

A Study on the Thermal Behavior and Phase Transformation of Iron-bearing Minerals in Clay of Cheju Island by Mössbauer Effect

Mössbauer 효과에 의한 제주도 찰흙의
함철 광물의 열적 거동과 상변환에 관한 연구

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ABSTRACT : Based on the X-ray powder diffraction (XRD) and Mössbauer spectroscopy, the thermal behavior and phase transformations of two clays are investigated for raw and fired conditions, which are collected from Kwangryeongli and Ildo district in Cheju Island. Mössbauer spectra at room temperature and 20K for two clays show that paramagnetic Fe^{2+} is the structural iron of the layer silicate and ferrihydrite, and superparamagnetic goethite has about 50% of the total iron contents. The XRD peaks of hematite for the fired clays appear from 800°C in Kwangryeongli clay and from 600°C in Ildo district clay, respectively. When the clays are fired ranging from 100°C to 1200°C with an interval of 100°C, a transformation of superparamagnetic goethite to hematite occurs at the range of 200°C~300°C for Kwangryeongli clay and 500°C~600°C for Ildo district clay, respectively. The structural Fe^{2+} was completely oxidized into Fe^{3+} at 400°C. For the temperature ranging from 400°C to 700°C~800°C, two fired clays exhibit the dehydroxylation of the clay mineral. A disintegration of the clay mineral structure is observed from 700°C~800°C to 1100°C, followed by the onset and spread of vitrification process. It is also shown that well-crystallized hematite phase is formed at the temperature higher than 1100°C and the relative absorption area decreases, which might be related to the recrystallization of alluminosilicate matrix.

요약 : 열처리하지 않은 찰흙과 열처리한 찰흙에서 함철 광물의 열적 거동과 상변환을 X-선 분말 회절 분석과 Mössbauer 분광법으로 조사하기 위하여 제주도 북제주군 광령리와 제주도 일도 지구에서 찰흙을 채취하였다. 상온과 20K에서 취한 Mössbauer 스펙트럼을 통해 열처리하지 않은 두 지역 찰흙에 함유된 상자성 Fe^{2+} 는 총형 규산염 광물과 ferrihydrite의 구조철이었고 초상자성 goethite가 전체 철 함량의 약 50%를 차지하고 있음을 확인하였다. 열처리한 찰흙에서 hematite의 X-선 회절 피크가 광령리 찰흙에서는 800°C에서부터 일도 지구 찰흙에서는 600°C에서부터 각각 나타났다. 두 지역 찰흙을 100°C에서 1200°C까지 100°C 간격으로 공기 분위기에서 열처리하였을 때 초상자성 goethite가 hematite로의 변환이 광령리 찰흙에서는 200°C와 300°C사이에서 일도 지구 찰흙에서는 500°C와 600°C사이에서 각각 일어남을 확인하였다. 열처리 온도 400°C에서 두 지역 찰흙의 구조철 Fe^{2+} 이 Fe^{3+} 로 완전히 산화되었다. 열처리 온도

400°C로부터 700°C~800°C에서 점토광물의 재수화가 나타났다. 700°C~800°C에서부터 1100°C 사이에서는 점토광물의 구조가 붕괴되면서 유리질화의 시작과 전개가 이어진 것으로 분석되었다. 1100°C 이상에서는 결정도가 높은 hematite가 형성된 반면에 알루미늄 규산염 matrix의 재결정화와 관련이 있을 것으로 여겨지는 상대 흡수면적비의 감소가 관측되었다.

INTRODUCTION

In the past decades, many works have been made on earthenwares and pottery excavated all over the world, in order to solve the questions of the provenance of raw material and the firing techniques, by using the analytical techniques such as XRD, Differential thermal analysis (DTA), Scanning electron microscope (SEM), Electron paramagnetic resonance (EPR), and Mössbauer spectroscopy. Among these, Mössbauer technique is ideally suitable for the investigation of the clay mineral transformations depending on the temperature and atmospheres, because of with the good sensitivity and high resolving power of ^{57}Fe Mössbauer spectroscopy to iron-bearing minerals.

In order to understand the Mössbauer spectra of earthenwares and pottery, it is necessary first to study both raw and fired clay. Works for the fired clay, based on the Mössbauer spectroscopy, have been carried out by some research groups (Simopoulos et al., 1975; Chevlier et al., 1976; Maeda et al., 1979; Maniatis et al., 1981; Stevens and Zhu, 1986; Zhou et al., 1992; Matsoka and Ikeya, 1995). Simopoulos et al. (1975) have heated a sample of an illitic clay in Athens for one hour at temperatures between 200°C and 1100°C with an interval of 100°C and studied Fe transformations induced by firing with Mössbauer spectroscopy. The similar behavior was observed by Chevlier et al. (1979) for a calcareous clay from Iran fired in air. They have shown that Fe transformations may be followed by measuring the changes in magnetic parameters such as spontaneous and

remanent magnetization and coercivity. These parameters provide a simple way to estimate what firing temperatures were used. By using Mössbauer spectroscopy and SEM, Maniatis et al. (1981) showed that an oxide particle size on firing at 700°C for both calcareous and noncalcareous clays increased. For temperatures higher than 700°C, the size of both clays continued to increase. However, unlike the size of noncalcareous clay, that of calcareous clay decreased at 1080°C.

More recently, Wagner et al. (1990) studied the iron mineralogy of illitic clays containing iron-rich impurities from eastern Bavaria fired systematically for 48 hours up to 1250°C with an interval of 50°C in air. They suggested that, in order to distinguish the contribution of oxides and silicates, it is important to take Mössbauer spectra at 4.2K or even below, because of the frequent presence of superparamagnetic iron oxides.

As for the Cheju Island soils resulted from the volcanic ashes, physical and chemical properties of soil minerals widely vary, because about 306 parasitic volcanos irregularly erupted during five main volcanic episodes and climate, topography, and year of formation differ with altitude. About 70% of the soils of Cheju Island formed by the volcanic activities have the typical characteristics of volcanic ash soil, and the parent material of the soil is originated mainly from basalt, and partly from trachyte or trachy-andesite.

Shin and Tavernier (1988) presented for five chronosequence soils of Cheju Island that soils developed from relatively old ash or alluvial deposits were mainly composed of

the primary minerals, ferromagnesian minerals and feldspars, and of the clay minerals, halloysite and vermiculites, by using XRD, Transmission electron microscope (TEM), and SEM techniques. Also, Kwon and Moon (1989) carried out mineralogical study on the clay minerals in Cheju Island by using XRD and SEM. Their results show that clay mineral assemblages vary slightly from sample to sample depending on the nature of parent materials and geological environments. However, chlorite, smectite, and illite show a preponderance in volcanic ash soils, while chlorite show a preponderance in magnesian soils. It is interesting to note that the XRD, TEM, and SEM techniques used by Kwon and Moon (1989) and Shin and Tavernier (1988) are not effective for analyzing oxidation state, electronic configuration, coordination number, magnetic state, and crystal symmetry of Fe atoms in the clay minerals or accessory minerals, for example, goethite or chlorite etc.. Therefore, this study related to the above properties of the Cheju soil is needed, using the Mössbauer spectroscopy.

The purpose of the present study is to investigate the thermal behavior and the transformation induced in the iron-bearing phases for samples collected from Kwangyeongli and Ildo district in Cheju Island, by using XRD and Mössbauer spectroscopy.

EXPERIMENTAL METHODS

The clay used in this study was collected from specific plowing fields located in Kwangyeongli and Ildo district. Clay collected in two areas was air-dried and ground with a medicine pestle to pass a 63 μ m sieve. Clay powders were used to examine by X-ray powder diffraction (XRD), X-ray fluorescence (XRF) and Mössbauer spectroscopy. Mössbauer absorbers of about 10mgFe/cm² were

prepared for the room temperature and 20K. Mössbauer spectroscopy by packing the clay powers in the brass rings in diameter 21mm and thickness 1mm sealed with Al-foil.

X-ray diffractometer (Philips PW3710) was used to investigate the mineralogical composition of raw clay and to monitor the phase transformation during firing. Pararell-oriented, 50mg samples of powdered clay on 25 by 75mm slide glass were analyzed by XRD techniques using Ni-filtered CuK α radiation ($\lambda=1.5406\text{\AA}$). XRD patterns of all samples were obtained in the 2θ range from 15° to 45° with a scanning speed 1°/min.

The chemical compositions of two clay samples were analyzed by X-ray fluorescence sequential spectrometer (Philips PW1480), and generator tension and current of the XRF spectrometer to obtain the measuring intensity were 40kV and 30mA, respectively.

The air-dried clay samples were fired in air atmosphere starting from 100°C and heating up to 1200°C with the step interval of 100°C. The firing procedure involved placing two samples within a muffle furnace and increasing the temperature by 200°C/h heating rate. After the samples were kept for 5 hours at the highest temperature constantly, they were allowed to cool down to the room temperature in the furnace.

Mössbauer spectra of the fired and raw clay samples were obtained at room temperature and 20K with a conventional constant acceleration spectrometer (Austin Co. S-600 type). The γ -ray source was 10mCi ⁵⁷Co (doped with Rh) at room temperature. An APCI cryogenic refrigeration systems were used to obtain spectra of clay samples held at 20K. Mössbauer spectra of the raw clay and the fired clay are obtained at room temperature and 20K. The velocity scale is calibrated by using an iron foil as the standard, before and after each spectrum is recorded.

Table 1. Chemical compositions of the clay sample by XRF

Sampling site	Unit: wt%											
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	L.O.I	Total
Kwangryeongli	59.86	18.52	6.34	1.38	0.01	0.31	0.87	1.47	0.66	0.09	10.53	100.04
Ildo district	61.73	16.30	8.03	1.35	0.13	0.46	1.37	2.12	1.60	0.10	6.89	100.08

*. FeO: Total Fe ** L.O.I: Loss on Ignition

Most samples are counted for 24 to 30 hours to get reasonable statistics, usually in the range of 5×10^5 to 3×10^5 counts per channel. Each spectrum is computer-fitted with a least square program which allows for the variation of parameters of sextet and doublet components.

RESULTS AND ANALYSIS

Chemical Compositions of Raw Clay

The chemical compositions analyzed with XRF of two clay samples are listed in Table 1. As shown in Table 1, they have a higher SiO₂ and a relatively lower Al₂O₃ content than the volcanic ash clay derived from basalts. Two clay samples belong to noncalcareous clay because CaO contents is less than 5%. The SiO₂ content of the two clay samples have a large difference, compared to that of volcanic ash soils derived from basic basalts. This means that two clay samples are not derived from a basic basalt but probably partly acid volcanic rocks such as trachyte. Especially, it is interesting to note that the content of Fe₂O₃ in two clay samples given by 6.34wt% and 8.03wt%, respectively is lower than that of volcanic ash soils in Cheju Island presented by Shin and Tavernier (1988) and Song and Yoo (1991).

X-ray Diffraction Analysis

XRD analysis was performed to identify the clay minerals and/or the phase transfor-

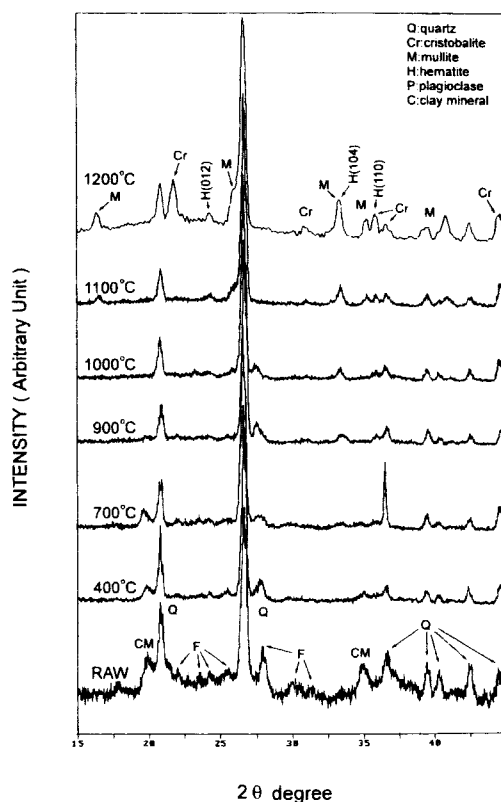


Fig. 1. XRD patterns of clay sample collected in Kangryeongli raw and fired at 300, 600, 800, 1000 and 1200°C in air atmosphere for 5 hours.

mations of iron oxides and the other Fe-bearing minerals in the raw and fired clay. Some of X-ray diffractograms for the raw and fired clay are shown in Fig. 1. As shown in Fig. 1, quartz and plagioclase is identified with some clay minerals. As shown in Fig. 1, no evidence of goethite and hematite phases is observed in XRD patterns of raw clay samples A and B, which is well explained by

Kodama et al. (1977) and Brown (1980). For the raw clay sample B, XRD peaks near 2.68 Å(104) and 2.50 Å(110), indicate hematite phases.

Shin and Tavernier (1988) and Song and Yoo (1991) have shown that a considerable amount of ferrihydrite, which is short-range-order hydrate iron oxide mineral, is present in volcanic ash soils in Cheju Island by selective dissolution techniques. In fact, an evidence of ferrihydrite is observed in XRD patterns (Fig. 1) in raw clay samples A and B.

As the firing temperature progressively increases, the relative intensity of plagioclase peaks gradually decreases, and it completely disappears above 1000°C. In XRD patterns of sample A given in Fig. 1, the clay minerals collapse between 900°C and 1000°C, and above 1100°C mullite phases appear. At 1200°C, peaks of cristobalite appear clearly. When the sample A is fired at the temperature higher than 800°C, peaks of hematite appear near 2.68 Å(104), 2.50 Å(110), and 3.66 Å(012). For sample B, the intensity of hematite strengthens gradually as the firing temperature increases above 600°C.

When raw clays are fired in air atmosphere, we can expect that the transformation of goethite and/or ferrihydrite into hematite depended on the firing temperature. From the result of XRD analysis, however, we can see that hematite phases appear for sample A at 600°C and for sample B at 800°C, respectively.

MÖSSBAUER SPECTROSCOPY ANALYSIS

Raw Clays

Mössbauer spectra obtained at the room temperature for raw clay samples A and B

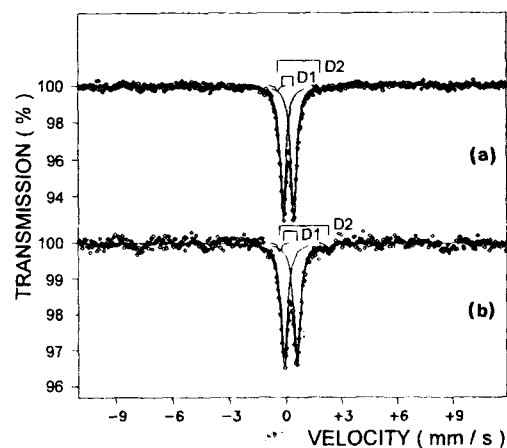


Fig. 2. Mössbauer spectra of raw clay samples obtained at room temperature. (a) Kwangryeongli (b) Ildo district.

are shown in Fig. 2. Each spectrum is fitted by two doublets. The structure of the observed spectra consists of two sets of doublet attributable to quadrupole splitting of the paramagnetic Fe^{3+} and Fe^{2+} , respectively. Mössbauer spectrum obtained at the room temperature for raw clay sample A shows no magnetic ordering. While spectrum for raw clay sample B shows insignificant magnetic hyperfine splitting attributable to magnetic oxides. The values of Mössbauer parameters for raw clays in this study are listed in Table 2.

The oxidation states of paramagnetic D1 and D2 component (Fig. 2) with isomer shift of 0.19mm/s and 0.25mm/s and of 0.77mm/s and 1.01mm/s display octahedral high spin Fe^{3+} and Fe^{2+} state, respectively. Also the values of the quadrupole splitting of these components are 0.57mm/s and 0.69mm/s, 2.26mm/s and 2.65mm/s, respectively. As shown in Fig. 2, the appearance of the paramagnetic Fe^{3+} doublet in raw clays commonly can be attributed to the presence of mainly super-paramagnetic goethite and/or Fe-bearing silicate minerals.

Mössbauer spectra of raw clay samples A

Table 2. Mössbauer parameters obtained at room temperature for raw clay collected in two areas.

Sampling site	Horizon	Fe ³⁺ doublet			Fe ²⁺ doublet		
		I.S.(mm/s)	Q.S.(mm/s)	R.A.(%)	I.S.(mm/s)	Q.S.(mm/s)	R.A.(%)
Kwangry-eongli	A-B ₃	0.19	0.57	98	0.90	2.26	2
Ildo district	C II B	0.25	0.69	96	1.01	2.65	4

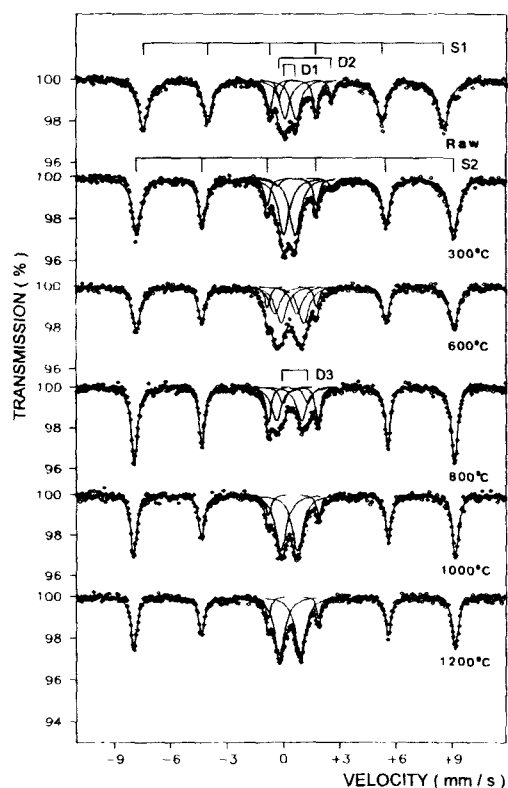


Fig. 3. Mössbauer spectra of clay in Kwangryeongli for raw and fired conditions at 300, 600, 800, 1000 and 1200°C in air atmosphere for 5 hours obtained at 20K.

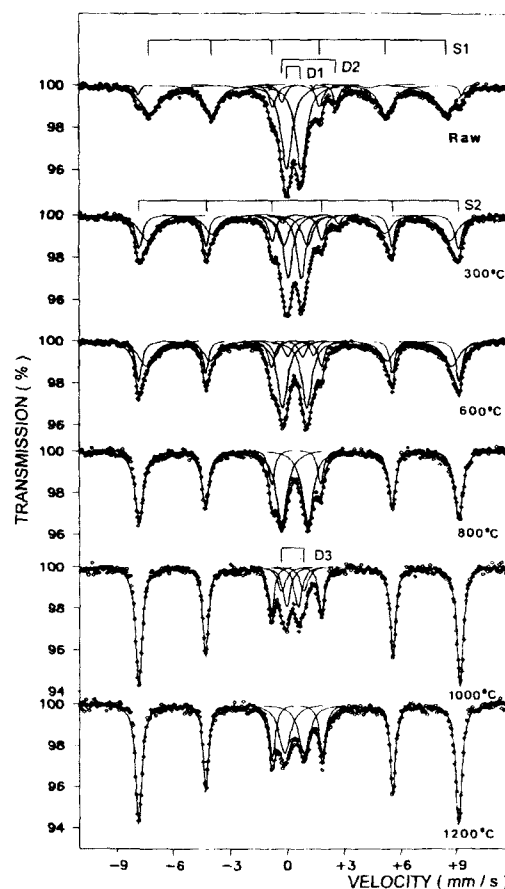


Fig. 4. Mössbauer spectra of clay in Ildo district for raw and fired conditions at 300, 600, 800, 1000 and 1200°C in air atmosphere for 5 hours obtained at 20K.

and B at 20K are shown in the top end of Fig. 3 and Fig. 4, respectively. These two spectra show very different figures in comparison with those obtained at room temperature. The decrease of the measuring temperature in sample A and B results in the clearly appearance and enhancement of the magnetic sextet of magnetic hyperfine splitting with depletion of a central paramagnetic doublet

(Fig. 3 and 4). The magnetic hyperfine field values of sextet S1 of two samples correspond to 492kOe and 487kOe, respectively. It is noted that the values of the magnetic hyperfine field for component S1 in raw clay samples A and B lie in that of synthetic goethite with the size smaller than 180Å measured

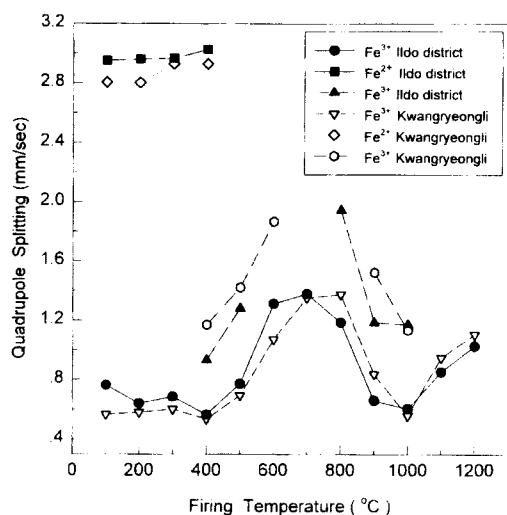


Fig. 5. Variation of the quadrupole splitting of the paramagnetic components of the Mössbauer spectra obtained at 20K with firing temperature.

at 77K (Van Der Kraan and Loaf, 1966).

The superparamagnetic relaxation effect of small iron oxides was observed in the Greese Attic clay by Gangas et al. (1972). Bigham et al. (1978a) and Murad and Johnston (1987) showed that it is difficult to characterize iron oxides with XRD analysis, in the case of iron oxide with the average grain size in the Mössbauer spectroscopy due to superparamagnetic relaxation effect (Fig. 3 and 4).

Fired Clays

Some of 20K Mössbauer spectra of clay samples A and B fired in the range from 100 °C to 1200 °C are shown in Fig. 3 and Fig. 4, respectively. The pattern of the observed spectra consists of two parts: two sets of paramagnetic doublet patterns due to quadrupole splitting of ferrihydrite and of the structural iron (Fe^{3+} , Fe^{2+}) in silicate minerals and a set of magnetic sextet pattern arising from

magnetic hyperfine splitting in magnetic oxides.

The quadrupole splitting of paramagnetic components of the spectra as a function of firing temperature is plotted in Fig. 5. From the figures we can recognize that the phase transformations of the Fe-bearing minerals occur successively in the domain of four temperatures as follows: room temperature to 300 °C, 400 °C to 700 °C~800 °C, 700 °C~800 °C to 1100 °C, above 1100 °C.

In the range from room temperature to 300 °C, the values of quadrupole splitting of paramagnetic Fe^{3+} and Fe^{2+} are not significantly changed because of the dehydration of absorption water and interlayer water in the clay mineral. At 400 °C, the quadrupole splitting of Fe^{3+} in samples A and B show a minimum value, which reaches 0.56 mm/s and 0.60 mm/s, respectively. In the regions of the firing temperature ranging from 400 °C to 600 °C for sample B and from 400 °C to 700 °C for sample A, distinctive changes occur. These regions have two features, the increase of the quadrupole splitting of doublet D1 and the growth of paramagnetic Fe^{3+} component D3 with high quadrupole splitting with depletion of doublet D1 observed below 400 °C. Two outstanding features of these are the appearance of doublet D3 with high quadrupole splitting at the temperature of near 400 °C and the disappearance above 600 °C for sample A and above 500 °C for sample B.

As shown in Fig. 3, 4, and 5, the two prominent changes observed are the fast increase of the quadrupole splitting and the variation of absorption linewidth of a central Fe^{3+} doublet D1 in temperature ranging from 400 °C to 600 °C. It implies that the electric field gradient is increased by the escape of crystal water OH^- ($2\text{OH}_{\text{inter}}^- \rightarrow \text{O}_{\text{inter}}^{2-} + \text{H}_2\text{O}_{\text{gas}}$) and by crystallographic deformation arising from dehydration (Farmer and Russel, 1972),

it clearly shows that the paramagnetic doublet D3 has higher quadrupole splitting and broader linewidth than doublet D1 observed below 400°C. Similar results have been found by Mackenzie (1969) and Simopoulos et al. (1975). It is believed that this change is associated with the beginning of dehydroxylation of the clay minerals.

At the firing temperature 500°C or higher, paramagnetic Fe²⁺ doublet D2 in 20K Mössbauer spectra of raw clay samples A and B almost disappears. This indicates that the ferrous iron is all-oxidized to the ferric form near the temperature where dehydration occurs (Fig. 3, 4, and 5). Our result agrees well with that of Hayashi et al. (1972) that ferrous iron in pure chlorites is completely oxidized by firing in air at between 400°C and 500°C. For fired sample A, quadrupole splitting of doublet D1 has increased slowly once again at near 700°C until it reached the maximum value of 1.37mm/s, but sample B showed a broad maximum at near 600°C until it reached the maximum value of 1.38mm/s in comparison with sample A. This shows the fact that the clay lattice is left severely disorganized with various defects and asymmetric coordinations for Fe³⁺, resulting in an increase of Z-component of the electric field gradient and in an increase in the linewidth as well. This result is supported by appearance of a paramagnetic Fe³⁺ D1 component with a broad linewidth given in Fig. 3 and Fig. 4.

On the other hand, there are many examples of the study of thermal analysis on the dehydroxylation process induced in clay minerals in firing within this range of temperatures. According to Grim (1968), thermal analysis (DTA) showed an endothermic peak corresponding to the loss of lattice water was observed in illite samples between 500°C and 700°C. The same result was obtained by

Smykatz-Kross (1974) from the study with various clay minerals fired between 500°C and 700°C. It appears therefore that firing the sample from 400°C to 700°C~800°C induces the increase of quadrupole splitting with broad linewidth due to dehydroxylation of Fe-bearing silicate minerals.

In the region of the firing temperature ranging from 700°C~800°C to 900°C, values of quadrupole splitting of doublet D1 components decrease quickly, but slowly between 900°C and 1000°C (Fig. 5). According to Tite and Maniatis (1975), the onset, spread, and completion of vitrification in fired clay are observed by SEM around 700°C, 900°C and 1080°C. Maniatis et al. (1981) also showed the successive decrease of the quadrupole splitting according to the onset, spread and completion of vitrification by using Mössbauer spectroscopy. As SEM results (Maniatis et al., 1981), new major changes in Fe-bearing silicate minerals occur at about 900°C, which can involve the appearance of silicate matrix of mullite and cristobalite, observed by XRD patterns given in Fig. 1. Therefore, Fe phase transformation occurring in the region of the firing temperature ranging from 700°C to 1100°C may be associated with vitrification process.

Additional variations in the pattern of the central paramagnetic part of the Mössbauer spectra shown in Fig. 3 and 4 are observed again in the range of firing temperature from 800°C to 1000°C. In this range of the firing temperature a second ferric component D3 reappears, and has splittings varying from 1.13 to 1.94mm/s and broad absorption linewidth. The paramagnetic D3 component with splittings 0.49mm/s and 0.80mm/s appeared in the Greece Attic clay fired in the temperature ranging from 500°C to 900°C (Simopoulos et al., 1975). Between the clay samples from two areas of Cheju Island and Greece Attic clay,

the differences in the firing temperature dependence of appearing and disappearing of paramagnetic D3 component may be varied due to differences in Fe-bearing mineral species and its mineral composition.

At a temperature higher than 1100°C, values of quadrupole splitting of paramagnetic doublet D1 are slightly higher than those of doublet D1 observed below 400°C, and they gradually increases and approaches 1.03mm/s and 1.10mm/s, respectively. It may imply that new Fe-bearing mineral phases are formed by a certain iron transformation different from vitrification process. These are shown in the XRD data (Fig. 1) which indicate clearly the disappearance of the plagioclase peaks and the appearance of the aluminosilicate matrix of mullite due to recrystallization and of the apparent cristobalite at a temperature higher than 1100°C. Two phase transformations occur between 500°C~600°C and 1100°C, corresponding to the following sequence of reaction. The Mössbauer data and XRD patterns are almost consistent with this reaction sequence.

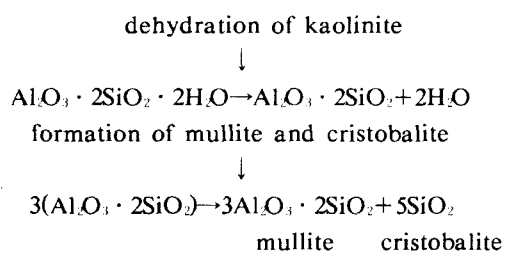


Fig. 6 shows the dependence on the firing temperature of the magnetic hyperfine field of iron oxide components induced by firing the clay samples for two areas in Cheju Island. The Mössbauer spectrum of sample A fired at 200°C has been fitted with two sets of sextet S1 and S2 attributable to hematite and goethite, but that at 300°C has been fitted with only one set of a sextet S2. This indicates that the transformation of goethite

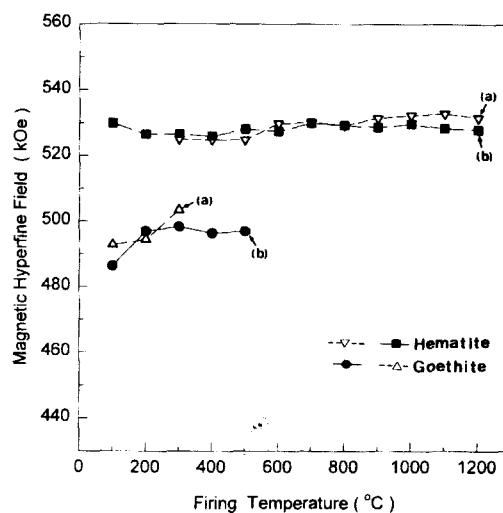


Fig. 6. Variation of the magnetic hyperfine field of the components of hematite and goethite of the Mössbauer spectra obtained at 20K with firing temperature.

into hematite occur in the firing temperature ranging from 200°C to 300°C, which indicates that the hematite with magnetic hyperfine field of 520kOe was formed by firing at 300°C in sample A. This value is slightly lower than that measured in synthetic hematite samples at 16K ($H_{\text{eff}}=534.5\text{kOe}$, Amarasiriwardena et al., 1988). In comparison with the magnetic hyperfine field of bulk samples, smaller reductions have been observed in small particles of hematite (Gangas et al. 1972).

The Mössbauer spectra of the sample B fired between room temperature and 500°C have been fitted with two sets of sextet S1 and S2 attributable to hematite and goethite and/or their compounds, while for the temperature higher than 600°C they have been fitted with a sextet S2 only. This result implies that phase transformation of goethite in raw clay sample B into hematite occurs in the firing temperature between 500°C and 600

°C. The values of magnetic hyperfine field of hematite formed from the clay samples A and B fired in the temperature ranging from 400 °C to 600°C are average 525kOe and show almost constant distribution (Fig. 6).

Further firing up to 800°C leads the slow increase of magnetic hyperfine field attributable to the increase of particle size and/or decrease of the substitution content of impurities such as Al³⁺ in hematite.

It has been reported that the magnetic hyperfine splitting values obtained from various soil iron oxides is influenced by at least two factors: random replacement of Fe atoms with nonmagnetic cations (Nalovic et al., 1975) such as Al³⁺ (Janot and Gibert, 1970) and particle size effect (Kandig et al., 1966; Van Der Kraan and Van Leof, 1966). In our study, particle size effects should be minimized at low temperatures (20K). Thus reductions in magnetic hyperfine fields may be mainly resulted from a disruption of internal magnetic ordering through replacement of Fe³⁺ with nonmagnetic cations including Al³⁺. In fact, Al-substituted goethite and hematite in soils have been identified by many workers (Bigham et al. 1978b; Golden et al. 1979; Pombo et al., 1982; Fabris et al., 1985; Fontes et al., 1991). Therefore, the reduced values of magnetic hyperfine field may be attributed primarily to the effect of diamagnetic Al-substitution. The chemical compositions of soil hematite and goethite have taken the form of $\alpha\text{-}(\text{Fe}_{1-x}\text{Al}_x)\text{O}_3$ and $\alpha\text{-}(\text{Fe}_{1-x}\text{Al}_x)\text{OOH}$, respectively, where x is the mole% of Al. In our study, the substitutions of Al for Fe in goethite and hematite were calculated from 20K Mössbauer data by using two relation formula which were proposed by Amarasiriwardena et al. (1988) and De Grave et al. (1988). As hematites in sample A FIRED AT 1000°C and the sample B fired at 1100°C exhibits the maximum value for magnetic hyper-

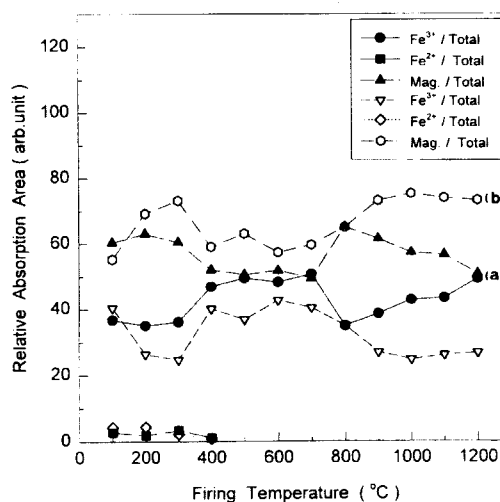


Fig. 7. Variation of the relative absorption areas of the paramagnetic and magnetic components of the Mössbauer spectra obtained at 20K as a function of firing temperature.

fine fields of 533kOe and 530kOe, respectively, and sextet with all the narrowest absorption linewidth as well, it appears that well-crystallized hematites are formed by firing in this range of temperatures. It indicates that hematites formed at 1000°C and 1100°C grow up to the maximum size, or diamagnetic Al³⁺ contents drop rapidly down to 7.6mol% in sample A and to 16.4mol% in sample B, respectively.

The relative amounts of magnetic iron oxides and of structural iron in the clay minerals can be conveniently obtained by the ratio of the resonance absorption area of the paramagnetic or magnetic components to the total resonance absorption area for 20K Mössbauer spectra with the firing temperature (this ratio will be referred to relative absorption area hereafter). If the equal recoil-free fractions can be assumed for all Fe, the figures represent the relative amounts of Fe in each phases. A plot of the relative absorption area versus firing temperature is given in Fig. 7. In

the region up to 300°C the characteristic features are that the relative absorption area of the structural iron (Fe^{3+} , Fe^{2+}) decreases due to silicate clay minerals and magnetic components increase. This result indicates that the phase transformation of superpara-magnetic goethite into hematite occurred between room temperature and 300°C. The reaction kinetics of hydrothermal transformation of α - FeOOH to α - Fe_2O_3 by heating has been investigated by Barb et al. (1990) with Mössbauer spectroscopy on synthetic samples. According to their results the transformation is completed in 2 h at 200°C, which well matches our experimental result.

In the temperature ranging from 400°C up to 600°C the relative absorption areas of the paramagnetic and magnetic components remains almost constant within experimental error at 50%:50% and 40%:60% for samples A and B, respectively, which indicates that no outstanding changes in two components occur in this temperature range. For sample A fired higher than 600°C, the relative absorption area of the paramagnetic Fe^{3+} component decreases and the corresponding hematite increases. Above 800°C, variation of the relative absorption areas for two components exhibits inversing variation. This results may be explained by an onset of the vitrification process in the aluminosilicates. Grim (1968) observed that the destruction of the illite structure starts at about 850°C. It appears that the decrease observed in the relative absorption areas at 800°C implies the initiation of disintegration of the Fe-bearing clay mineral structure. Especially, for sample B, the relative absorption area of paramagnetic component decrease continuously from 700°C to 1000°C and increase very slowly for the temperature higher than 1000°C, which indicates a decrease in the recoil-free fractions. From these results, the opposite trends

between 900°C and 1100°C may be explained by depletion of Fe in the aluminosilicates and/or a increase in particle size due to reactions of iron oxides with the aluminosilicate matrix of mullite formed during the continuous vitrification. Similarly the decreasing trend observed generally in the relative absorption area of hematite in sample A fired between 900°C and 1100°C (Fig. 7) may be understood as a result of a decrease in particle size and/or the partial dissolution of Fe due to the recrystallization of the aluminosilicate matrix of mullite. However, it is noted that other aspects of the effect of firing are the apparent increases in particle size of hematite of the clay samples according as the firing temperature increases (Simopoulos et al., 1975).

Therefore, the decrease of the relative absorption area in two samples A and B fired above 800°C and 1000°C, respectively, may suggest that the growth of hematite is suppressed by a certain reaction which traps Fe. It is believed that In the case of sample B the velocity of the spread of vitrification and the recrystallization of aluminosilicate matrix according to the disintegration of the clay mineral structure is very slow in comparison with in the case of sample A.

CONCLUSIONS

The results presented in this paper can provide a detailed information of the iron-bearing phases in a soil and of the iron transformations during firing.

The X-ray powder diffraction peaks of hematite are observed near 2.68Å(104), 2.50Å(110), and 3.66Å(012) in firing two clays progressively to 600°C and 800°C, respectively, but no peaks of hematite and goethite were observed in the raw clays in both areas.

The raw clays in two areas in Cheju Is-

land contains mainly iron, in the form of superparamagnetic goethite and structural iron (Fe^{3+} and Fe^{2+}) in the silicate clay minerals. The majority of paramagnetic components are in high spin Fe^{3+} state. Two clays exhibited strong superparamagnetic relaxation, a collapse of the Mössbauer magnetic splitting at room temperatures due to small size of the oxide particles and/or partial substitution of Al^{3+} for Fe^{3+} in the oxide structures.

A transformation of superparamagnetic goethite into hematite is observed in firing progressively to 300°C for the clay in Kwangryeongli and in firing progressively to 600°C for the clay in Ildo district.

Through the dependence on firing temperatures of quadrupole splitting and relative absorption area for Fe^{3+} component contained in the fired clay, the phase transformation of the iron-bearing silicate minerals is observed in the domain of four temperatures. The dehydration of silicate minerals is observed in the region of firing temperature from room temperature to 300°C , and Fe^{2+} contained in the raw clays is completely oxidized into Fe^{3+} at 400°C . In the region of firing temperature from 400°C to $700^\circ\text{C}\sim 800^\circ\text{C}$ large increases in the values of quadrupole splitting and of absorption linewidth is observed, due to paramagnetic Fe^{3+} leaving crystal lattice of iron-bearing silicate minerals and is associated with dehydroxylation process of clay minerals. It is believed that a sudden decrease in the value of quadrupole splitting from $700^\circ\text{C}\sim 800^\circ\text{C}$ to 1000°C is associated with the desintegration of the clay mineral structure and with the onset and spread of vitrification process at the same time. Magnetic hyperfine fields and crystallization of hematite phase arising from vitrification increase, but the relative absorption area decreases in firing up to 1100°C or high-

er. It is believed that the decrease of the relative absorption area is related to the recrystallization of alluminosilicate matrix.

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