher $Na/(K+Na)$ ratios. The hydrothermal solutions that deposited high-Na alunite, may be encountered with

Table 4. Representative chemical composition and structural formulae of alunites from the Seongsan mine.

Sample	8705 1701 (10)**	8705 1822 (9)**	8705 1411 (11)**	8610 1904 (15)**	8705 1510 (11)**	8705 1503 (6)**	8705 1505 (9)**	8705 1504 (5)**	8705 1701 (13)**	8705 1628 (21)**	8705 1627 (18)**	8610 1907 (10)**	8610 1905 (15)**
Al ₂ O ₃	37.08	37.46	37.57	36.39	37.78	37.45	37.11	36.81	37.06	36.22	37.09	38.80	37.70
Fe ₂ O ₃	0.15	0.03	0.00	0.19	0.47	0.23	0.00	0.00	0.11	0.10	0.01	0.00	0.01
K ₂ O	10.41	9.94	10.18	10.57	10.30	10.09	9.29	10.17	10.50	9.93	10.90	10.25	9.37
Na ₂ O	0.24	0.44	0.19	0.19	0.34	0.08	0.43	0.37	0.29	0.33	0.04	0.69	0.80
SO ₃	39.09	39.26	39.29	40.54	39.28	39.67	40.12	40.12	38.77	40.04	38.73	38.48	39.27
Total	86.97	87.13	87.70	87.69	87.25	87.52	86.95	87.47	86.73	87.02	86.77	87.50	87.15
Numbers of atoms on the basis of 11 oxygen													
Al	3.006	2.995	3.012	2.929	3.000	2.967	2.946	2.920	3.096	2.993	3.027	3.099	2.952
Fe	0.008	0.002	0.024	0.010	0.000	0.012	0.000	0.000	0.006	0.005	0.001	0.000	0.001
K	0.956	0.928	0.923	0.959	0.913	0.993	0.926	0.902	0.998	0.993	0.998	0.837	0.942
Na	0.032	0.058	0.026	0.025	0.045	0.010	0.057	0.049	0.040	0.044	0.005	0.093	0.106
S	2.018	2.031	2.005	2.078	2.036	2.052	2.078	2.077	2.009	2.078	2.012	1.994	2.063
Total	6.025	6.014	5.990	6.068	5.994	6.034	6.007	5.948	6.139	6.042	6.043	6.023	6.064
Na/K+Na	0.030	0.060	0.030	0.030	0.050	0.010	0.050	0.050	0.040	0.040	0.010	0.100	0.100

Contents are wt.% determined by EPMA.

* Total Fe as Fe₂O₃. ** Number of analyses.

Table 5. Representative chemical composition and structural formula of alunites from the Ogmaesan mine.

Sample	8610 1607 (11)**	8910 1806 (8)**	8910 1502 (5)**	8910 1807 (11)**	8910 1504 (30)**	8910 1603 (10)**	8910 1803 (9)**	8910 1905 (13)**	8910 1816 (15)**	8910 1818 (17)**	8910 1608 (7)**	8910 1906 (5)**	8910 1804 (11)**
Al ₂ O ₃	34.60	35.08	35.78	35.57	35.29	35.54	34.86	34.78	35.07	37.13	35.53	35.36	34.59
Fe ₂ O ₃ *	0.07	0.05	0.05	0.00	0.00	0.03	0.00	0.04	0.04	0.07	0.05	0.10	0.00
K ₂ O	10.60	7.67	7.04	7.99	10.56	10.03	9.50	11.60	9.96	8.27	8.74	10.21	9.74
Na ₂ O	0.82	1.90	2.15	1.58	0.25	0.34	0.24	0.46	0.67	1.67	1.40	0.33	0.40
SO ₃	40.23	38.93	39.15	38.59	40.84	41.00	40.45	39.27	40.07	39.47	39.53	39.93	40.94
Total	86.37	83.63	84.17	84.73	86.96	86.00	85.51	86.27	85.97	86.61	85.32	86.00	85.69
Numbers of atoms on the basis of 11 oxygen													
Al	2.804	2.905	2.932	2.904	2.944	2.902	2.946	2.849	2.843	2.906	2.898	2.874	2.913
Fe	0.004	0.003	0.003	0.000	0.000	0.002	0.000	0.002	0.002	0.007	0.003	0.006	0.000
K	0.930	0.687	0.624	0.706	0.950	0.909	0.907	1.028	0.874	0.725	0.772	0.898	0.885
Na	0.087	0.259	0.290	0.212	0.035	0.046	0.033	0.049	0.071	0.214	0.188	0.044	0.056
S	2.076	2.053	2.043	2.058	2.029	2.051	2.036	2.048	2.068	2.022	2.054	2.066	2.053
Total	5.904	5.907	5.892	5.880	5.959	5.916	5.923	5.983	5.869	5.874	5.919	5.894	5.907
Na/K+Na	0.090	0.270	0.320	0.230	0.020	0.050	0.040	0.050	0.080	0.230	0.200	0.050	0.060

Contents are wt.% determined by EPMA.

* Total Fe as Fe₂O₃. ** Number of analyses.

halite-rich beds in the sedimentary rocks, and may not have experienced sufficiently higher temperatures so that the Na/(K+Na) ratio in the solution did not increase by the exchange with the volcanic host rocks.

Chemical Analysis of Specimens from Clay Deposits

Because Al₂O₃ content is comparatively constant in the altered zones except for the Clay zones

(Pyrophyllite zone, Alunite zone, Kaolin zone, Kaolin-Quartz zone, Quartz zone and Sericite zone), Al_2O_3 seems to be an inert component in these zones. Assuming that Al_2O_3 has not undergone any significant mobilization, the contents of various components with respect to Al_2O_3 were plotted in order to investigate the mobility of each component.

Seongsan mine

Results of the chemical analyses are shown in Table 6. Oxide-variation diagrams plotted against the Al_2O_3 contents are shown in Fig. 6. The chemical variations of the major components in the altered zones are summarized as follows:

SiO_2 content is 68~87 wt.% in the Chlorite zone, Sericite zone and Kaolin-Quartz zone. It goes up to 98~99 wt.% in the Quartz zone. Then it decreases to 43~48 wt.% in the Kaolin zone. Except for the Quartz, Kaolin-Quartz and Kaolin 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 wt.%. It increases to 10~21 wt.% in the Kaolin-Quartz zone, and Al_2O_3 content of the Kaolin zone is more than 36 wt.%. CaO content is less than 0.3 wt.% throughout most of the zones, except for the Chlorite zone. In the Chlorite zone, some rocks have CaO content more than 0.3 wt.%. Fe_2O_3 content, which means total iron as mentioned above, is about 1~3 wt.% in the Chlorite and Sericite zones. It decreases to less than about 1 wt.% in the Quartz, Kaolin-Quartz and Kaolin zones. Except for the Chlorite zone, Na_2O content is less than 0.3 wt.%. It increases more than 2 wt.% in the Chlorite zone. K_2O content is 3~4 wt.% in the Chlorite zone. It increases to 4~9 wt.% in the Sericite zone. Then it decreases to less than 0.5 wt.% in the Quartz, Kaolin-Quartz and Kaolin zones. MgO content is less than 0.3 wt.% throughout most of the zones, except for the Chlorite zone. MgO content of the Chlorite zone is within the range of 0.3~0.6 wt.%. Ignition loss is less than 3 wt.% throughout most of the zones, except for the Kaolin-Quartz and Kaolin zones. It increases to 4~9 wt.% in the Kaolin-Quartz zone, and comes up to 10~14 wt.% in the Kaolin zone. P_2O_5 content is less than 0.1 wt.% in Quartz, Sericite and Chlorite zones. It increases to 0.1~0.15 wt.%, and comes up to 0.1~0.3 wt.%. MnO and TiO_2 contents were less than about 1 wt.% throughout all of the zones, and do not show any remarkable tendency.

Ogmaesan mine

Results of the chemical analyses are shown in Table 7. Oxide-variation diagrams plotted against the Al_2O_3 contents are shown in Fig. 7. The chemical variations of the major components in the altered zones are summarized as follows:

SiO_2 content is 74~80 wt.% in the Chlorite and Sericite zones. It decreases to 43~81 wt.% in the Kaolin zone, and further decreases to 12~69 wt.% in the Alunite zone. Then it goes up to 96~98 wt.% in the Quartz zone. Al_2O_3 content is in the range from 10 to 14 wt.% in the Chlorite and Sericite zones. It increases to 12~41 wt.% in the Kaolin and Alunite zones. Al_2O_3 content of the Quartz zone is less than 2 wt.%. CaO content is less than 0.1 wt.% throughout most of the zones, except for the Chlorite zone. Some rocks in the Chlorite zone have CaO content more than about 2 wt.%. Fe_2O_3 content, which means total iron as mentioned above, is more than 1 wt.% in the Chlorite and Sericite zones. It decreases to less than about 1 wt.% in the Kaolin, Alunite and Quartz zones. Except for the Chlorite and Sericite zones, Na_2O content is less than 0.3 wt.%. It increases to 1~2 wt.% in the Sericite zone, and increases to more than 4 wt.% in the Chlorite zone. K_2O content is 2~4 wt.% in the Chlorite zone. It increases to 4~6 wt.% in the Sericite zone, and comes up to 3~10 wt.% in the Alunite zone. Then it decreases to less than about 0.5 wt.% in the Kaolin and Quartz zones. MgO content is less than 0.3 wt.% throughout most of the zones, except for the Chlorite zone. MgO content of the Chlorite zone is about 0.3 wt.%. Ignition loss is less than about 1 wt.% throughout most of the zones, except for the Kaolin and Alunite zones. It increases to 4~17 wt.% in the Kaolin zone, and comes up to 15~45 wt.% in the Alunite zone. P_2O_5 content is less than 0.1 wt.% in Chlorite zone. It decrease to 0.05 wt.% in Sericite zone. It increases to 0.1~0.25 wt.% in Kaolin and Alunite zones. Then decrease to less than 0.5 wt.%. MnO and TiO_2 contents were less than about 0.5 wt.% throughout all of the zones, and do not show any remarkable tendency.

Haenam mine

Results of the chemical analyses are shown in Table 8. Oxide-variation diagrams plotted against the Al_2O_3 contents are shown in Fig. 8. The chemical variations of the major components in the altered zones are summarized as follows:

SiO_2 content is 72~75 wt.% in the Chlorite zone, and it increases to 76~80 wt.% in the Sericite zone. It decreases to 62~81 wt.% in the Pyrophyllite zone. Then it goes up to 91~97 wt.% in the Quartz zone.

Table 6. Chemical composition of altered rocks of clay deposits in the Seongsan mine.

Zone	KZ	KZ	KZ	KZ	KZ	KZ	KQZ	KQZ	KQZ	KQZ	KQZ	KQZ	QZ	QZ
Sample	8610 1902	8705 1515	8705 1602	8705 1626	8706 1507	8705 1408	8610 1903	8610 1906	8705 1306	8705 1508	8705 1616	8706 1503	8801 1204	8705 1611-1
SiO ₂	44.58	47.16	44.31	44.72	43.71	48.68	73.70	85.21	76.45	68.59	69.71	83.57	98.41	99.02
TiO ₂	0.09	0.16	0.11	0.03	0.22	0.18	0.07	0.08	0.04	0.21	0.22	0.20	0.07	0.04
Al ₂ O ₃	40.70	38.94	40.38	40.36	40.83	36.89	19.26	10.24	16.84	21.30	21.75	11.88	0.00	0.00
Fe ₂ O ₃	0.51	0.10	0.46	0.05	0.81	0.05	0.06	0.11	0.10	0.05	0.05	0.41	0.10	0.10
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.01	0.02	0.05	0.03	0.03	0.01	0.00	0.00	0.04	0.04	0.04	0.04	0.00
CaO	0.00	0.01	0.00	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.03	0.01	0.06	0.00
Na ₂ O	0.14	0.00	0.01	0.01	0.07	0.01	0.06	0.13	0.03	0.06	0.01	0.06	0.01	0.01
K ₂ O	0.03	0.04	0.02	0.02	0.04	0.05	0.05	0.00	0.05	0.33	0.05	0.05	0.05	0.05
P ₂ O ₅	0.08	0.21	0.11	0.13	0.30	0.15	0.07	0.10	0.09	0.07	0.13	0.09	0.02	0.02
Ig.loss	14.28	13.54	14.45	14.12	14.42	12.84	6.85	3.55	6.32	9.64	7.70	4.66	1.08	0.72
Total	100.41	100.17	99.87	99.78	100.45	99.42	100.13	99.42	99.84	100.29	100.14	100.97	99.80	99.96
Zone	QZ	QZ	QZ	SZ	SZ	SZ	SZ	SZ	SZ	SZ	SZ	CZ	CZ	CZ
Sample	8705 1514	8705 1611-1	8705 1813	8705 1702	8705 1705	8705 1406	8705 1907	8705 1403	8705 1902	8705 1911	8705 1912	8705 1305	8705 1806	8705 2012
SiO ₂	99.45	98.37	99.63	76.11	76.12	82.95	79.13	82.59	77.19	82.51	80.84	76.32	76.02	72.58
TiO ₂	0.06	0.09	0.07	0.13	0.11	0.09	0.07	0.04	0.03	0.08	0.04	0.15	0.15	0.16
Al ₂ O ₃	0.00	0.00	0.00	13.15	13.54	11.83	11.34	9.14	11.70	12.16	10.94	13.34	13.18	13.52
Fe ₂ O ₃	0.05	0.05	0.41	1.32	1.53	0.15	0.71	0.51	0.91	0.15	0.56	0.91	1.17	1.42
MnO	0.00	0.00	0.00	0.02	0.00	0.02	0.09	0.05	0.00	0.14	0.06	0.11	0.00	0.05
MgO	0.04	0.00	0.00	0.24	0.11	0.11	0.28	0.03	0.05	0.19	0.21	0.31	0.16	0.20
CaO	0.00	0.00	0.01	0.26	0.15	0.20	0.39	0.07	0.00	0.31	0.30	0.30	0.09	0.19
Na ₂ O	0.01	0.01	0.50	0.01	0.01	0.03	0.37	0.24	0.24	0.01	0.23	2.16	2.75	1.98
K ₂ O	0.05	0.05	0.07	4.67	4.23	2.17	6.04	5.81	9.46	3.63	5.75	4.70	4.35	5.47
P ₂ O ₅	0.02	0.02	0.02	0.04	0.04	0.03	0.04	0.04	0.04	0.02	0.03	0.05	0.04	0.05
Ig.loss	0.34	0.60	0.80	3.02	3.60	1.96	1.40	1.08	0.70	0.74	0.72	1.64	2.28	2.16
Total	100.02	99.19	101.06	98.97	99.44	99.54	99.86	99.60	100.34	99.94	99.74	99.99	100.19	100.48
Zone	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ
Sample	8705 1303	8705 1314	8705 1901	8705 1909	8801 2220	8705 1307	8705 1906-1	8705 1309	8705 1906-2	8802 0204-2	8802 0204-1	8801 2015	8802 0214	8705 1302
SiO ₂	75.19	82.27	78.61	80.88	79.07	72.27	75.56	74.45	75.89	74.92	74.88	74.91	76.81	76.80
TiO ₂	0.14	0.04	0.11	0.05	0.06	0.21	0.06	0.14	0.15	0.15	0.17	0.08	0.07	0.06
Al ₂ O ₃	13.20	10.19	11.42	9.38	10.77	14.62	14.46	14.54	13.63	13.95	13.98	14.45	13.73	12.42
Fe ₂ O ₃	1.35	0.07	1.05	0.71	1.13	1.76	0.51	1.58	1.22	1.12	1.56	0.56	0.71	0.05
MnO	0.06	0.00	0.04	0.03	0.08	0.08	0.04	0.05	0.07	0.04	0.05	0.03	0.00	0.00
MgO	0.07	0.01	0.06	0.03	0.03	0.27	0.03	0.46	0.33	0.33	0.32	0.19	0.19	0.03
CaO	0.20	0.05	0.01	0.09	0.21	0.00	0.07	0.41	0.80	0.31	0.03	0.35	0.42	0.25
Na ₂ O	2.11	2.15	2.10	2.10	2.78	4.13	7.47	3.69	3.44	3.85	4.77	4.14	6.03	3.47
K ₂ O	5.18	4.23	4.67	4.59	5.42	3.44	0.13	3.63	4.14	3.40	3.44	4.59	1.59	4.81
P ₂ O ₅	0.02	0.02	0.03	0.03	0.01	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.04	0.02
Ig.loss	1.15	1.04	1.54	0.94	0.84	1.60	1.32	1.40	0.88	1.02	1.07	1.06	0.50	0.60
Total	98.67	100.07	99.66	98.83	100.38	98.34	99.80	100.38	100.59	99.22	100.42	100.39	100.08	98.51

Table 6. Continued.

Zone	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	Pure SZ	Pure SZ	Pure SZ	Pure SZ	Pure SZ	Pure SZ	Pure SZ
Sample	8705 1310	8705 1313	8705 1402	8705 1809	8801 2010	8801 2201	8802 0205-1	8802 0205-2	8610 1808	8706 1510	8706 1512	8705 2511	8705 2513	8705 2514		
SiO ₂	87.43	75.70	73.84	77.75	72.89	72.61	68.60	69.08	46.81	46.24	47.36	48.89	53.18	50.25		
TiO ₂	0.06	0.11	0.09	0.14	0.13	0.24	0.24	0.25	0.19	0.07	0.15	0.60	0.12	0.18		
Al ₂ O ₃	12.24	13.49	14.96	12.33	14.56	15.03	16.06	14.90	37.16	36.36	36.30	234.67	32.71	35.10		
Fe ₂ O ₃	0.86	1.11	1.13	1.34	1.84	2.00		1.57	0.07	0.87	0.88	0.49	0.21	0.17		
MnO	0.08	0.06	0.06	0.08	0.09	0.07	0.07	0.17	0.01	0.13	0.11	0.02	0.03	0.09		
MgO	0.16	0.18	0.28	0.31	0.35	0.55	0.63	0.54	0.09	0.88	0.64	0.39	0.60	0.50		
CaO	0.30	0.31	0.38	0.33	1.42	0.70	1.62	3.32	0.00	0.00	0.00	0.05	0.07	0.05		
Na ₂ O	4.33	4.17	4.56	3.79	3.71	4.19	3.87	3.45	0.30	0.34	0.26	0.00	0.00	0.00		
K ₂ O	3.52	4.29	3.36	3.39	3.49	3.93	4.18	4.08	8.65	8.65	8.64	8.23	8.02	8.59		
P ₂ O ₅	0.03	0.00	0.04	0.04	0.07	0.08	0.09	0.07	0.10	0.05	0.04	0.43	0.03	0.10		
Ig.loss	1.08	0.42	0.96	0.68	1.80	1.62	2.62	3.36	5.76	5.64	5.62	6.07	4.87	4.76		
Total	100.09	99.84	99.66	100.16	99.85	100.86	99.98	100.79	99.14	99.23	99.45	99.84	99.82	99.75		

Abbreviations: KZ; Kaolin zone, KQZ; Kaolin-Quartz zone, QZ; Quartz zone, SZ; Sericite zone, CZ; Chlorite zone, and Ig.loss; Ignition loss. Contents are in wt. %.

Table 7. Chemical composition of altered rocks of clay deposits in the Ogmaesan mine.

Zone	Qz	QZ	AZ	AZ	AZ	AZ	AZ	KZ	KZ	KZ	KZ	KZ	KZ	KZ
Sample	8910 1807	8910 1610	8910 1806	8910 1804	8910 1502	8910 1504	8910 1905	8910 1607	8910 1803	8910 1603	8801 2218	8903 1203-1	8910 1802	8910 1605
Height	1 m	2 m	3 m	4 m	5 m		6 m	7 m		8 m		9 m		
SiO ₂	98.22	96.51	69.32	38.43	22.98	12.29	12.88	43.17	44.51	47.04	58.72	55.98	55.49	79.46
TiO ₂	0.07	0.15	0.32	0.38	0.10	0.03	0.21	0.37	0.00	0.11	0.12	0.28	0.33	0.12
Al ₂ O ₃	0.73	1.72	12.61	24.11	30.21	32.59	30.85	37.96	41.03	38.48	29.81	32.09	32.11	14.53
Fe ₂ O ₃	0.25	0.18	0.03	0.06	0.03	0.05	0.08	0.09	0.01	0.01	0.09	0.11	0.12	0.19
MnO	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.02
CaO	0.00	0.01	0.03	0.02	0.00	0.01	0.03	0.03	0.02	0.01	0.03	0.04	0.05	0.05
Na ₂ O	0.04	0.05	0.21	0.41	0.48	0.27	0.22	0.07	0.04	0.13	0.11	0.11	0.19	0.13
K ₂ O	0.05	0.21	2.93	5.96	7.11	9.09	9.98	0.59	0.45	0.54	0.06	0.07	0.09	0.04
P ₂ O ₅	0.03	0.02	0.11	0.15	0.18	0.13	0.15	0.25	0.17	0.20	0.19	0.15	0.14	0.16
Ig.loss	0.52	0.85	14.95	30.64	38.93	45.54	45.66	17.34	14.07	13.78	10.89	11.43	11.54	4.97
Total	99.93	99.72	100.52	100.17	100.04	100.01	100.06	99.87	100.30	100.30	100.04	100.26	100.07	99.67
Zone	KZ	KZ	KZ	KZ	KZ	KZ	KZ	KZ	SZ	SZ	SZ	CZ	CZ	CZ
Sample	8903 1203-3	8903 1203-2	8910 1902	8910 1602	8910 1903	8910 1503	8910 1805	8906 1705	8910 1202	8903 1204	8801 2217	8903 1205	8801 2216	8903 1201
Height	10 m	11 m	12 m		13 m	14 m	15 m					16 m		
SiO ₂	66.09	71.63	76.53	78.11	81.51	81.01	79.11	70.17	80.07	78.16	77.98	75.00	74.11	74.18
TiO ₂	0.32	0.13	0.09	0.11	0.33	0.25	0.24	0.21	0.09	0.08	0.07	0.17	0.18	0.09
Al ₂ O ₃	24.02	20.61	16.61	15.64	12.81	13.31	14.43	20.49	10.71	12.85	13.78	11.42	13.21	13.74
Fe ₂ O ₃	0.17	0.18	0.09	0.15	0.12	0.11	0.13	0.90	1.14	1.17	1.38	1.63	1.72	1.49
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.07	0.16	0.13	0.11
MgO	0.04	0.00	0.00	0.01	0.02	0.04	0.00	0.07	0.04	0.19	0.27	0.34	0.33	0.15
CaO	0.00	0.01	0.03	0.02	0.04	0.03	0.02	0.02	0.01	0.10	0.11	2.96	2.42	0.22
Na ₂ O	0.43	0.58	0.12	0.05	0.06	0.18	0.29	0.97	0.98	2.11	1.87	4.57	4.31	4.49
K ₂ O	0.05	0.07	0.05	0.04	0.06	0.08	0.10	0.12	6.21	4.79	4.21	2.99	2.71	4.72
P ₂ O ₅	0.14	0.16	0.16	0.13	0.17	0.15	0.14	0.13	0.08	0.05	0.05	0.09	0.08	0.08
Ig.loss	8.98	6.81	5.71	5.63	4.56	4.81	5.23	6.71	1.19	0.60	0.57	0.57	0.52	0.50
Total	100.24	100.18	99.39	99.89	99.69	99.97	99.69	99.79	100.52	100.16	100.36	99.90	99.72	99.77

Abbreviations: QZ; Quartz zone, AZ; Alunite zone, KZ; Kaolin zone, SZ; Sericite zone, CZ; Chlorite zone, and Ig.loss; Ignition loss. Contents are in wt. %.

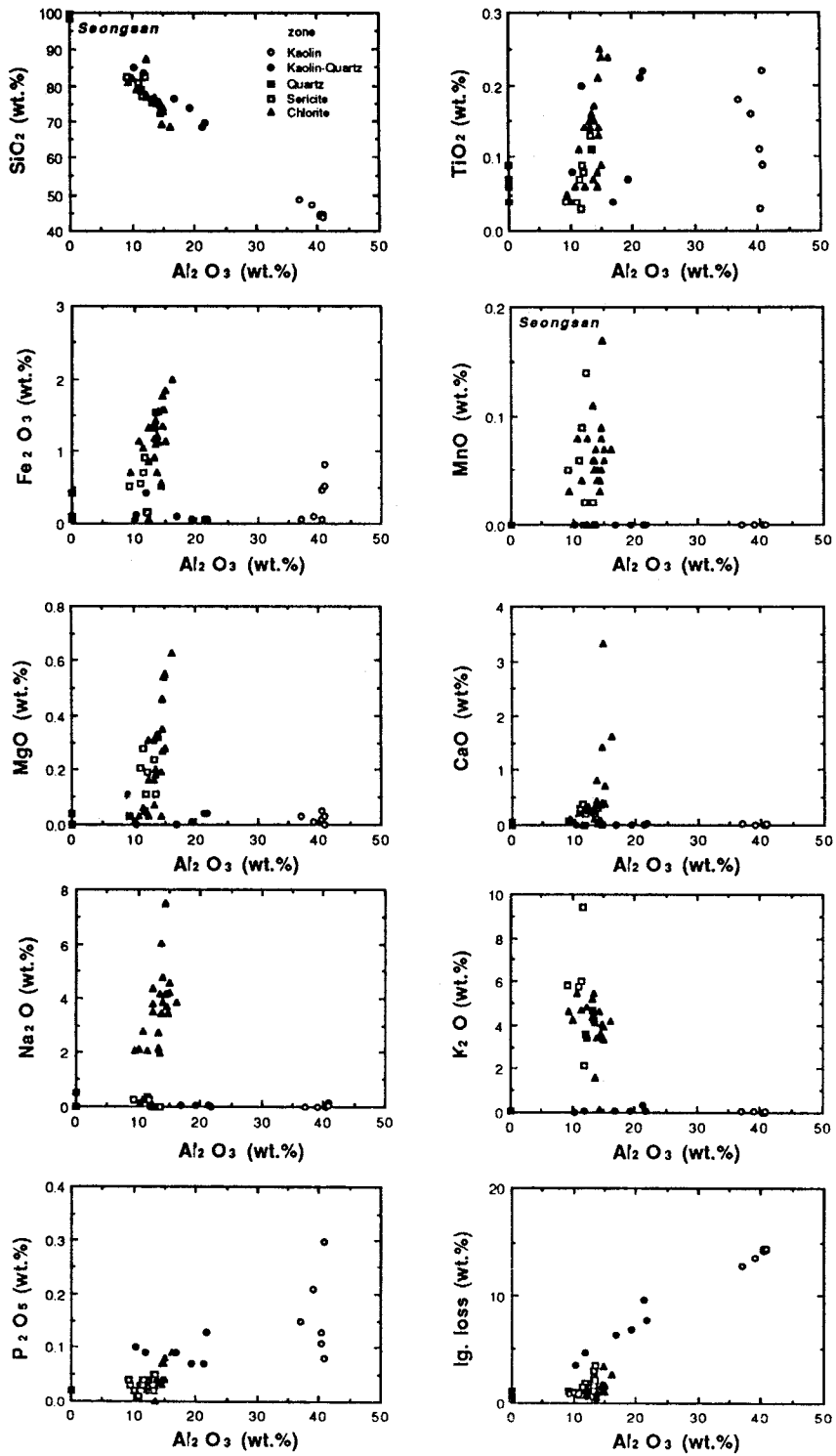


Fig. 6. Oxides vs. Al_2O_3 variation diagrams of altered rocks in the Seongsam mine.

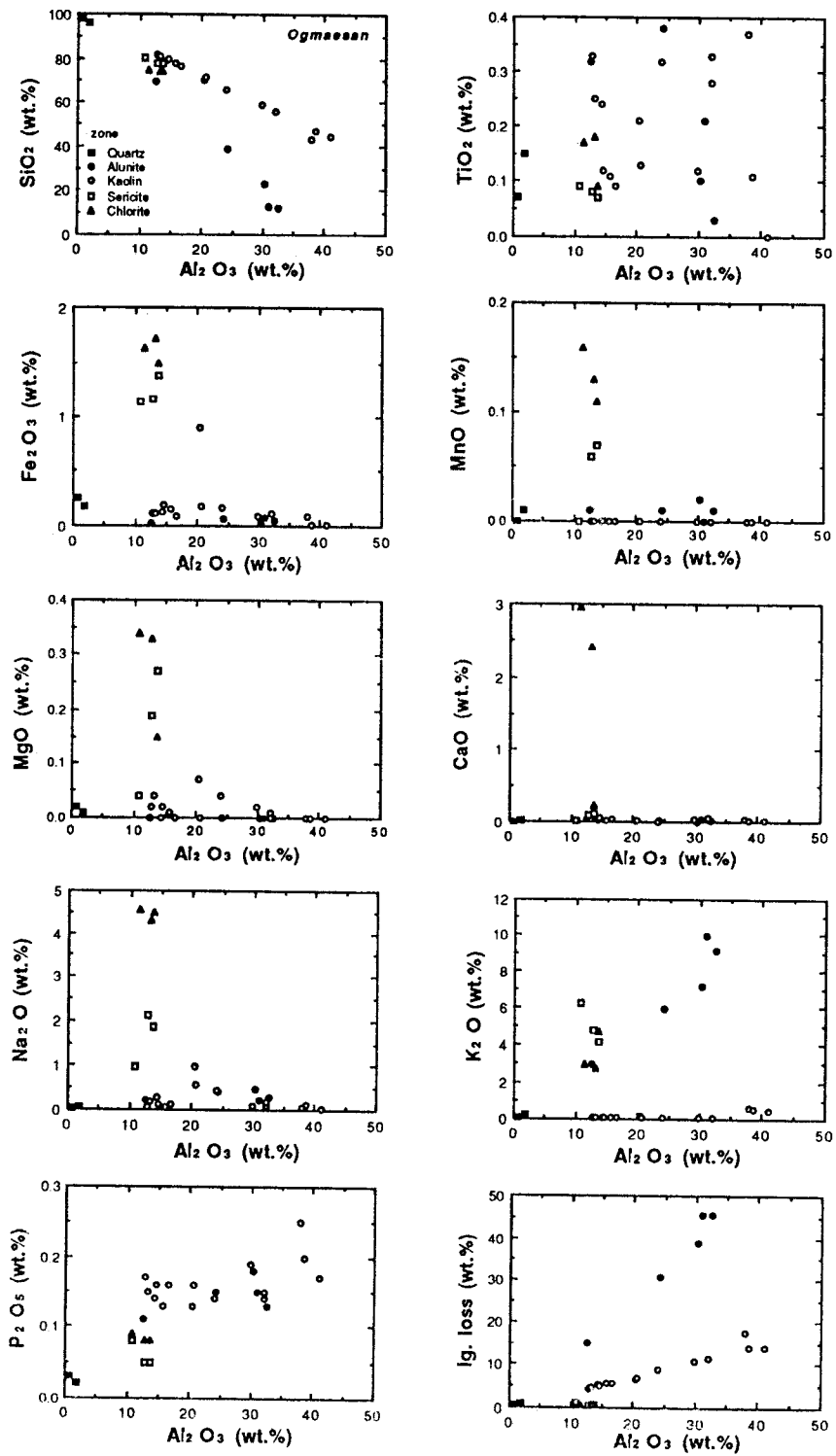


Fig.7. Oxides vs. Al_2O_3 variation diagrams of altered rocks in the Ogmaesan mine.

Table 8. Chemical composition of altered rocks of clay deposits in the Haenam mine.

Zone	QZ	QZ	QZ	PZ	PZ	PZ	PZ	PZ	PZ	PZ	PZ	PZ	PZ	PZ	SZ	SZ	
Sample	8911 0409	8903 1108-1	8911 0301	8903 1108-3	8903 1108-4	8911 0518	8911 0516	8911 0410	8903 1108-2	8903 1108-2	8911 0510	8911 0512	8911 0411	8911 0414	8911 0507	8911 0407	
# = Pit	# 1	# 3				# 3	# 3	# 1			# 3	# 3	# 1	# 1	# 3	# 1	
Height	5 m	4 m				1 m	3 m	4 m			7 m	5 m	1 m	3 m	10 m	10 m	
SiO ₂	97.91	93.42	91.29	62.14	65.26	62.71	75.06	81.41	78.47	74.36	71.82	75.20	62.16	62.45	76.91	76.37	
TiO ₂	0.05	0.09	0.18	0.06	0.07	0.109	0.10	0.15	0.08	0.06	0.09	0.10	0.06	0.08	0.05	0.07	
Al ₂ O ₃	1.12	3.71	5.64	30.91	28.34	30.47	20.36	14.88	16.67	19.40	20.18	17.59	30.11	28.27	15.71	15.30	
Fe ₂ O ₃	0.09	0.17	0.19	0.42	0.68	0.53	0.19	0.06	0.49	0.71	0.55	0.89	0.16	0.76	1.13	0.74	
MnO	0.00	0.00	0.00	0.00	0.00	0.53	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	
MgO	0.00	0.02	0.01	0.10	0.01	0.00	0.00	0.07	0.06	0.04	0.00	0.11	0.02	0.13	0.00	0.10	
CaO	0.00	0.00	0.06	0.00	0.00	0.09	0.05	0.07	0.00	0.00	0.07	0.11	0.05	0.10	0.07	0.06	
Na ₂ O	0.05	0.41	0.31	0.28	0.42	0.09	0.00	0.24	0.12	0.16	0.00	0.00	0.63	0.71	0.00	0.49	
K ₂ O	0.12	0.60	1.45	0.39	0.09	0.24	0.28	0.22	0.55	2.36	3.33	2.68	1.58	2.59	2.94	4.53	
P ₂ O ₅	0.03	0.05	0.01	0.06	0.05	0.07	0.03	0.04	0.05	0.05	0.03	0.02	0.11	0.02	0.02	0.02	
Ig.loss	0.51	0.85	1.02	5.52	4.95	5.53	3.67	2.54	3.09	3.37	3.49	3.62	5.44	5.02	3.18	2.73	
Total	99.88	99.32	100.16	99.88	99.87	99.91	99.65	99.68	99.58	100.51	99.56	100.32	100.32	100.13	100.01	100.43	
Zone	SZ	SZ	SZ	SZ	SZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	CZ	
Sample	8911 0408	8911 0502	8911 0503	8911 3124	8801 3126	8801 0808	8911 3111	8910 3105	8911 4005	8911 0501-2	8910 3112	8911 0810	8911 0501-1	8911 0403	8911 0401	8910 3104	8903 1107
# = Pit	# 1	# 3	# 3						# 1	# 3		# 3	# 1	# 1			
Height	7 m	16 m	14 m						13 m	18 m		19 m	17 m	24 m			
SiO ₂	78.27	78.68	77.68	81.36	80.95	74.04	75.02	74.95	73.69	74.49	72.27	72.68	72.83	73.31	73.49	75.17	73.35
TiO ₂	0.07	0.05	0.07	0.01	0.21	0.05	0.04	0.06	0.21	0.04	0.12	0.06	0.24	0.11	0.14	0.08	0.11
Al ₂ O ₃	13.17	12.78	14.13	12.08	11.60	15.21	14.46	14.74	16.79	15.55	16.28	15.51	15.29	15.12	15.55	13.24	13.37
Fe ₂ O ₃	1.26	1.91	1.83	0.95	0.92	1.98	1.48	1.22	1.98	1.62	1.89	1.29	2.41	1.84	1.62	1.34	1.53
MnO	0.01	0.02	0.01	0.02	0.01	0.04	0.02	0.01	0.03	0.06	0.04	0.03	0.02	0.04	0.06	0.03	0.05
MgO	0.09	0.15	0.08	0.09	0.14	0.23	0.24	0.1	0.27	0.23	0.09	0.05	0.08	0.11	0.02	0.40	0.46
CaO	0.08	0.08	0.04	0.02	0.03	0.08	0.13	0.26	0.15	0.13	0.39	0.43	0.56	0.59	0.33	1.76	1.91
Na ₂ O	0.42	0.00	0.15	0.00	0.00	2.41	2.87	2.16	1.44	2.89	3.79	3.48	3.87	3.13	3.89	5.05	5.97
K ₂ O	3.63	3.49	3.43	3.52	3.53	5.33	5.36	5.16	5.06	4.98	4.28	4.66	4.34	4.98	4.43	2.42	2.74
P ₂ O ₅	0.03	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.03	0.01	0.04	0.02	0.07	0.02	0.01	0.02	0.13
Ig.loss	2.89	3.40	3.08	2.447	2.87	0.79	0.60	0.66	0.71	0.69	0.37	0.49	0.62	0.43	0.30	0.78	0.35
Total	99.92	100.59	100.53	100.51	100.29	100.19	100.24	99.35	100.36	100.69	99.56	98.70	100.33	99.68	99.84	100.29	99.97

Abbreviations: QZ; Quartz zone, PZ; Pyrophyllite zone, SZ; Sericite zone, CZ; Chlorite zone, #1 and #3; Open pit number, and Ig.loss; Ignition loss. Contents are in wt. %.

Al₂O₃ content is in the range from 11 to 16 wt.% in the Chlorite and Sericite zones. It increases to 14~30 wt.% in the Pyrophyllite zone. Al₂O₃ content of the Quartz zone is 1~5 wt.%. CaO content is less than 0.1 wt.% throughout most of the zones, except for the Chlorite zone. Some rocks in the Chlorite zone have CaO content more than about 0.3 wt.%. Fe₂O₃ content, which means total iron as mentioned above, is more than 1 wt.% in the Chlorite and Sericite zones. It decreases to less than about 1 wt.% in the Pyrophyllite and Quartz zones. Except for Chlorite zone, Na₂O content is less than 0.7 wt.%. It increases

more than 2 wt.% in the Chlorite zone. K₂O content is 2~5 wt.% in the Chlorite and Sericite zones. It decreases to less than about 0.5 wt.% in the Pyrophyllite and Quartz zones. In some parts of the Pyrophyllite zone, its content is 1~3 wt.% due to the presence of sericite. MgO content is less than 0.1 wt.% throughout most of the zones, except for the Chlorite zone. MgO content of the Chlorite zone is about 0.3 wt.%. Ignition loss is less than about 1 wt.% throughout most of the zones, except for the Sericite and Pyrophyllite zones. It increases to 2~3 wt.% in the Sericite zone, and comes up to 3~5 wt.% in the

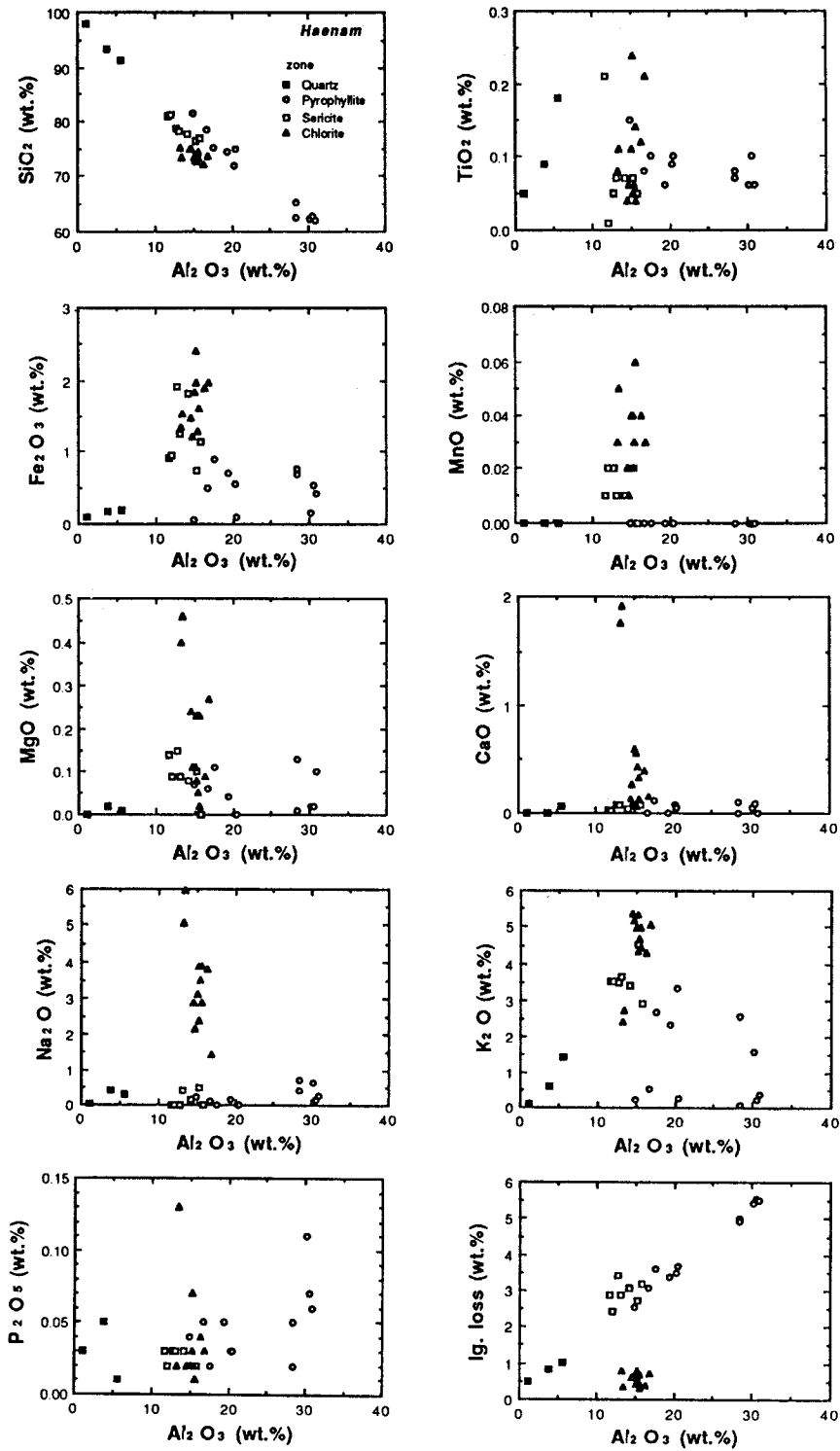


Fig. 8. Oxides vs. Al_2O_3 variation diagrams of altered rocks in the Haenam mine.

Pyrophyllite zone. MnO, TiO₂ and P₂O₅ contents were less than about 0.5 wt.% throughout all of the zones, and do not show any remarkable tendency.

DISCUSSION

From the above data, the following features can be considered on the zones in the Seongsan, Ogmaesan and Haenam deposits.

The Kaolin zone shows much higher contents of aluminium and water than other zones. Silica content in this zone is low in comparison with other zones, and other elements are nearly zero in the zone. Silica, alumina and water are fixed in kaolin minerals, and other are depleted from the rocks by the solution. The Kaolin-Quartz zone has similar aspect to the Kaolin zone except that silica is fixed both in kaolin minerals and quartz. The Quartz zone has very high content of silica, while other elements are nearly zero. This fact indicates that other elements are dissolved into the solution. In the Alunite zone, silica, aluminium, potassium, water and sulfur are fixed in alunite and quartz, and other elements are depleted from the rocks by the solution. In the Pyrophyllite zone, silica, aluminium and water are fixed in pyrophyllite and quartz, and potassium is fixed in sericite. Other elements are depleted from the rocks by the solution. In the Sericite zone, potassium, magnesium and iron are fixed in sericite, and sodium, and calcium are fixed in plagioclase. The content of all elements in the Chlorite zone is thought to be close to those in original rocks.

Therefore, it can be noticed that chemical constituents of the rocks are partly removed and added through the interaction of the hydrothermal solutions, which were subsequently changed to a series of the altered zones. The major chemical constituents of the original rocks are SiO₂, Al₂O₃, Fe₂O₃, FeO, MgO, CaO, Na₂O, K₂O, sulfur and water. Fe₂O₃, FeO and MgO are contained mainly in biotite, magnetite and glass in the original rocks, and some of them might be fixed in chlorite, hematite and pyrite after the alteration. SiO₂, Al₂O₃, Fe₂O₃, FeO, Na₂O, K₂O and water are the responsible constituents for the formation of the minerals which are characteristic in each altered zone. In addition to H₂O and SO₃, SiO₂ is considered as an excess component in the alteration processes, because the presence of quartz is commonly recognized in all of the alteration zones. It can be considered that the mobility of these major elements is related to mineral assemblages in each altered

zone.

Alunite phase relations were discussed by Hemley et al. (1969). In terms of aqueous K₂SO₄ versus H₂SO₄ activity, alunite, K-mica and kaolinite, in a quartz-saturated system, can coexist at an isothermal, isobaric invariant point. At aqueous K₂SO₄ values above this point, alunite is stable against K-mica and at sufficiently high K₂SO₄ values, 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 and Ogmaesan deposits, alunite is stably present. 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, this will produce pyrophyllite. If not, kaolinite will be stable. This is the case in the Seongsan and Ogmaesan deposits. With fluoride and chloride added, pyrophyllite and zunyite or topaz may be sometimes produced (Rosenberg, 1972). In the Haenam deposit, pyrophyllite is present. Then, formation temperature, pH and silica activity for the Haenam deposits are higher than those for the Seongsan and Ogmaesan deposits. Whereas, potassium activity for the Haenam deposit is lower than that of the Seongsan and Ogmaesan deposits.

In addition, very small amounts of enargite is also present in the Ogmaesan deposits. Knight (1977) reported that enargite is reacted at 200°C with the rock composed of alunite, quartz and kaolinite. Enargite and three minerals are encountered in the reaction path (alunite goes to kaolinite, kaolinite goes to muscovite and muscovite goes to K-feldspar) in his experimental study. Then, enargite-quartz-kaolinite-alunite becomes a stable assemblage, and no zoning is predicted between enargite veins and quartz-kaolinite-alunite rocks. Furthermore, Meyer (1967) suggested that enargite mineralization is most likely to take place in the basal part of the ground-water zone, where magmatic fluids could be quenched and oxidized without undergoing major dilution. Einaudi (1977 and 1982) favored enargite generation in situations where small, relatively high-level stocks are emplaced into rocks saturated with ground water. Furthermore, Sillitoe (1983) pointed out that enargite is localized in permeable channel ways, particularly fault zones, where part of a magmatic vapor plume containing a high flux of SO₂, H₂S, HCl and volatile metal species. Ogmaesan deposits, therefore, is thought to have been formed

at relatively shallow level and from the solution with low pH.

Stoffregen (1985) pointed out that at a pH less than about 2 appreciable aluminum mobility would inhibit alunite deposition, resulting in a solution that would dissolve most rock-forming minerals except quartz and pyrite, creating the observed vuggy silica assemblage. The alteration sequence of vuggy silica, alunite, quartz-kaolinite and illite, from center to outer, is clearly the result of decreasing acidity away from the center. If vuggy silica exists at the deposits, the pH of the center at the deposits is less than about 2. In the Ogmaesan deposits, vuggy silica occurs in the Quartz zone, thus the pH of the Quartz zone is less than 2. Alunite occurs in the deposits, the pH of alunite zone of the deposits is about 2 to 4. In the Seongsan deposits, alunite also observed. Thus, pH of the Seongsan deposits is about 1 to 4 in the center of the Acidic zone. However, in the Haenam deposits, alunite does not occur in any zones, and formation temperature is higher than that of Seongsan and Ogmaesan deposits. Therefore, pH of the Haenam deposits is considered to be about 3 to 4 in the center of the Acidic zone, because Stoffregen (1985) pointed out that pH of the solution decreases with the increase of formation temperature. Then, it is thought that alunite in the area was formed by oxidation of hydrogen sulfide in the steam-heated environment or by oxidation of sulfide in the hypogene environment, and it is considered that all deposits were formed by acid-sulfate or acid hydrothermal alteration under the steam-heated environment of shallow depth.

CONCLUDING REMARKS

All clay deposits belong to high-sulfidation (acid-sulfate) system. The hydrothermally altered rocks of the clay deposits are classified into the following altered zones from the center to the margin of the alteration: Kaolin zone, Kaolin-Quartz zone, Quartz zone, Sericite zone and Chlorite zone in the Seongsan deposits; Quartz zone, Alunite zone, Kaolin zone, Sericite zone and Chlorite zone in the Ogmaesan deposits; Quartz zone, Pyrophyllite zone, Sericite zone and Chlorite zone in the Haenam deposits. These alteration zones can be grouped in two large zones: Acidic zone such as Pyrophyllite zone, Alunite zone, Quartz zone, Kaolin zone, Kaolin-Quartz zone and a part of Sericite zone; Propylitic zone such as Chlorite zone and a part of Sericite zone.

On the basis of bulk chemical composition of the hydrothermally altered rocks, it was found that many components such as SiO_2 , TiO_2 , Fe_2O_3 , CaO , MgO , K_2O and Na_2O were considerably mobilized from the original rocks. Therefore, it can be considered that the movement of these major elements is related to mineral assemblages in each altered zone.

Polytypes of sericite are determined as $2M_1$ and $1M$ by XRD. The amount of $2M_1$ is nearly equal to that of $1M$ in the Seongsan deposits, and is less than that of $1M$ in the Ogmaesan deposits, and is higher than that of $1M$ in the Haenam deposits. These facts indicate that formation temperature of sericite is relatively high in the Haenam deposits, moderate in the Seongsan deposits, and low in the Ogmaesan deposits.

The exchanged values of $\text{Na}/(\text{K}+\text{Na})$ for alunite in the Ogmaesan deposits are higher than those of in the Seongsan deposits from the mineralogical study by EPMA. Thus, the alunite of the Ogmaesan deposits must have been formed from solutions with high aqueous $\text{Na}/(\text{K}+\text{Na})$ ratios, low pH and high temperature than the alunite of the Seongsan deposits.

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한국 서남부, 해남지역에서 백악기 산성마그마티즘에 관련된 열수점토광상의 누대분배, 광물조합의 지구화학적 연구

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요 약: 본 논문에서는 해남지역의 점토광상인 성산, 옥매산 및 해남광상을 연구대상으로 하였다. 열수변질을 받은 각 점토광상은 중심으로부터 주변부로 감에 따라 변질대를 형성하고 있는데, 성산광상의 경우 카올린대, 카올린-석영대, 견운모대 및 녹니석대의 변질대가, 옥매산광상의 경우 석영대, 명반석대, 카올린대, 견운모대 및 녹니석대의 변질대가, 그리고 해남광상의 경우 석영대, 납석대, 견운모대 및 녹니석대의 변질대가 각각 나타나고 있다. 이같은 변질대들은 두 종류의 변질 작용으로 구분될 수 있는데, 하나는 납석대, 명반석대, 석영대, 카올린대 및 카올린-석영대와 같은 산변질작용 (acidic alteration)이고, 다른 하나는 녹니석대와 일부 견운모대와 같은 프로필리틱 (prophyllitic alteration) 이다. 모든 점토광상은 high sulfidation (acidic-sulfate) 계에 속한다. 산변질작용의 암석은 납석, 명반석, 카올린광물, 견운모, 석영 및 황철석 등으로 구성되어 있다.

전암화학분석의 결과 SiO_2 , TiO_2 , Fe_2O_3 , MgO , CaO , K_2O 및 Na_2O 와 같은 원소들은 원암의 조성과 상당한 차이를 보여주고 있는데, 이같은 주원소들의 유동성은 각 변질대의 광물조합과 관련되어 이들에 영향을 주고 있다. 견운모의 폴리타일 (polytype) 은 X-선 회절분석결과, $2M_1$, 및 $1M$ 형으로 밝혀졌다. 성산광상의 경우 $2M_1$ 및 $1M$ 형이 거의 같은 비율로 나타나고, 옥매산광상의 경우 $1M$ 형이 우세한 반면, 해남광상의 경우 $2M_1$ 형이 우세하게 나타나고 있다. 이같은 현상은 견운모의 형성온도를 반영하는 것으로, 해남광상이 가장 고온에서, 성산광상은 중간온도에서, 그리고 옥매산광상이 가장 저온에서 형성되었음을 시사해 준다. 전자현미 분석결과, 명반석의 $\text{Na}/(\text{K}+\text{Na})$ 의 비율이 옥매산광상의 것이 성산광상의 명반석이 성산광상의 것보다 높은 것으로 나타났는데, 이는 옥매산광상의 것보다 상대적으로 고온에서 높은 $\text{Na}/(\text{K}+\text{Na})$ 값과 낮은 pH 값을 갖는 용액에서 형성되었음을 시사해 준다. 모든 분석결과를 종합하여 볼 때, 명반석은 hypogene 기원이며, steam-heated 환경에서 hydrogen sulfide의 산화작용에 의하여, 그리고 오늘날의 열수계에서 관찰할 수 있는 solfataric alteration의 결과로 형성되었음을 알 수 있다.