Laihunite in planetary materials: An FTIR and TEM study of oxidized synthetic and meteoritic Fe-rich olivine

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In situ mid-infrared transmission measurements of matrices from carbonaceous chondrites heated up to 572 °C in air were conducted by FTIR spectroscopy. The FTIR spectra of the matrices mainly showed olivine bands. With increasing temperature, up to 477 °C, the spectra did not show significant changes. However, at 572 °C, the ~11-μm band split into a doublet, and the intensity of the ~10-μm band relative to that of the ~11-μm band increased significantly. In synthetic Fe-rich olivine (Fo₄₇) samples heated at 600 °C in air, their mid-infrared spectra showed changes similar to those in meteoritic samples. A TEM observation of the recovered meteoritic samples showed that most olivine grains had a stacking disorder on (001). Selected area electron diffraction patterns of the grains also exhibited extra reflections, corresponding to a similar superstructure to three-fold periodicity along *c*_{ol} known as laihunite-3*M* in Fe₂SiO₄. Although the synthetic Fe-rich olivine did not have any defect structures before heating, the olivine commonly had a stacking disorder on (001) after heating at 600 °C. Therefore, the changes in mid-infrared spectra of the matrices of carbonaceous chondrites were not caused by chemical reactions among their constituent minerals, but were mainly caused by oxidation of iron within the olivine structure. The mid-infrared spectra of olivine-dominating samples from this study are potential reference data for the oxidation state of olivine in in situ mid-infrared measurements on the Martian surface, in partially oxidized meteorites, on asteroidal surfaces, and in interplanetary dust particles.

Keywords: Fe-rich olivine, Laihunite, Carbonaceous chondrites, Infrared spectroscopy, Transmission electron microscopy

INTRODUCTION

The oxidation state of iron in planetary materials such as meteorites and dust particles is the key to understanding *f*_{O₂} conditions and water activities that these planetary materials have experienced. Among silicates in planetary materials, olivine is one of the major hosts of iron. At high *f*_{O₂} conditions, iron-bearing olivine transforms to ferric iron-bearing phases such as magnetite, hematite, and a superstructure of olivine known as laihunite (e.g., Shen et al., 1986; Tamada et al., 1983). Laihunite forms in a variety of terrestrial processes such as metasomatism of man-

tle olivine (Banfield et al., 1992). Moreover, meteoritic and planetary materials may also be exposed to oxidizing environments during aqueous alteration or metasomatism on their parent bodies (Brearley, 2003; Tomeoka and Buseck, 1990). Hence, knowledge of the effects of oxidation on the dominating Fe-bearing minerals is crucial; it allows the determination of the formation environment. Since olivine is a very common phase in meteoritic and planetary materials, oxidation-related changes to this mineral are of high interest.

Recent findings have shown that the environment on Mars was much more “wet” and oxidizing in the past (Ehlman et al. 2011; Wiseman et al. 2010). As a secondary phase in Martian meteorites, laihunite proved to be a

useful marker to estimate the formation environment. Micro-Raman spectroscopy, scanning electron microscopy, transmission electron microscopy (TEM), and X-ray diffraction studies of crack- and vein-fillings in nakhlites suggested fluid-assisted alteration in the 400 °C to 800 °C range (Noguchi et al., 2009; Rost et al., 2006). This laihunite-like phase was also rich in Li, which is a fluid-mobile element, and the phase was regarded to be a reaction product of fayalite with water in nakhlite magma (Rost et al., 2006). TEM, micro-Raman, Mössbauer, electron spin resonance, and optical spectroscopic studies on brown-colored olivine in shergottites and chassignites suggested that the ferric iron was produced by oxidation during heavy shock metamorphism on the Martian surface (Bläß et al., 2010; Ostertag et al., 1984). In addition, laihunite was considered to be a potential phase occurring on the surface of Venus (Fegley et al., 1992).

Laihunite also occurs as a sensitive marker for the oxidation environment of interplanetary dust particles (IDPs). The mineral was found in chondritic-porous IDPs (Keller et al., 1992, 1996; Rietmeijer, 1993). In this case, laihunite probably formed as a result of the heat pulse during atmospheric entry of the IDPs (Greshake et al., 1994; Guofei and Rietmeijer, 1994; Keller et al., 1992). However, laihunite also formed in laboratory studies of annealed vapor condensates while investigating dust formation in protoplanetary environments (Guofei and Rietmeijer, 1994). In more recent experiments (Nozaki et al., 2006) to simulate heating of micrometeorites during atmospheric re-entry, laihunite formed in samples of the Orgueil CI chondrite at ~ 900 °C and 0.8 torr.

In this study, which is part of a project to investigate environmental effects on the mid-infrared spectral properties of planetary materials, we report the oxidation of Fe in synthetic and meteoritic olivines to laihunite, based on Fourier transform infrared spectroscopy (FTIR) and TEM. In FTIR measurements, direct structural information from both crystalline and amorphous materials can be obtained from a few samples. In addition, FTIR is a non-destructive measurement and has better sensitivity for minor components than Raman spectroscopy. Therefore, it is useful not only to analyze the oxidation state of meteorites but also for in situ measurements of rocks by future Mars landers and rovers (Anderson et al., 2005).

Thus far, laihunite has been mainly investigated with terrestrial applications in mind. However, mid-infrared analyses of laihunite are very rare and have either focused on the study of water content (Banfield et al., 1992) or been of very low resolution (Huggins, 1970; Schaefer, 1985; Zhang et al., 1981). In the present study, we aimed to inspect this sensitive marker for redox states of mineral assemblages in the context of their occurrences in plane-

tary and meteoritic environments.

EXPERIMENTAL METHODS

The matrices of the carbonaceous chondrites used in this study were from samples obtained from the collection of the Natural History Museum in London: Vigarano (CV) (catalogue number: BM1911, 174), Ningqiang (CV) (BM2000, M1), and Ornans (CO) (BM1985, M149). CV and CO matrices consist mainly of olivine and lesser amounts of pyroxene, Fe-metal, Fe-sulfide, and Fe-oxide (Buseck and Hua, 1993). Matrix olivines in the samples are rich in Fe with Fo₄₇₋₈₅ (Vigarano: Lee et al., 1996), Fo₂₆₋₆₅ (Ningqiang: Zolensky et al., 2003), Fo₄₀₋₅₂ (Ornans: Brearley and Jones, 1998) compositions. The materials were crushed to a very fine powder (<1 µm) using a diamond compression cell and placed on infrared transparent KBr pellets using a tungsten needle. In situ mid-infrared transmission/absorption spectra (2.5 µm to 25.0 µm) of the samples at temperatures up to 572 °C were taken using a Perkin Elmer AutoIMAGE FT-IR microscope at the Natural History Museum, equipped with a calibrated heating stage (Linkam FTIR), using a spectral resolution of 4 cm⁻¹. Fifty scans were completed for each measurement. The heating path consisted of ~ 100 °C steps (5 °C/min), with a 5 min equilibration time before each infrared measurement. After cooling, the samples were analyzed by the same method with synthetic olivine as described below.

To compare the results of meteoritic samples, synthetic Fe-rich olivine (Fo₄₇) was also investigated by FTIR. The olivine was crushed using agate mortar and directly put on a Pt foil and a KBr pellet. Respective samples were heated up to 600 °C in 1 h and kept at the temperature for 0.5 h in air in an electric furnace, and then cooled to room temperature in 1 h. These synthetic olivines were analyzed by an FTIR spectrometer before and after heating. An FTIR spectrum of the Fe-rich olivine was obtained using the KBr-pellet technique. Here, a sub-micron powder of sample was ground well with KBr, of which 200 mg was pressed into a pellet. Analyses were carried out using a Nicolet Nexus 670 FTIR workbench at the Kyoto Pharmaceutical University, with 512 scans completed. Spectral resolution in all cases was 4 cm⁻¹. The results of absorbance [$A = \log_{10}(100/T)$] were corrected using a baseline joining of the low-points in the spectra between 7 and 16 µm. Following this, spectra were normalized to the weakest and strongest silicate bands. Further details of the sample preparation and measurements of FTIR are described in Morlok et al. (2006).

Mineral aggregates of cooled Vigarano and Ningqiang samples were removed from the KBr pellets by a

tungsten needle and were embedded in epoxy. They were processed to thin foils of 70–75 nm thickness using an ultramicrotome. Synthetic Fe-rich olivine powder before and after heating on a platinum foil was directly mounted on Cu grids, which were covered with a formvar/carbon film. All samples were examined using a transmission electron microscope (JEOL JEM-2010) at the Kobe University, operated at an accelerating voltage of 200 kV. The crystal structure was identified by selected area electron diffraction (SAED) and high-resolution imaging.

RESULTS

FTIR measurements

In the FTIR spectra of the matrix of the Vigarano chondrite, strong absorption bands were observed at $\sim 10\ \mu\text{m}$, $\sim 11\ \mu\text{m}$, and $\sim 12\ \mu\text{m}$ (Table 1 and Fig. 1). The 10–11 μm and 12 μm bands were attributed to asymmetric (ν_3) and symmetric (ν_1) Si–O stretching vibrations within the SiO_4 tetrahedra of the olivine structure, respectively (Hofmeister, 1987). The 11- μm band was the strongest, and the 10- μm one was the second strongest among the three bands. At temperatures up to 286 °C, no significant change was observed. Above 382 °C, the intensity of the 10- μm band conspicuously increased, and became the strongest band at 572 °C. Another major spectral change observed was the splitting of the 11- μm band into a double band (Table 1 and Fig. 1). After cooling to room temperature, the splitting of the 11- μm band into separate bands at 11.2 μm and 11.6 μm became more obvious. Additionally, a band at 12.2 μm and a shoulder at $\sim 9.8\ \mu\text{m}$ appeared.

The Ningqiang matrix showed similar changes in mid-infrared spectra to those of Vigarano, except the presence of a $\sim 9.3\ \mu\text{m}$ band of minor pyroxene (Chihara et al., 2002). At 572 °C, the intensity inversion from the 10- μm band to 11- μm band was also observed, as was the split of the 11- μm band. The splitting into bands at 11.2 μm and 11.6 μm also remained after cooling (Table 1 and Fig. 2). In addition to the bands at 9.8 μm and 12.2 μm , a band at 14.4 μm clearly appeared in the cooled sample.

The Ornans matrix also showed similar changes in mid-infrared spectra to those of Vigarano and Ningqiang. No significant change was observed up to 382 °C. Above 477 °C, the intensity of the 10- μm band relative to that of the 11- μm band began to increase. Intensity inversion of the 10- μm band to the 11- μm one or the splitting of the 11- μm band did not occur, even at 572 °C (Table 1 and Fig. 3). However, splitting into bands at 11.2 μm and 11.6 μm was clearly observed after cooling. A 9.1- μm band appeared in the spectrum while heated above 477 °C, and a shoulder at $\sim 9.8\ \mu\text{m}$ in the spectrum after cooling also

appeared (Fig. 3).

FTIR spectra of the synthetic olivine (Fo_{47}) before heating showed strong olivine bands at $\sim 10\ \mu\text{m}$, 11 μm , and 12 μm , as in the meteoritic samples (Fig. 4). In the spectra from the synthetic olivine sample on a KBr pellet obtained at room temperature after heating at 600 °C in air, the intensity of the 10- μm band increased relative to that of the 11- μm band, but no inversion was observed. In addition, the 11- μm band split into two bands at 11.2 μm and 11.5 μm (Fig. 4). A further band appeared at 12.3 μm . FTIR spectra of olivine after heating at 600 °C on a platinum foil yielded more noise, but showed the same spectral bands as that of the heated olivine on a KBr pellet. Figure 5 shows a comparison of infrared spectra among synthetic olivine and the matrices of chondrites taken after cooling. The Vigarano and Ningqiang samples showed splitting of the 11- μm band and a large increase in the intensity of the 10- μm band relative to that of the 11- μm one. On the contrary, the above spectral changes were observed to be less significant for the Ornans matrix and synthetic olivines.

TEM observations

Under TEM observation, microtomed Vigarano samples after cooling mainly consisted of Fe-rich olivine ($<1\ \mu\text{m}$ in size) and a lesser amount of Si-rich amorphous material. Selected area electron diffraction (SAED) patterns of olivine grains showed strong diffraction spots from the olivine structure. However, most of the olivine grains also had weaker extra reflections along c^*_{ol} (Fig. 6). These extra spots correspond to a superstructure of three-fold periodicity along the c axis of olivine. High-resolution TEM images could not be taken owing to a difficulty in making enough thin olivine grains for this purpose.

Ningqiang samples after cooling consisted mainly of Fe-rich olivine, high-Ca pyroxene, and a lesser amount of Si-rich amorphous material and hematite. All mineral grains were smaller than 1 μm in size. Most of the olivine grains showed superlattice reflections along the c^* axis of olivine, similar to heated Vigarano samples (Figs. 7a and 7b). Minor amounts of grains had streaking diffraction along the olivine c^* axis and extra reflections different from those of the superstructure of olivine. The extra reflections were from a magnetite structure. The SAED pattern clarified that olivine and magnetite exhibit the following crystallographic orientation: $(100)_{\text{ol}} // \{111\}_{\text{mag}}$ and $(001)_{\text{ol}} // \{101\}_{\text{mag}}$ (Figs. 7c and 7d). $(100)_{\text{ol}}$ and $\{111\}_{\text{mag}}$ correspond to close-packed oxygen layers of olivine and magnetite. This topotaxial olivine-magnetite intergrowth was previously reported in experimentally heated olivine in the Murchison meteorite (Nozaki et al., 2006).

Table 1. FTIR band positions in the heated and original samples

T (°C)	25	96	191	286	382	477	572	25 (Cooled)
Vigarano								9.8(sh)
	10.12	10.12	10.12	10.12	10.1 (br)			10.25
	10.42	10.46	10.46	10.46	10.46	10.50	10.46	
						10.82*	11.26*	11.15*
	11.31*	11.31*	11.31*	11.31*	11.31*	11.31*	11.63*	11.55*
Ningqiang	12.02	12.02	12.02	12.02	12.0(sh)		12.32	12.23
								16.15
								19.49
	9.33	9.33	9.33	9.3(sh)	9.43	9.43	9.4(sh)	9.8(sh)
	10.29	10.29	10.25	10.25	10.20	9.9(sh)	9.9(sh)	10.27
Ornans				10.42	10.46	10.20	10.37	
	11.42*	11.42*	11.42*	11.42*	11.42*	11.47*	11.47*	11.20*
	12.02	12.02	12.02	12.02	12.0(sh)		11.63*	11.57*
	14.20	14.89	14.20	14.53	14.53	14.53	12.32	12.20
								14.44
Synthetic Fo ₄₇ (KBr)						9.1 (sh)	9.1(sh)	16.20
	10.12	10.12	10.12	10.12	10.12			19.64
	10.42	10.42	10.42	10.42	10.42			21.25
	11.31*	11.36*	11.36*	11.36*	11.36*	11.36*	11.6(sh)	9.8(sh)
	12.02	12.02	12.08	12.08	12.08	12.1(sh)		10.39
Synthetic Fo ₄₇ (Pt)	10.41							11.22*
								11.55*
	11.37*							11.98
	12.00							12.2(sh)
	17.22							16.36
Synthetic Fo ₄₇ (Pt)	20.66							19.64
	10.41							9.8 (sh)
								10.39
								11.15
								11.22*
Synthetic Fo ₄₇ (Pt)								11.47*
								11.55
								12.26
								16.5(br)
								10.39
Synthetic Fo ₄₇ (Pt)								10.76
								11.12
								11.22*
								11.47*
								11.60
Synthetic Fo ₄₇ (Pt)								11.71
								12.29
								16.5(br)

All values are in microns.

*, Split bands at ~ 11 μ m.

Notes: "sh" and "br" denote shoulders and broad bands with no clear peak, respectively.

The Fo₄₇ olivine before and after heating at 600 °C on a platinum foil was also examined by TEM. In the unheated olivine sample, none of the grains showed stacking disorder (Fig. 8a). On the contrary, in the heated olivine sample, half of the olivine grains exhibited stacking disorder

on the (001) plane (Fig. 8b), and some of them showed superlattice reflection along the c^* direction, as in olivine from the meteoritic samples (Fig. 8c). The diffraction spots of magnetite were not observed in this sample. In the high-resolution TEM image, only fringes with 1.8

Figure 1. In situ mid-infrared spectra from 5 μm to 25 μm of the matrix of the Vigarano (CV) carbonaceous chondrite heated up to 572 $^{\circ}\text{C}$ and that after cooling. The band around 15 μm comes from CO_2 gas in air. Note that the $\sim 11\text{-}\mu\text{m}$ band splits into a doublet in the spectrum after cooling (indicated by dotted lines).

Figure 3. In situ mid-infrared spectra from 5 μm to 25 μm of the matrix of the Ornans (CO) carbonaceous chondrite heated up to 572 $^{\circ}\text{C}$ and that after cooling.

Figure 2. In situ mid-infrared spectra from 5 μm to 25 μm of the matrix of the Ningqiang (CV) carbonaceous chondrite heated up to 572 $^{\circ}\text{C}$ and that after cooling.

Figure 4. Mid-infrared spectra of cooled Fo_{47} olivines after heating at 600 $^{\circ}\text{C}$ in air on a KBr pellet (average of 5 spectra) and a platinum foil (average of 7 spectra), Fo_{47} olivines before heating, hematite (Fe_2O_3), and magnetite (Fe_3O_4). Data of iron oxides are from Salisbury et al. (1992).

Figure 5. Mid-infrared spectra of heated Fo_{47} olivine and the matrices of carbonaceous chondrites. The positions of major olivine bands are shown as dotted lines.

nm spacing, corresponding three-fold length of the olivine c -axis, could be recognized because of the high stacking disorder on the (001) plane (Fig. 8d).

DISCUSSION

The three-fold superstructure of Fe-bearing olivine observed by TEM in the present study was previously reported in natural and synthetic oxidized fayalite, known as laihunite, which was first discovered in terrestrial rocks (Kitamura et al., 1984; Kondoh et al., 1985; Shen et al., 1986). Laihunite has an olivine structure with a composition of $v_x\text{Fe}_{2-3x}^{2+}\text{Fe}_{2x}^{3+}\text{SiO}_4$, where v is the vacancy (Kitamura et al., 1984; Shen et al., 1986). It has a monoclinic unit cell of $a = 0.481$ nm, $b = 1.019$ nm, $c = 0.580$ nm, and $\alpha = 91.0^\circ$ in the Fe_2SiO_4 composition (Tamada et al., 1983). However, natural and synthetic laihunites often have superlattices with two-fold ($2M$ structure) and three-fold ($3M$ structure) periodicities along the c axis of fayalite, owing to the ordering of the cation and vacancy sites (Kondoh et al., 1985; Kitamura et al. 1984; Shen et al., 1986). The laihunite identified by TEM in the present study corresponded to the $3M$ superstructure. The $3M$ phase was also found in more Mg-rich olivine (Fo_{89}) experimentally heated at 600 °C and 700 °C and high f_{O_2} (0.2 atm) conditions (Khisina et al., 1995).

Concerning mass balance, the oxidation of Fe-bearing

Figure 6. A matrix olivine grain from a heated Vigarano chondrite. (a) Transmission electron micrograph. (b) Selected area electron diffraction (SAED) pattern. Super-lattice reflections corresponding to three-fold periodicity along the c axis of olivine are present.

ing (Fo_{47}) olivine observed in this study can be expressed as the following equation:

In this reaction, the amount of magnetite is much less than that of laihunite. This is consistent with our results, since magnetite was not observed much under TEM or in the FTIR spectra (Figs. 4 and 5). Laihunite- $2M$ was not found in either synthetic or meteoritic olivines in our TEM observations. Previous oxidation experiments of fayalite at 400–700 °C for 5–480 h clarified that fayalite initially transforms to the $3M$ structure, and further oxidation produces the $2M$ structure (Kondoh et al., 1985). The relatively short heating duration in the present study (<3 h) may have prevented progression of the oxidation of olivine to form the $2M$ phase.

The following effects can be considered when investigating causes of changes in mid-infrared spectra in chondrite matrices during heating: (1) Fe-oxide formation by oxidation breakdown of Fe-rich olivine, (2) reactions

Figure 7. Olivine grains in the matrix of a heated Ningqiang chondrite after cooling. (a) Transmission electron micrograph of an olivine grain with stacking disorder on the (001) plane. (b) SAED pattern taken from the grain in (a) shows weak reflections along the c^* direction corresponding to those of laihunite-3M. (c) Transmission electron micrograph of an olivine grain containing magnetite. (d) SAED pattern taken from the grain in (c). Diffuse scattering are shown along the c^* direction of olivine (Ol). Weaker diffraction spots indicated by triangles correspond to those of magnetite (Mag).

Figure 8. Synthetic olivine grains with Fo_{47} composition. (a) Electron micrograph of unheated olivine. The olivine grain does not have any stacking disorder. SAED pattern of the olivine grain is in the inset. (b) Transmission electron micrograph of olivine heated at 600 °C showing stacking disorder. (c) SAED pattern taken from the grain in (b). (Inset) Superlattice reflections of three-fold periodicity along the c axis of olivine. (d) High-resolution electron micrograph of heated olivine showing 1.8 nm spacing of the laihunite-3M structure.

among constituent minerals of the chondrite matrices, and (3) chemical reactions between matrix minerals and KBr pellets.

As for (1), ferric-iron bearing minerals such as hematite and magnetite did not exhibit their characteristic bands in the wavelength range of $\sim 10\text{--}12\ \mu\text{m}$ in the FTIR

spectra (Fig. 4). This suggests that the mid-infrared spectra in this range were not affected by the Fe-oxides, even if those produced by heating are in a high amount. As for (2), the Vigarano, Ningqiang, and Ornans chondrites consisted mainly of Fe-rich olivine and lesser amounts of pyroxene, Fe-metal, Fe-sulfide, and Fe-oxide (Rubin et al.,

1988; Buseck and Hua, 1993; Lee et al., 1996). However, both chondritic matrices and synthetic olivine samples showed similar spectral changes in major bands for olivine in the range of ~ 10 – $12\ \mu\text{m}$. As for (3), there was no obvious difference in the FTIR spectra of Fe-rich olivine between the sample heated on a KBr pellet and on a platinum foil. Therefore, a chemical reaction with a KBr pellet can be ruled out as a cause of spectral change by heating. The major spectral changes would have been caused by structural modification of olivine, as speculated in the above oxidation reaction, rather than by effects of other mineral constituents before and after heating. The mid-infrared spectra of the oxidized olivines in the present study were similar to that of natural laihunite (ferrifayalite) in terrestrial rocks (Huggins, 1970; Zhang et al., 1981; Schaefer, 1985), with a relatively high intensity of the $10\text{-}\mu\text{m}$ band with respect to the intensity of the $11\text{-}\mu\text{m}$ band; however, natural laihunite does not exhibit the split of the $11\text{-}\mu\text{m}$ band, which was observed in this study.

The band positions of olivine increased to longer wavelengths with increasing fayalite content (Koike et al., 2003; Morlok et al., 2006). The Mg/Fe ratio in oxidized olivine (laihunite) is higher than non-oxidized olivine in the oxidation reaction mentioned above. If the splitting of the $\sim 11\text{-}\mu\text{m}$ band was caused by dissociation to non-oxidized olivine and oxidized olivine with different Mg/Fe ratios, the $\sim 10\text{-}\mu\text{m}$ and $12\text{-}\mu\text{m}$ bands should also have split, because these band shifts are also sensitive to fayalite content (Koike et al. 2003; Morlok et al. 2006). However, splitting of the $\sim 10\text{-}\mu\text{m}$ and $\sim 12\text{-}\mu\text{m}$ bands was not observed in the samples in the present study. Therefore, the splitting of the $\sim 11\text{-}\mu\text{m}$ band was not simply caused by the Mg/Fe ratio in olivine, but by the formation of a slightly different vibration mode of Si-O in the laihunite structure from those of non-oxidized olivine at the $\sim 11\text{-}\mu\text{m}$ region. Ferric iron sites and/or vacancy sites in the laihunite structure could locally change the frequency of the Si-O stretching vibration. The degree of splitting of the $11\text{-}\mu\text{m}$ band and the intensity ratio of the $10\text{-}\mu\text{m}$ and $11\text{-}\mu\text{m}$ bands could explain relative abundances of oxidized and non-oxidized domains in the samples.

As mentioned above, in the samples of Ornans (CO3) and synthetic olivines after cooling, the splitting of the $11\text{-}\mu\text{m}$ band and the increase in the intensity of the $10\text{-}\mu\text{m}$ band relative to that of the $11\text{-}\mu\text{m}$ band were less significant than the Vigarano and Ningqiang (CV3) samples, despite identical heating duration ($\sim 3\text{ h}$). In general, CV3 and CO3 chondrites are nominally anhydrous, but contain up to $\sim 4.5\text{ wt\%}$ of water (Jarosewich, 1990), mostly as structural water in minerals such as phyllosilicates found in chondrule rims in the Vigarano CV3 chon-

drite (Tomeoka and Tanimura, 2000). It was experimentally clarified that Fe-rich olivine is oxidized to form laihunite in alkaline aqueous solutions at $300\text{ }^{\circ}\text{C}$ and 100 bar (Iishi et al., 1997). The spectral differences among the samples may have been caused by different degrees of oxidation of Fe-rich olivine, depending on the amount of water in each sample. In particular, the synthetic olivine contained only trace amounts of water, if at all. In which case, the above changes in the FTIR spectra of the synthetic olivine would be the least significant among the samples, although more quantitative studies of water effects on the oxidation process are necessary.

The present study found that oxidation of Fe-rich olivine in complex mineral assemblages, such as chondritic materials including pyroxene, Fe-metal, Fe-sulfide among others, could be recognized by the effects on the Si-O vibration modes in mid-infrared spectroscopy. The changes in mid-infrared spectra of olivine-dominating samples are potential reference data for oxidation state of olivine in planetary materials.

Detailed infrared laboratory studies on the formation of environmentally sensitive phases like laihunite are necessary for better interpretation of laboratory analyses of planetary samples. Successful sample return missions, e.g., STARDUST (Keller et al., 2006) and recently HAYABUSA (Kitajima et al., 2011), all included micro-FTIR studies as one of the first steps for the analysis of the precious and fine-grained returned materials, since they allow the non-destructive study of these rare and unique samples. A detailed database including indicator phases, especially for environmental conditions, is crucial for the interpretation of these results. This is also of special interest regarding the upcoming/planned sample return missions NASA OSIRIS-Rex, JAXA HAYABUSA-2 (Kawaguchi et al., 2008), and ESA MarcoPolo-R (Barucci et al., 2012) of carbonaceous chondrite type near-Earth asteroids, where the identification of any hydrous or oxidized phases will be crucial for the understanding of the degree of alteration of these bodies (Lauretta et al., 2012). The results from this study also provide new data to investigate alteration in related IDPs, which are also analyzed using micro-FTIR studies (Brunetto et al., 2011).

Furthermore, these results have potential application for astronomical infrared studies of dust in comets or in young, forming solar systems (e.g., debris disks), where dust from oxidized planetesimals and asteroids are observed (Currie et al., 2011; Lisse 2009; Morlok et al., 2010). That is, FTIR analyses have the potential to link and apply laboratory studies of planetary materials with astronomical observations.

Finally, these results are also of interest for planetary lander/rover missions. FTIR is a potential instrument for

future in situ measurements on the Martian surface, as it is one of fundamental instruments in cosmochemistry, which allows analyses of both mineral and organic compounds. Previously, a Mössbauer spectrometer equipped on the Mars rover Opportunity successfully detected jarosite $[(K,Na)(Fe,Al)_3(SO_4)_2(OH)_6]$ and hematite-containing ferric iron, suggesting high- f_{H_2O} and high- f_{O_2} conditions on Mars (Klingelhöfer et al., 2004). FTIR provides the entire range of structural information on not only Fe-bearing minerals but also Fe-free ones. Therefore, it has an advantage to obtain comprehensive data sets on mineralogy and biochemistry of Martian rocks (Anderson et al., 2005).

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