Fourier Transform Infrared Spectroscopic Studies of Hydrothermal Illites

열수변질 기원 일라이트의 FTIR 연구

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ABSTRACT : The purpose of this study is to interpret vibrational spectra of hydrothermal $1M_d$ and $2M_1$ illites using Fourier transform infrared spectroscopy (FTIR) in both the far-IR (<200 cm^{-1}) and mid-IR (400-4000 cm^{-1}) regions. The illites were obtained from the hydrothermal clay deposits, western Pusan, Korea. The Al-O-Al and Al-O-Si bonding of $2M_1$ polytype is stronger than that of $1M_d$ polytype. Three bondings of K atom are observed in the interlayer sites; interlayer torsional mode at the 111-114 cm^{-1}, out-of-plane vibration at 135-143 cm^{-1}, and lattice mode of vibration at 167-168 cm^{-1}. The most noticeable difference between the two polytypes lies in the bonding state of the interlayer sites. The $1M_d$ illite shows broad bands in the far-infrared region and its band positions differ from those of the $2M_1$ type. The interlayer bonding of the $2M_1$ polytype is stronger than that of the $1M_d$ type. In the case of the $2M_1$ polytype, the K cation is more firmly fixed on the interlayer site. The K-O$_{inner}$ bands increase with increasing frequency of the hydroxyl stretching vibration. The frequency of hydroxyl stretching vibration increases with increasing (Fe+Mg) cations.

Keyword : far-IR region, hydrothermal illites, mid-IR region, polytype, vibration

요약 : Fourier transform 적외선 분광기를 사용하여 및 원적외선 (<200 cm^{-1}) 영역과 중간적외선 (400-4000 cm^{-1}) 영역에서 열수기원 일라이트의 층간 결합상태와 화학조성간의 관계를 해석하였다. 중간 적외선 영역에서는 $2M_1$ 다형의 Al-O-Al 및 Al-O-Si 결합이 $1M_d$ 형의 것보다 강한 것으로 나타났다. 원적외선 영역에서는 세 종류의 K-O 결합이 111-114, 135-143 및 167-168 cm^{-1}에서 인지되었다. $2M_1$ 과 $1M_d$ 다형간의 가장 큰 차이는 $2M_1$형의 층간결합이 $1M_d$형보다 상대적으로 강하여 K가 층간에 보 다 강하게 결합되어 있다는 점이며, 두 다형의 층간결합의 상태는 서로 상이하다. K-O$_{inner}$ band는 (OH) stretching band의 진동수가 높을수록 커지며, (OH) stretching band는 팔면체의 양이온 (Fe+Mg) 의 함량에도 영향을 받는 것으로 나타났다.

주요어 : 원적외선영역, 열수기원 일라이트, 중간적외선영역, 다형, 진동수

Introduction

Natural clay minerals occurring in the hydro-thermal systems show complex structures and chemistry. Spectroscopic techniques can provide information on the nature of the interactions between interlayer cations and the structures of clays minerals. Infrared spectroscopy has been widely used for the structural study of clay minerals and as a probe of interatomic forces (Farmer, 1974). The mid-infrared region is used to study strong absorptions such as the Si-O stretching and bending vibrations of silicate minerals. The far-infrared contains fundamental absorptions associated with metal-oxygen vibra-tions and complex deformations of polymeric units. The far-infrared region of the spectrum is generally limited to the frequencies below 200 cm^{-1}. The assignment of the bands in the 80-200 cm^{-1} region were firstly made by Ishii *et al.* (1967) using a normal mode analysis that predicts infrared-active and interlayer vibrational modes. However, the spectral range below <200 cm^{-1} is still difficult to interpret because the low energy range is related to vibrations of several atoms in complex modes and many absorption bands are generally weaker than those in the mid-infrared region. Nevertheless, the interpretation of infrared spectra in the far-infrared region becomes to be more important for clay minerals because the frequencies are primarily dependent on the cation-O bonds and vary as the cation is exchanged.

Studies of far- and mid-infrared absorption spectra on clay minerals provide insight into the causes of vibrational modes of OH and cations of tetrahedral, octahedral, and interlayer sites (Farmer and Russell, 1964; Vedder, 1964; Farmer, 1974, Velde, 1983; Velde and Couty, 1985; Prost, *et al.*, 1989; Johnstone *et al.*, 1990; Schroeder, 1990). Until recently, the advent of the Fourier transform infrared spec-trometer has made possible measurement of absorption spectra with high resolution in the far-infrared frequency range of 50-200 cm^{-1} as well as in the mid-infrared region (Velde and

Couty, 1985; Prost and Laperche, 1990; Laperche and Prost, 1991).

The purpose of this study is to interpret infrared spectra of hydrothermal illites obtained from clay deposits, using Fourier transform infrared spectroscopy in both the mid- and far-infrared regions.

Materials and Methods

$2M_1$ and $1M_d$ illites are found in the clay deposits in the western Pusan (referred to as Noksan, Kimhae-gun until mid 1990s). $2M_1$ illite is the predominant in the sericite-rich clays of the Bobae mine located in western Pusan. $1M_d$ illite that occurs as pale green veinlets is a trace mineral in the pyrophyllite-rich clays of the Kimhae mine at the Noksan area, western Pusan. Both clay deposits were formed by the hydrothermal alteration of late Cretraceous volcanoclastic rocks such as rhyo-dacitic tuff, andesitic tuff, and tuffaceous shale (Kim *et al.*, 1991, 1993; Choo, 1996).

X-ray powder diffraction (XRD) analysis was used to identify the clay minerals and to cal-culate the cell parameters of illite. The original clay samples were crushed gently in an agate mortar and dispersed in distilled water using an ultrasonic vibrator. After overnight sedimenta-tion, the <2 μm fractions were separated from the dispersed solution by centrifugation. XRD results indicated that all illitic samples separated for the present study are monomineralic and contain no impurity. An automated X-ray dif-fractometer (Rigaku RAD3-C) equipped with a Cu target and Kα radiation was operated at 40 kV/30 mA and 0.5°-0.15 mm-1.0° slits. Calcu-lated unit cell parameters for the $1M_d$ polytype illite are a=5.098Å, b=8.999Å, c=10.071Å, and β=94.55° and those for the $2M_1$ polytype average a=5.179Å, b=9.006Å, c=20.059Å, and β=95.76°. The cell parameters of the $2M_1$ polytype are slightly larger than those of the $1M_d$ polytype.

Chemical compositions of minerals were analyzed on the polished thin sections using an electron microprobe (JEOL Superprobe 733)

fitted with automated wavelength-dispersive spectrometers. The instrumental conditions by the electron microprobe were set to a beam diameter of 5 μm, an accelerating voltage of 15 kV and a beam current of 10 nA, with 20-seconds counts per element. Both Na and K were counted first so as to avoid alkali loss during the analyses. Quantitative analyses were performed using a ZAF X-ray intensity correction.

Infrared spectra were obtained using a Bomem DA-8 Fourier transform infrared spectrometer. The FTIR spectrometer incorporates a KBr beamsplitter and a mercury-cadmium-telluride detector (MCT) cooled by liquid-nitrogen for the mid-infrared range. Bolometer cooled by liquid-helium was adapted for the far-infrared experiment. All samples were prepared by the pellet technique.

FTIR spectra in the mid-infrared region were recorded in the frequency range 400-4000 cm^{-1}, with a resolution of 1 cm^{-1}. Pellets were made of a mixture of 198 mg of KBr and 2 mg of clay. Far-infrared absorption spectra were recorded in the 50-200 cm^{-1} region, with a resolution of 0.2 cm^{-1}. Aside from polyethylene or silicon wafer, there have been few supporting materials used for the powdered samples in far-infrared experiment. Previous workers used polyethylene (Prost and Laperche, 1990; Laperche and Prost, 1991), self-supporting film (Tateyama et al., 1977; Velde and Couty, 1985; Laperche and Prost, 1991; Schroeder, 1992) or silicon

wafer (Schroeder, 1990, 1992). For the present study, Teflon powder was used as a matrix material because it does not give any spectra overlapped with those of clay minerals. During the infrared spectroscopy experiments the FT spectrometer was operated under the vacuum condition and constantly purged with dry nitrogen in order to remove atmospheric water vapor.

Results and Discussion

IR Spectra in the Mid-IR Region

Fig. 1 and Table 1 show representative IR spectra of hydroxyl stretching bands in illites. The $1M_d$ illite has an OH asymmetric stretching band at 3630 cm^{-1} with a tailing toward higher frequency. The $2M_1$ illite also shows one OH asymmetric stretching band at 3628-3630 cm^{-1}. These bands are due to OH ions coordinated to two octahedral cations of AlAl. These OH ions are close to a vacant octahedral site, so they are tilted toward the vacancy (Vedder and McDonald, 1963; Vedder, 1964). The main cause of hydroxyl orientation basically originates from structural characters of dioctahedral mica that contains vacant octahedral sites.

Vibrations near 1000 cm^{-1} are due to Si-O stretching. Substitution of Al for Si in the silicon-oxygen lattice modifies Si-O vibrations, and causes new bands ascribed to Si-O-Al vibrations that appear in the 600-900 cm^{-1} region

Table 1. Frequency of IR bands and K content of illites (per O_{11}).

Sample	K_1-O bond (cm^{-1})	K_2-O bond (cm^{-1})	K_3-O bond (cm^{-1})	ν(OH) (cm^{-1})	K	polytype
B7-22	112	143	170	3628	-	$2M_1$
B7-32	112	143	169	3628	-	$2M_1$
B7-33	111	140	170	3628	-	$2M_1$
B8A-3	111	142	168	3630	0.89	$2M_1$
B10-2	111	139	168	3630	0.86	$2M_1$
B20-1	110	142	168	3628	0.89	$2M_1$
B36	110	142	168	3629	0.88	$2M_1$
J3	111	142	167	3631	0.85	$2M_1$
J4	111	141	168	3631	0.85	$2M_1$
1Md	111	135	167	3630	0.81	$1M_d$

- ; not measured
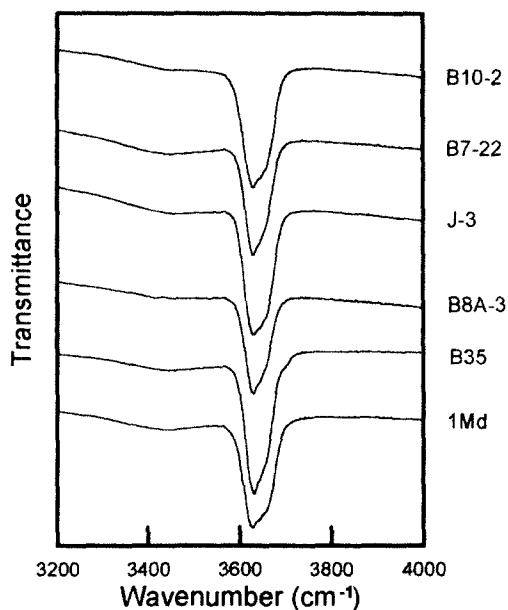
Fig. 1. Frequency of the hydroxyl stretching of illites.

Fig. 2. Far-infrared spectra of illites. Sample numbers are the same as in Fig. 1.

(Farmer and Russell, 1964). The (AlAl)-OH bending vibration occurs at 905 cm^{-1} in both illite polytypes. The tetrahedral Al-O vibration occurs at 800 cm^{-1}. Its intensity exhibits an increase from $1M_d$ to $2M_1$ type. It suggests that the Al-O-Al bonding of $2M_1$ polytype is stronger than that of $1M_d$ polytype. The bands at 828-830 cm^{-1} are due to dipole moment perpendicular to the (001) direction and the bands at 735-725 cm^{-1} are attributed to Al-O-Si bonding. The intensity of these bands is also weak in $1M_d$ polytype. The O-Si-O vibration including apical and basal oxygens appears at 530 cm^{-1}. The ordering between Al and Si does not affect the stacking (Velde, 1983). The difference between the two polytypes is not observed at this lower frequency region.

IR Spectra in the Far-IR Region

The vibrations in this region are related to interlayer M-O stretching modes or interlayer ion translations (Ishii *et al.* 1967). Fig. 2 and Ta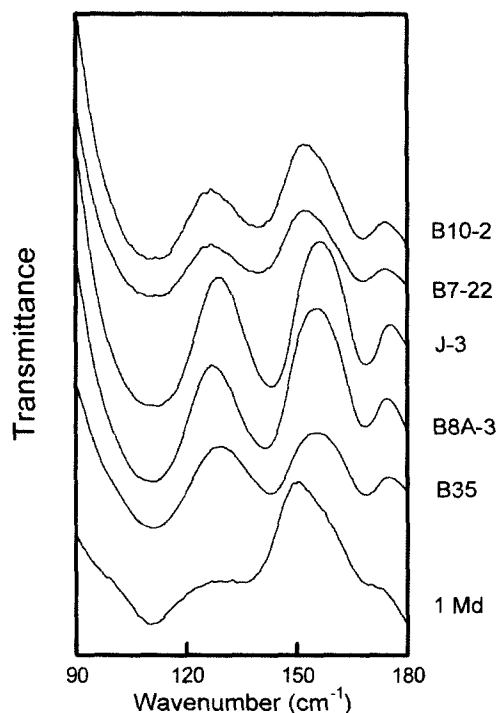ble 1 show spectra of illites in the far-infrared region. The frequency of interlayer bands is strongly correlated with the charge and mass of the interlayer cations, and compositions of the octahedral layer (Fripiat, 1982; Prost and Laperche, 1990; Schroeder, 1992). Three bands are observed at the 110-112, 135-143, and 167-168 cm^{-1} regions. The $1M_d$ illite shows broad bands in the far-infrared region and its band positions and shapes differ from those of $2M_1$ type. The $1M_d$ polytype is prominently differentiated from $2M_1$ type in the bands at 135-143 cm^{-1}.

The interlayer torsional mode is observed at the 111-114 cm^{-1}. This band is attributed to the K-O stretching vibrational motions (Ishii *et al.*, 1967). Bands at 135-143 cm^{-1} are ascribed to the out-of-plane vibrations of K atom and those at 167-168 cm^{-1} are due to a lattice mode of vibration (Laperche and Prost, 1991). In contrast to the torsional mode, these modes exhibit much weaker absorbance value.

Interlayer Bonding of the Two Polytypes

The most noticeable difference between the two polytypes of illite, as confirmed by far-infrared spectroscopy, lies in the bonding state of the interlayer sites. On the basis of the intensities and positions of the present far-infrared spectra, there seems to be no doubt that the interlayer bonding of the $2M_1$ polytype is stronger than that of the $1M_d$ type. In the case of the $2M_1$ polytype, the K cation is more firmly fixed on the interlayer site. The reason why the interlayer bonding in the $2M_1$ type is stronger than in the $1M_d$ type can be explained by crystal chemistry. The bonding between layers of the muscovite structure arises from the electrostatic attraction between the uncompensated ionic charges of cations in the layers and interlayers. The uncompensated charge is mainly due to the Al substitution for Si in the tetrahedral sites, and minimal substitution in octahedral sites can occur as well. All negative charge is very close to the interlayer K, leading to a strong electrostatic attraction between layers. For the present samples studied, the total layer charge and the content of interlayer cations (mainly K) of the $2M_1$ polytype are higher than those of the $1M_d$ type.

Relation between IR Frequency and Crystal Chemistry

Hydroxyl stretching frequency decreases with increasing K content, although there is some scatter of the data (Fig. 3). The out-of-plane vibrations of K atom at 135-143 cm^{-1} are slightly dependent on the K content in illites. At the 135-143 cm^{-1} region, the difference of the frequency position and intensity between the two polytypes of illite is noticeable. The frequency of 110 cm^{-1} region is a function of the bond length between K and the basal inner oxygen of the ditrigonal cavity (Tateyama et al., 1977). With increasing bond length between K and the basal inner oxygen of the ditrigonal cavity distance, the specific interaction between
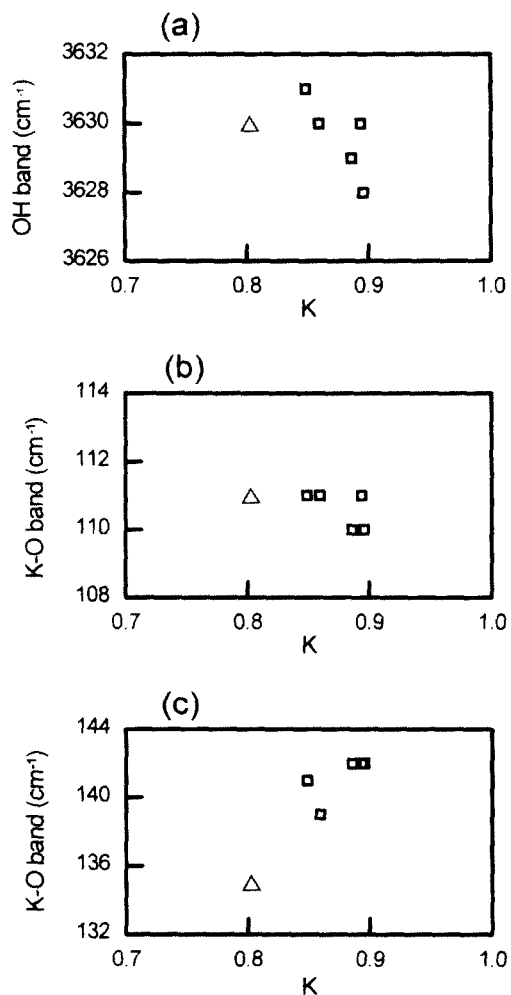

Fig. 3. The variations in frequency as a function of K content in illites. Cation content is normalized on the basis of 11 oxygens. (a) The relation between OH stretching band and K. (b) The relation between K-O band at 110 cm^{-1} and K. (c) The relation between K-O band at 135-145 cm^{-1} and K. Seven samples analyzed.

K and structural OH groups theoretically decreases. Tateyama et al. (1977) and Schroeder (1990) derived linear correlation equations between the frequency and K-O distance from known lattice parameters and infrared data of K-micas, although there is a lack of consistency between different samples used. The K-O$_{inner}$ distance of $1M_d$ illite, which is calculated by
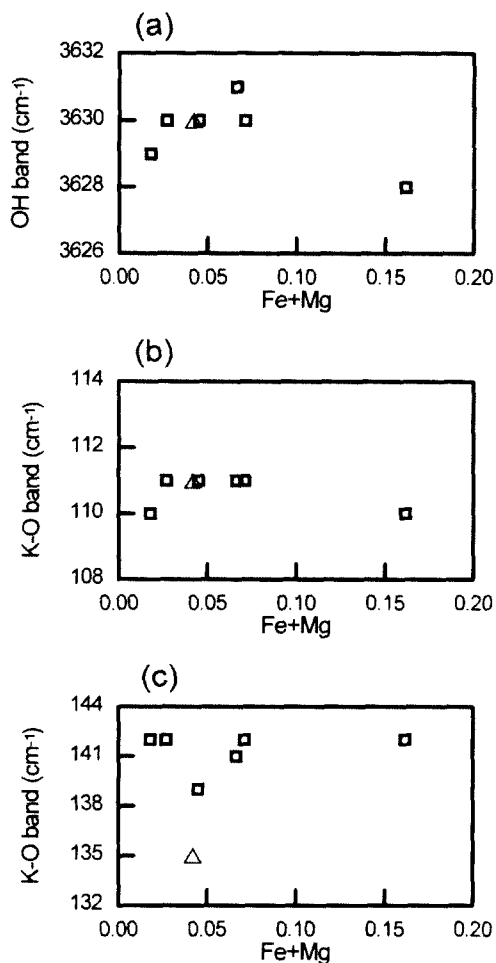
Fig. 4. Variations in frequency position as a function of octahedral (Fe+Mg) contents. Cation content is normalized on the basis of 11 oxygens. (a) The relation between OH stretching band and (Fe+Mg). (b) The relation between K-O band at 110 cm⁻¹ and (Fe+Mg). (c) The relation between K-O band at 135-145 cm⁻¹ and (Fe+Mg). Sample numbers are the same as in Fig. 3.

Fig. 5. Relation between frequency of hydroxyl stretching and frequency of K-O interlayer torsional mode. Sample numbers are the same as in Fig. 1.

The frequency of hydroxyl stretching vibration increases with increasing (Fe+Mg) cations in octahedral sites, with one exception of data (Fig. 4). Much substitution in octahedral sites seems to be related to shorter K-O bond distance, and K is strongly fixed in the ditrigonal ring of interlayer. The K-O$_{inner}$ bands at 110-114 cm⁻¹ and 135-143 cm⁻¹ regions appear to have little relationship with (Fe+Mg) content.

Variations in K-O bond lengths are closely related to the hydroxyl orientation (Kodama *et al.*, 1974). The K-O bands at 110-114 cm⁻¹ increase with increasing frequency of the hydroxyl stretching vibration, as shown in Fig. 5. The vibrations of hydroxyl groups are affected by the nature of cations to which the OH group is directly coordinated by hydrogen bonding. The vibrational frequency of K, therefore, is a function of the electric potential in the cage where K is located. The OH stretching frequency changes positively with K and the (Fe+Mg) contents. This result is compared with the data by Prost and Laperche (1990) showing that the frequency was influenced by the orientation of structural-OH groups and by the Fe^{2+} content of the micas.

their equation, shows similar to that of 2M₁ polytype. Hydroxyl stretching frequency varies with substitutions in the octahedral and tetrahedral sheets or with the K content in the interlayer. Therefore, it is expected that the hydroxyl stretching band is related to octahedral composition and the torsional or transitional vibrational frequencies in the far-infrared region.
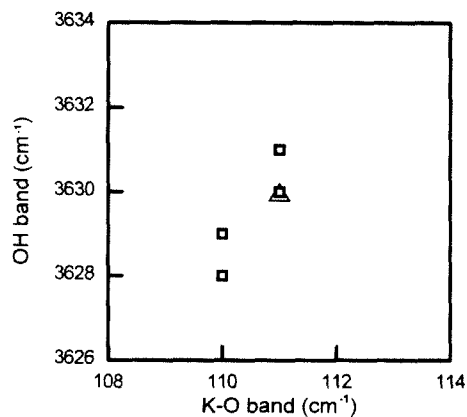
Summary

The most noticeable difference between the

two polytypes of illite, as confirmed by far-infrared spectroscopy, lies in the bonding state of the intelayer sites. The interlayer bonding of the $2M_1$ polytype is stronger than that of the $1M_d$ type. The Al-O-Al and Al-O-Si bonding of $2M_1$ polytype is stronger than that of $1M_d$ polytype. In the case of the $2M_1$ polytype, the K cation is more firmly fixed on the interlayer site. The $1M_d$ illite shows broad bands in the far-infrared region and its band positions differ from those of $2M_1$ type. The frequency of hydroxyl stretching vibration increases with increasing (Fe+Mg) cations. The K-O_{inner} bands increase with increasing frequency of the hydroxyl stretching vibration. Although far-infrared spectroscopy has the potential to ascertain the bonding state of interlayer sites in illite, thorough characterization of the infrared spectra for many illites with varying crystal chemistry is also needed to better understand the bonding characters, together with the high frequency region.

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