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Oxygen and Hydrogen Isotope Studies of the Hydrothermal Clay Deposits and Surrounded Rocks in the Haenam Area, Southwestern Part of the Korean Peninsula

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ABSTRACT: In the present study, three representative hydrothermal clay deposits, named the Seongsan, Ogmaesan and Haenam deposits, were selected for oxygen and hydrogen isotope studies. Oxygen and hydrogen isotopic compositions of quartz, sericite, alunite and kaolin minerals from Seongsan, Ogmaesan, Haenam deposits and surrounded rocks of clay deposits have been measured. The $\delta^{18}O$ values of quartz, kaolin, sericite and alunite in the Seongsan mine are +8.4 to +11.1‰, +3.6 to 5.4‰, +4.8 to +5.8‰ and +3.0 to +6.6‰, respectively. In the Ogmaesan mine, the $\delta^{18}O$ values of quartz, kaolin, sericite and alunite are +8.0 to +13.6‰, +2.8 to +6.7‰, +4.8 to +8.4‰ and +0.9 to +2.4‰, respectively. The $\delta^{18}O$ values of the Haenam mine range from +7.9 to +10.1‰ for quartz and from +4.5 to +6.5‰ for sericite. The $\delta^{18}O$ values of the whole-rocks range from +3.0 to +7.8‰ for the granitic rocks. The $\delta^{18}O$ values of the whole-rocks range from +3.2 to +10.7‰ for the volcanic rocks. The δD values of kaolin, sericite and alunite in the Seongsan mine are −78 to −86‰, −71 to −90‰ and −43 to −77‰, respectively. In the Ogmaesan mine, the δD values of kaolin, sericite and alunite are −73 to −80‰, −74 to −88‰ and −57 to −98‰, respectively. The δD values of the Haenam mine range from −76 to −85‰ for sericite. The δD values of the whole-rocks range from −77 to −105‰ for the granitic rocks. The δD values of the whole-rocks range from −76 to −100‰ for the volcanic rocks.

The main result obtained oxygen and hydrogen isotope data can lead to the following interpretations on the origin of hydrothermal fluids in the clay deposits: Through the oxygen isotopic study, the formation temperature of the clay deposits was estimated from the coexisting minerals such as quartz-kaolin minerals and -sericite. Formation temperature of the acidic alteration zone is 165 to 280℃ in the Seongsan deposits, 175 to 250℃ in the Ogmaesan deposits and 250 to 350℃ in the Haenam deposits. Three clay deposits has been formed by magmatic water mixed with meteoric water. Furthermore, from this isotopic data, it is clarified that kaolin minerals and alunite are hypogene in origin, and has been formed by oxidation of hydrogen sulfide in the steam-heated environment, and that alunite has been produced in the spectacular solfataric alteration observed at the surface of some present-day hydrothermal systems. Oxidation of the H_2S is thought to be generated when the vapor phase generated by boiling of the deep-seated water under the water table.

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 Hayba et al., 1986 and 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).

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 Haenam deposits in the area are generally considered to be genetically related to Cretaceous felsic

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magmatism. Since the clay deposits of the area were first described by Kinosaki (1935), many revisions on geology and genesis of the clay deposits in the area, have been made by numerous geologist. Recently, there are many workers have been studied to the hydrothermal clay deposits. For example, mineralogical (Kim, 1989, 1991 and 1992b) and geochemical (Cheong and Chon, 1990; Kim, 1989, 1991, 1992a and 1992b) studies were reported. Kim (1989, 1990a, 1990b, 1991, 1992a and 1992b) has described alteration zoning and fluid inclusion study. Kim et al. (1990), Chon et al. (1991) and Kim et al. (1993) discussed sulfur isotope study. K-Ar ages of the hydrothermal clay deposits and their surrounded rocks have been reported by Kim et al. (1990) and Kim and Nagao (1993).

Oxygen and hydrogen isotope studies of the clay deposits were reported by Cheong and chon (1990) and Kim et al. (1990). In the present work, the author studied oxygen and hydrogen isotope of the clay deposits from for mines and surrounded rocks. The regional variation of oxygen and hydrogen isotopic compositions of the clay deposits is of great interest from the viewpoint of material source and formation mechanism of the hydrothermal clay deposits. In this paper, special attention is focused on the oxygen isotopic compositions of coexisting minerals in the clay deposits.

The purposes of the present investigation are to obtain oxygen and hydrogen isotopic data on coexisting minerals minerals from the clay deposits, to consider what factors are impotant for controlling oxygen and hydrogen isotopic compositions of kaolin minerals, sericite and alunite in these deposits, to elucidate the origin of kaolin minerals and alunite for these deposits, and to estimate ore formation temperature.

GEOLOGICAL SETTING

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).

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. Biotite gneiss, hereafter called Sanyi gneiss, is distributed in the central and eastern parts of the area. The rock is a fine- to medium-grained and foliated. Mica schist is distributed in the western part

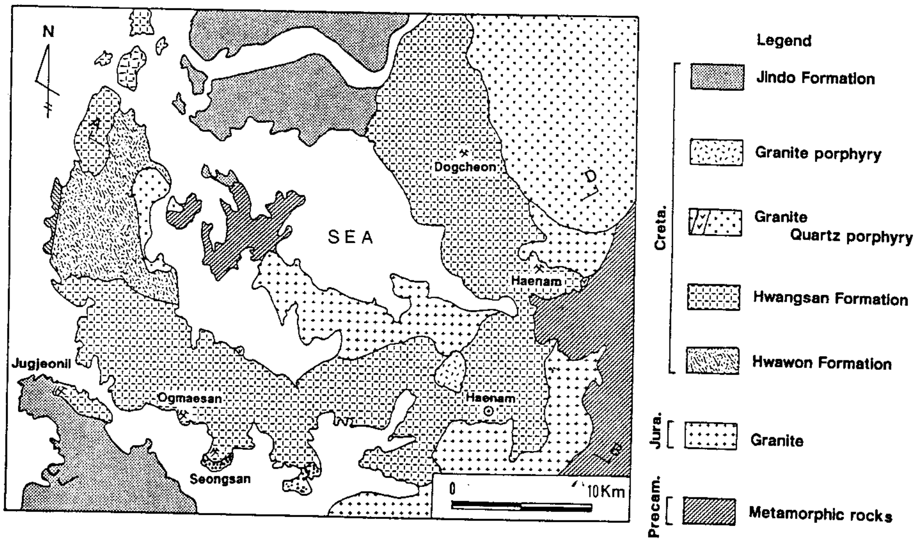

Fig. 1. Geological map of the Haenam area. The location of clay deposits are shown.

of the area.

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 seperated from the Weolgagsan granite were reported by Kim (1991) and Kim and Nagao (1993). They composed of hornblende-biotite, biotite and two mica granites. Hornblende-biotite granite is a medium- to coarse-grained and slightly porphyritic rock. Biotite granite is a fine- to medium-grained one with slightly porphyritic texture. Two-mica granite is a fine- to medium-grained equigranular rocks. In the some part of the area, these rocks have weakly altered.

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 fault-contact. 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. Kim (1991) and Kim and Nagao (1993) 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. Hwawon basalt is mainly composed of basalt having a flow texture, and intercalating small amounts of tuffaceous sandstone. The rocks show poikilitic texture. The rock is weakly propylitized. Inji andesite is composed mostly of andesite, andesitic welded tuff and andesitic tuff breccia. The size of breccia fragments in the rock is 5 to 40 cm in length. Volcanogenic sediments and sedimentary rocks are intercalated in some parts. These intercalated rocks are composed of tuffaceous sandstone, sandstone, oily shale, black shale and chert. These rocks are called Uhangri formation by Lee and Lee (1976). The Inji andesite is dark grey to pale green in color, and shows flow and welding textures. The rock is also weakly propylitized. Hwangsan Formation is divided into the Hwangsan dacite and Weolho rhyolite. 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. Kim (1991) and Kim and Nagao (1993) reported the ages of Hwangsan Formation as follows: Hwangsan dacite gives 84.5 to 86.4 Ma and Weolho rhyolite 811.4 to 81.8 Ma. The total thickness of the Formation exceeds 500 m. The Formation conformably overlies Hwawon Formation. Hwangsan dacite is widely distributed in the area, and is mainly composed of dacite flow, welded tuff and small amounts of ash tuff and lapilli tuff. The rock shows light grey to pale green in color, and has flow, bubble wall and welding textures. The rock includes xenoliths of andesite and pre-Cretaceous basements. The rock is widely propylitized. In some parts, it has suffered strong hydrothermal alteration, and makes clay deposits. The original textures of the rock is still preserved even in some clay deposits. Weolho rhyolite is mainly distributed in the northwestern and northeastern parts of the area. It conformably overlies Hwangsan dacite. The rock is commonly red in color, and usually shows flow texture and rarely spherulitic texture. White-colored rhyolite flow is observed in some parts. The rhyolite flow changes to rhyolitic tuff breccia in some parts. Rock fragments in tuff breccia are mainly rhyolite flow and small amounts of shale. The size of breccias is commonly smaller than 50 cm in length. The Formation is weakly propylitized, and also altered to clay deposits in some parts. 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) and Kim and Nagao (1993) 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 Formation is about 600 m. Samji tuff is mainly composed of welded tuff and crystal tuff. The rock is propylitized. Welded tuff shows welding and bubble wall textures. Crystal tuff includes rock fragments of rhyolitic composition, and weakly shows bubble wall texture. Jindo rhyolite is mainly distributed in the southwestern part of the area. The rock ovrelies the Samji tuff and intrudes Hwangsan dacite in a small scale at some parts. The rock is deep red in color, with numerous spherulites, and shows flow structure. It is very weakly propylitized. Gaji tuff is distributed in the northwestern part of area. The rock consists of lapilli and breccia tuffs, most of which include not only breccias of aphanitic rhyolite fragments and coarse volcanic ash but also accidental breccias of all rocks in the area, such as, red- and black-shale, sandstone, and granitic rock fragments. The rock shows very weak propylitic alteration.

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; Kim and Nagao, 1993). It is composed of hornblende-biotite and biotite granites. Hornblende-biotite granite is medium-grained. Biotite granite is a fine- to medium-grained and has slightly porphyritic texture. Weolchulsan Granite is distributed in the eastern part of the area, and intrudes Precambrian basements, Weolgagsan Jurassic granite and Hwangsan Formation. Kim (1991) and Kim and Nagao (1993) reported that K-Ar ages of K-feldspar and whole rock of Weolchulsan granite show 77.0 and 81.2 Ma. It is biotite granite. Biotite granite is medium- to coarse-grained rock with porphyritic texture. 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; Kim and Nagao, 1993). The rock shows typical porphyritic texture. Jangseong Granite Porphyry occurs in the central part of the area. Kim (1991) and Kim and Nagao (1993) reported that Jangseong granite porphyry gives 71.8 Ma. It intrudes Weolgagsan Jurassic granite and Hwangsan Formation. It is fine-grained, and shows micrographic textures.

OUTLINE OF 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 Hyounsan 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 magmatisms 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; Kim and Nagao, 1993). 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 Haenam and Dogcheon mines. Center of zone in the Seongsan clay deposits is Kaolin zone, whereas that in the Ogmaesan 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.

ANALYTICAL PROCEDURES

Oxygen Isotope

The whole-rock samples, which represent the least altered rocks in the area, were used for oxygen isotope analysis. Clay minerals were separated from the rock specimen using gravitational techniques. Purity of the separated samples was determined to be higher than 95% using XRD.

Oxygen in samples was extracted by the BrF_5 technique (Clayton and Mayeda, 1963). The pulverized samples about 13 to 20 mg each were placed in nickel reaction tubes, and were reacted with BrF_5 at 550 to 600℃ for 11 hours. The outline of the gas preparation line used during the experiment was given by Matsuhisa et al. (1971). CO_2 gas was obtained from the oxygen by combustion with a resistance heated graphite rod (Taylor and Epstein, 1962). Oxygen isotope ratios of the resulting CO_2 gas was measured with a Nier-Mckinney type mass spectrometer (VG Micromass 903) of the Institute for Study of the Earth's Interior, Okayama University. The results of the isotope analysis are given in the $\delta^{18}O$ value as defined by:

$$\delta^{18}O(‰) = [(^{18}O/^{16}O)sample/(^{18}O/^{16}O)standard - 1] \times 10^3.$$

Isotopic data is given in terms of conventional expression in per mil relative to SMOW (Standard Mean Ocean Water [Craig, 1961]) for $^{18}O/^{16}O$ ratio. Reproducibility of $\delta^{18}O$ analysis using the standard of NBS-28 was estimated to be about ±0.1‰ Some samples were measured twice, and the results were identical within this error range.

Hydrogen Isotope

The same samples prepared for the oxygen isotope study were used during the experiment for hydrogen isotope study. The analytical technique for extraction of hydrogen from the samples is similar to that described by Friedman and Smith (1958), Godfrey (1962) and Suzuoki and Epstein (1976). After outgassing of the adsorbed water at 200℃ for at least 2 hours in vacuum, the remaining water was extracted by inductive heating at 1300 to 1400℃. A small amounts of hydrogen gas generated by reaction of water with ferrous iron during the dehydration process was reconverted to water by heating with CuO at 400℃. The water thus extracted was passed over a heated uranium metal (650℃) and converted to hydrogen gas. The hydrogen was manometrically measured to give the H_2O^+ content. The hydrogen isotopic composition of H_2 gas was determined with a McKinney type mass spectrometer (Hitachi mass spectrometer Kagaku L770) of the Institute for Study of the Earth's Interior, Okayama University. The results of δD values are expressed by:

$$\delta D(‰) = [(D/H)sample/(D/H)standard - 1] \times 10^3.$$

All of the hydrogen isotopic ratios are reported as conventional D-notation in ‰ deviation from SMOW (Standard Mean Ocean Water [Craig, 1961]). The reproducibility of measurement using a reference sericite sample was about ±1.0‰ for δD. Some samples were measured twice, and the results were identical within this error range.

RESULT

The oxygen isotope data obtained are given in Table 1 and 2. Results obtained from the oxygen isotope data in this study are summarized as follows.

The $\delta^{18}O$ values of quartz, kaolin, sericite and alunite in the Seongsan mine are +8.4 to +11.1‰, +3.6 to +5.4‰, +4.8 to +5.8‰ and +3.0 to +6.6 ‰, respectively. In the Ogmaesan mine, the $\delta^{18}O$ values of quartz, kaolin, sericite and alunite are +8.0 to +13.6‰, +2.8 to +6.7‰, +4.8 to +8.4‰ and +0.9 to +2.4‰, respectively. The $\delta^{18}O$ values of the Haenam mine range from +7.9 to +10.1‰ for quartz and from +4.5 to +6.5‰ for sericite. The $\delta^{18}O$ values of the whole-rocks range from +3.0 to +7.8‰ for the granitic rocks. The $\delta^{18}O$ values of the whole-rocks range from +3.2 to +10.7‰ for the volcanic rocks.

The hydrogen isotope data obtained are given in Table 1 and 2. Results obtained from the hydrogen isotope data in this study are summarized as follows.

The δD values of kaolin, sericite and alunite in the Seongsan mine are −78 to −86‰, −71 to −90 ‰ and −43 to −77‰, respectively. In the Ogmaesan mine, the δD values of kaolin, sericite and alunite are −73 to −80‰, −74 to −88‰ and −57 to −98‰, respectively. The δD values of the Haenam mine range from −76 to −85‰ for sericite. The δD values of the whole-rocks range from −77 to −105‰ for the granitic rocks. The δD values of the whole-rocks range from −76 to −100‰ for the volcanic rocks.

Temperature of ore formation was calculated based on oxygen isotopic fractionations between quartz and kaolinite, and between quartz and sericite (Table 1). Fractionation equations of coexisting minerals presented by Suzuoki and Epstein (1976), Friedman and O'Neil (1977), Matsuhisa et al. (1979), Kulla and Anderson (1978), and Lambert and Epstein (1980) were used. Then, δD and $\delta^{18}O$ values for water in equilibrium with the minerals at equilibrium temperatures were calculated as given in Table 1, and shown in Fig. 2.

DICUSSION AND CONCLUSIONS

In order to distinguish the alunites formed from primary or secondary supergene, it is necessary to

Table 1. Oxygen and hydrogen isotopic values of clay deposits.

Sample	Mineral	$\delta^{18}O$ (‰)	δD (‰)	H_2O (%)	$\delta^{18}O_{H_2O}$ (‰)	δD_{H_2O} (‰)	$T=\Delta_{Qz\text{-}Ka}$ (T=℃)	$T=\Delta_{Qz\text{-}Se}$ (T=℃)
Clay deposis								
Seongsan mine								
87062504	Quartz	11.1			0.9		224	164-169
87051514	Quartz	10.8			−0.2		210	169-193
87051611	Quartz	9.2			1.6		281	228
87051813	Quartz	8.4			0.6		274	
87062502	Kaolin	3.6	−90	13.97	0.6	−82	274	
87051515	Kaolin	4.8	−94	13.82	−0.1	−86	210	
87051602	Kaolin	5.4	−98	13.39	1.0	−78	224	
86101902	Kaolin	4.5	−91	13.55	0.7	−80	281	
87062511	Sericite	5.5	−93	5.31	−3.1	−90		164
87062513	Sericite	5.8	−84	4.11	−2.5	−81		169
87062514	Sericite	5.8	−84	3.96	−2.5	−81		169
87061512	Sericite	5.5	−83	4.80	−2.8	−80		169
87051410	Sericite	5.8	−74	4.76	−1.3	−74		193
87051705	Sericite	4.8	−74	3.35	−0.8	−71		228
86101905	Alunite	3.0	−83	12.79	−2.9	−77		
87051628	Alunite	5.4	−64	12.21	−0.5	−58		
87061504	Alunite	6.6	−49	11.30	0.7	−43		
Ogmaesan mine								
89101908	Quartz	13.6			0.3		175	183
89101610	Quartz	10.7			−1.7		194	204
89101807	Quartz	10.0			−3.3		175	183
89101704	Quartz	8.0			−0.9		250	
89101903	Kaolin	6.7	−78	13.61	0.3	−75	175	
89101604	Kaolin	4.3	−74	13.72	1.0	−73	194	
89101804	Kaolin	3.1	−86	13.49	−3.3	−83	175	
89101706	Kaolin	2.8	−87	13.99	−0.8	−80	250	
89101901	Sericite	8.4	−77	3.08	0.3	−74	173	183
89101801	Sericite	5.9	−84	4.72	−1.5	−83	187	204
89101601	Sericite	4.8	−91	2.95	−3.3	−88	173	183
89101905	Alunite	2.3	−68	12.55	−5.8	−59		
89101504	Alunite	2.4	−66	11.30	−5.7	−57		
89101502	Alunite	0.9	−107	12.13	−7.2	−98		
Haenam mine								
89031108-1	Quartz	7.9			2.1			310-344
89110409	Quartz	8.7			2.5			250-321
8911-507	Quartz	10.1			2.9			291
89031108-7	Sericite	4.6	−89	4.72	1.7	−79		321
89031108-8	Sericite	4.5	−87	3.76	1.4	−78		310
89110406	Sericite	4.6	−92	3.96	−0.2	−85		250
89110407	Sericite	5.4	−89	4.40	2.5	−79		321
89110502	Sericite	6.5	−91	4.43	2.9	−76		291
Other clay deposits								
Gushi mine								
88020413	Sericite	8.3	−84	4.84	3.8	−68		260
88020418	Sericite	6.4	−83	5.18	1.9	−67		260
Nohwa mine								
86092902	Sericite	8.0	−84	3.73				

Abbrreviation: Qz; Quartz, Ka; Kaolin, and Se; Sericite.

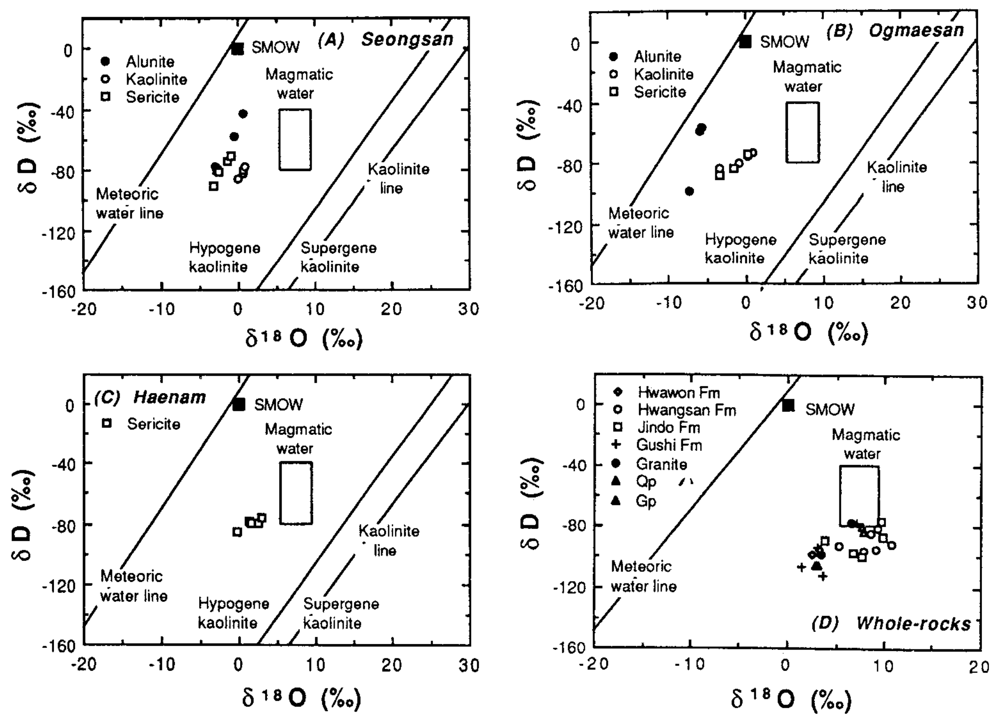

Fig. 2. δD(‰) vs. $\delta^{18}O$(‰) of clay deposits and whole-rocks. (A) Seongsan mine, (B) Ogmaesan mine, (C) Haenam mine, and (D) Whole-rocks. Abbreviations: Fm; Formation, Qp; Quartz porphyry, and Gp; Granite porphyry.

investigate the associated kaolinites. Hydrogen and oxygen isotopes can be used to distinguish between primary (or hypogene) and supergene (or secondary) kaolinite as reported by Taylor (1974). Marumo et al. (1982) reported that supergene kaolinites are plotted very close to the "kaolinite line" defined by Savin and Epstein (1970) and Lawrence and Taylor (1971), which is the line representing the locus of hydrogen and oxygen isotopic compositions for kaolinites formed by weathering and assumed to be in equilibrium with meteoric waters. While, hypogene kaolinites are plotted away from the "kaolinite line" (Maumo et al., 1982). These kaolinites, formed from the mixing between magmatic water and meteoric water, are considerably removed from the meteoric water line and very close to the dashed line which marks the compositions of kaolinites in equilibrium with meteoric water at temperature of 100℃. In the study area, calculated δD and $\delta^{18}O$ values for water in equilibrium with the minerals at isotopic temperatures are shown in Fig. 2A, 2B and 2C. Kaolin minerals of the Seongsan and Ogmaesan deposits are plotted away from the "kaolinite line" (Fig. 2A and 2B). Thus, kaolin minerals of two deposits can be considered to be primary (or hypogene). They were formed by shallow acid-sulfate alteration at mixing between magmatic water and meteoric water at 250℃ in the Seongsan deposit and at 200℃ in the Ogmaesan deposit (Table 1). These results well agree with each other.

Oxygen and hydrogen isotopes of alunite and kaolin mineral (this study), and sulfur isotope study of alunite (Kim et al., 1993) in acid-sulfate alteration can give some informations about origin of the acid-sulfate solution. In addition, they can be used to distinguish between primary and secondary origins for shallow acid-sulfate alteration zones. K-Ar age determinations on alunite can also be used to distinguish between supergene and primary origins as has been done at Goldfield by Mehnert et al. (1973) and at Round Mountain by Tingley and Berger (1985). Bethke (1984) reported that K-Ar ages from hypogene alunite are concordant with its mineralization.

Kim (1991) and Kim and Nagao (1993) reported that K-Ar ages of alunites (80.8 to 81.4 Ma) from the Seongsan, Ogmaesan and Dogcheon deposits are conformable with those of sericites (78.1 to 80.2 Ma). Although alunite is not present in the Haenam deposit, K-Ar ages of sericites (78.9 and 79.6 Ma) are

Table 2. Oxygen and hydrogen isotopic values of whole-rocks.

Sample	Fm	Rock type	$\delta^{18}O$(‰)	δD(‰)	H_2O(%)
Granitic rocks					
89062702	JYS	Gr	6.5	−77	1.07
89061501	WCS	Gr	3.5	−98	0.43
89031206	WGD	Qp	7.6	−80	0.39
90102801	WGD	Qp	7.8	−83	0.73
89061701	JS	Gr	3.0	−105	0.25
Valcanic rocks					
87070201	IJ	An	3.2	−95	1.72
89061606-6	HW	Da	3.8	−89	0.93
89103005	HW	Da	5.3	−93	0.96
89031204	HW	Da	9.0	−95	0.85
88020207	HW	Da	7.7	−100	1.67
89103112	WH	Rhy	7.8	−96	1.48
89031201	SJ	Tuff	9.2	−81	0.60
89061704	SJ	Tuff	9.9	−87	0.39
89070102-1	SJ	Tuff	2.5	−98	1.53
89063004	JD	Rhy	8.6	−84	0.39
88012220	JD	Rhy	6.8	−97	0.31
89031102	GJ	Tuff	10.7	−91	0.40
89031103-1	GJ	Tuff	9.7	−76	0.66
Other volcanic rocks					
90110301	GS	Ba	1.4	−107	1.35
88020401	GS	Da	3.1	−94	1.09
88020204	GS	Tuff	3.6	−112	3.28
88020409	GS	Rhy	7.1	−77	1.47

Abbreviations: JYS; Jiyoungsan, WCS; Weolchulsan, WGD; Weolgangdu, JS; Jangseong, IJ−Inji, HW; Hwangsan, WH; Weolho, SJ; Samji, JD; Jindo, GJ; Gaji, GS; Gushi, Fm; Formation, Gr; Granite, QP; Quartz porphyry, An; Andesite, Da; Dacite, Rhy; Rhyolite, and Ba; Basalt.

the same as those of other deposits. Furthermore, K-Ar ages of these minerals (78.1 to 81.4 Ma) are in good agreement with those of host rocks (Hwangsan Formation, 81.4 to 86.4 Ma) and heat source rocks (Cretaceous granitic rocks, 77.1 to 81.5 Ma).

Table 3 summarizes the isotopic features currently available for determining the origin of acid-sulfate alteration. It is considered that all deposits were formed by acid-sulfate or acid hydrothermal alteration under the steam-heated environment of shallow depth. Furthermore, based on all isotopic data, kaolin minerals and alunite are hypogene in origin, and are thought to have been formed by oxidation of hydrogen sulfide in the steam-heated environment, that produces the spectacular solfataric alteration seen at the surface in hydrothermal system. The clay deposits, therefore, were formed through the hydrothermal activities caused by circulation of hydrothermal solution (magmatic water mixed with meteoric water) of magmatic origin from the thermal effects of the granitic intrusions.

Table 3. Characteristics of acid-sulfate alteration of different origins (Bethke, 1984).

	Oxidation of H_2S	Disproportiontion of H_2S	Supergene Oxidation
$\delta^{34}S_{alunite}$	=Sulfides	>>Sulfides	=Sulfides
$\delta^{18}O_{kaolin}$	Far from Kaolin Line	Far from Kaolin Line	Near to Kaolin Line
$K/Ar_{alunite}$	Concordant	Concordant	Younger

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REFERENCES

Bethke, P. M. (1984) Contols on base and precious metal mineralization in deeper epithermal environments. U.S. Geol. surv. Open-File Report, 84-890, 40p.

Cheong, Y. W. and Chon, H. T. (1990) Geochemistry of pyrophyllite deposits in Hwasoon-Dado-Haenam areas in Korea. Jour. Korean Inst. Mineral Min Eng., v. 27, p. 63-76(in Korean).

Chon, H. T., Cheong, Y. W. and Kim, I. J. (1991) Oxygen and sulfur isotope composition, and genesis of some pyrophyllite deposits distributed in the Keongnam and Ceonnam provinces. Jour. Korean Inst. Min. Geol., v. 24, p. 97-105 (in Korean).

Clayton, R.N. and Mayeda, T.K. (1963) The use of bromine pentafluorid in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim. Cosmochim. Acta, v. 27, p. 43-52.

Craig, H. (1961) Isotopic variations in meteoric waters. Science, v. 133, p. 1702-1703.

Friedman, I. and O'Neil, J.R. (1977) Compliation of stable isotope fraction factors of geochemical interest. in Fleisher, M., ed., Data of Geochemistry, Sixth Edition. U.S. Geol. Surv. Prof. Paper, 440-KK, KK1-KK2.

Friedman, I. and Smith, R.L. (1958) The deterium content of water in some volcanic glasses. Geochim. Cosmochim. Acta, v. 15, p. 218-228.

Godfrey, J.D. (1962) The deterium content of hydrous minerals from the east-central Sierra Nevada and Yosemite National Park. Geochim. Cosmochim. Acta, v. 26, p. 1215-1245.

Hayba, D.O., Bethke, P.M., Heald, P. and Foley, N.K. (1986) The geological, mineralogical and geochemical characteristics of volcanic-hosted epithermal deposits. in Berger, B.R. and Bethke, P.M. eds., Geology and geochemistru of epithermal systems. Rev. in Ecom. Geol., v. 2, p. 129-167.

Heald, P.W., Foley, N.K. and Hayba, D.O. (1987) Comparative anatomy of Volcanic-hosted epithermal deposits: Acid-sulfate and adularea-sericite types. Econ. Geol., v. 82, p. 1-25.

Hedenquist, J.W. (1987) Mineralization associated with volcanic-related hydrothermal systems in the Circum-Pacific basin. In: Transactions of the Fourth Circum-Pacific Energy and Mineral Resources Conference, Singapore., Horn, M.K., ed., Am. Assoc. Per. Geol., p. 513-524.

Hemley, J.J., Hostertle, P.B., Gude, A.J. and Mountjoy, W.T. (1969) Some stability relations of alunite. Econ. Geol., v. 64, p. 538-567.

Hemley, J.J., Montoya, J.W., Marineko, S.W. and Luce, R.W. (1980) Equilibria in the system Al_2O_3-SiO_2-H_2O and some general implication of alteration/mineralization process. Econ. Geol., v. 75, p. 210-228.

Iwao, S. (1972) Genesis of clay (II). Jour. Clay Sci. Japan, v. 12, p. 81-95 (in Japanese).

Kamitani, M. (1974) Hydrothermal alteration at the Uku "Roseki" mine, Yamaguchi Prefecture. Min. Geol. Japan, v. 24, p. 31-43 (in Japanese).

Kinosaki, Y. (1935) Alunite deposits in Kimhae, Haenam, Jindo and Muan districts in Korea. The Government-General of Korea, Investigate of Mining, Korea, v. 8, p. 17-99 (in Japanese).

Kim, I.J. (1989) Hydrothermal alteration of the felsic volcanic rocks in the southwestern part of Korean Peninsula. M.S. These of University of Tokyo, 144p.

Kim, I.J. (1990a) Hydrothermal alteration of the felsic volcanic rocks in the Seongsan mine area, southwestern part of Korean Peninsula (abst). Mining Geol. Japan., v. 40, p. 52-53 (in Japanese).

Kim, I.J. (1990b) Hydrothermal alteration of the felsic volcanic rocks in the Seongsan mine, Korea (abst). Official Program, Fifth Circum-Pacific energy and Mineral Resources Conference and Exhibition, p. 51-52.

Kim, I.J. (1991) Geochemistry of hydrothermal alteration and clay deposits in the Haenam area, Southwestern Korea. D.S. Thesis of University of Tokyo, 238p.

Kim, I.J. (1992a) Hydrothermal Alteration Related to Cretaceous Felsic Magmatism in the Seongsan Dickite deposits, Korea-Estimation of Ore Forming Temperature and aNa^+/aK^+ Ratio of the Hydrothermal Fluid-. Jour. Korean Inst. Min. Geol. v. 25, p. 259-273.

Kim, I.J. (1992b) Alteration zoning, mineral assemblage and geochemistry of the hydrothermal clay deposits related to Cretaceous felsic magmatism in the Haenam area, southwest Korea. Jour. Korean Inst. Min. Geol., v. 25, p. 397-416.

Kim, I.J., Kim, S.Y. and Moon, H.S. (1993) Genetic environment of the hydrothermal clay deposits in southwest Korea. Jour. Earth Sci. Asso. (in Press).

Kim, I.J. and Nagao, K. (1993) K-Ar ages of the hydrothermal clay deposits and their surrounded rocks in southwest Korea. Jour. Korea Soc. Petrol. v. 1 (in Press).

Kim, Y.H., Moon, H.S., You, J.H. and Kim, J.H. (1990) Hydrothermal alteration and mineralogy of alunite and kaolinite in Ogmae deposits, southwest Jeonnam. Korean Inst. Min. Geol., v. 23, p. 207-308 (in Korean).

Kulla, J.B. and Anderson, T.F. (1978) Experimental oxygen isotope fraction between kaolinite and water. U.S. Geol. Surv. Open-File Report, 78-701, p. 234-235.

Lambert, S.J. and Epstein, S. (1980) Stable isotope investigations of an active geothermal system in Valles caldera, Jamez mountains, New Mexico. Jour. Volcanol. Geotherm. Res. v. 8, p. 111-129.

Lawrence, J.R. and Taylor, H.P.Jr. (1971) Deterium and oxygen correlation: Clay minerals and hydroxides in Quaternary soils compared to meteoric waters. Geochim. Cosmochim. Acta, v. 35, p. 993-1003.

Lee, D.S. (1987) Geology of Korea. The Kyohak-sa Publishing Co. Seoul, 1st ed., 514p.

Lee, D.S. and Lee, H.Y. (1976) Geological and geological study on the rock sequences containing oily materials in southern coast area of Korea. Jour. Korean Inst. Min. Geol., v. 9, p. 45-74 (in Korean).

Marumo, K., Matsuhisa, Y. and Nagasawa, K. (1982) Hydrogen- and oxygen-isotopic compositions of kaolin minerals in Japan. in Van Olphan, H. and Veniale, F., eds., Developments in Sedimentology 35, International Clay Conference, 1981, Elsevier, p. 315-320.

Matsuhisa, Y., Goldsmith, J.R. and Clayton, R.N. (1979) Oxygen isotopic fraction in the system quartz-albite-anorthite-water. Geochim. Cosmochim. Acta., v. 43, p. 1131-1140.

Matsuhisa, Y., Matsubaya, O. and Sakai, H. (1971) BrF5-technique for the oxygen isotopic analysis of silicates and water. Mass Spectr., v. 19, p. 124-133 (in Japanese).

Mehnert, H.H., Lipman, P.W. and Steven, T.A. (1973) Age of mineralization at Summitville, Colorado, as

indicated by K-Ar dating of alunite. Econ. Geol., v. 68, p. 399-412.
Moon, H. S., Kim, Y. H., Kim, J. H. and You, J. H. (1990) K-Ar ages of alunite and sericite in altered rocks, and volcanic rocks around the Haenam area, Southwest Korea. Jour. Korean Inst. Min. Geol., v. 23, p. 135-141 (in Korean).
Rye, R. O., Bethke, P. M. and Wasserman, M. D. (1989) Diverse origins of alunite and acid-sulfate alteration: stable isotope systematics. U.S. Geol. Surv. Open-File Report, 89-5, 33p.
Savin, S. M. and Epstein, S. (1970) The oxygen and hydrogen isotope geochemistry of clay minerals. Geochim. Cosmochim. Acta., v. 34, p. 25-42.
Sawkins, F. J. (1984) Metal deposits in relation to plate tectonics. Springer-Verlag, 340p.
Suzuoki, T. and Epstein, S. (1976) Hydrogen isotope fractionation between OH-bearing minerals and water. Geochim. Cosmochim. Acta, v. 40, p. 1229-1240.
Taylor, H. P. Jr. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Econ. Geol., v. 69, p. 843-883.
Taylor, H. P. Jr. and Epstein, S. (1962) Relationship between $^{18}O/^{16}O$ ratios in coexisting minerals of igneous and metamorphic rocks, part I: Principles and experimental results. G. S. A. Bull., v. 74, p. 461-480.
Tingley, J. V. and Berger, B. R. (1985) Lode gold deposits of Round Mountain, Nevada. Nevada Bureau of Mines and Geology, Bulletin, v. 100, 60p.

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한국 서남부, 해남지역의 열수 점토광상과 주변암에 대한 산소 및 수소동위원소 연구

김인준 · 日下部実

요 약: 본 연구에서는 세개의 대표적인 열수점토광상인 성산, 옥매, 해남광상으로 부터 채취한 석영, 견운모, 명반석과 카올린광물 및 광상들의 주변암에 대해 산소 및 수소동위원소 연구를 실시하였다. 성산광상의 석영, 견운모, 명반석과 카올린광물에 대한 산소동위원소값은 각기 +8.4에서 +11.1‰, +4.8에서 +5.8‰, +3.0에서 +6.6‰, +3.6에서 +5.4‰의 값을 나타낸다. 옥매산광상의 석영, 견운모, 명반석과 카올린광물에 대한 산소동위원소값은 각기 +8.0에서 +13.6‰, +4.8에서 +8.4‰, +0.9에서 +2.4‰, +2.8에서 +6.7‰의 값을 나타낸다. 해남광상의 석영과 견운모에 대한 산소동위원소값은 각기 +7.9에서 +10.1‰과 +4.5에서 +6.5‰의 값을 나타낸다. 화강암류와 화산암류에 대한 산소동위원소값은 각기 +3.0에서 +7.8‰과 +3.2에서 +10.7‰의 값을 나타낸다. 성산광상의 견운모, 명반석과 카올린광물에 대한 수소동위원소값은 각기 −71에서 −90‰, −43에서 −77‰, −78에서 −86‰의 값을 나타낸다. 옥매산광상의 견운모, 명반석과 카올린광물에 대한 수소동위원소값은 각기 −74에서 −88‰, −57에서 −98‰, −73에서 −80‰의 값을 나타낸다. 해남광상의 견운모에 대한 수소동위원소값은 −76에서 −85‰의 값을 나타낸다. 화강암류와 화산암류에 대한 수소동위원소값은 각기 −77에서 −105‰과 −76에서 −100‰의 값을 나타낸다.

산소 및 수소동위원소비 분석결과로부터 점토광상에서 열수의 기원에 대해 다음과 같은 해석을 할 수 있다. 산소동위원소 분석결과로부터 공존하는 광물 즉, 석영-카올린광물과 석영-견운모광물로부터 점토광상의 형성온도를 구하였다. 성산광상은 165~280℃, 옥매산광상은 175~250℃, 해남광상은 250~350℃로 나타났다. 이들 세개의 광상은 magmatic water와 meteoric water의 혼합으로 형성되었다. 이러한 동위원소비 분석결과로부터 카올린과 명반석광물은 hypogene 기원으로 나타났고, steam-heated 환경에서 황화수소의 산화로서 형성되었다. 황화수소의 산화작용은 지하수면 아래에서 deep-seated water의 boiling에 기인된 수증기상에서 기인된 것으로 해석된다.