Spectral Deconvolution Analysis on Olivine-Orthopyroxene Mixtures with Simulated Space Weathering Modifications

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Abstract Olivine and pyroxene are important mineral end-members for studying the surface material compositions of mafic bodies. The profiles of visible and near-infrared spectra of olivine-orthopyroxene mixtures systematically varied with their composition ratios. In our experiments, we combine the RELAB spectral database with a new spectral data obtained from some assembled olivine-orthopyroxene mixtures. We found that the commonly-used band area ratio (BAR, Cloutis et al. 1986) does not work well on our newly obtained spectral data. To investigate this issue, an empirical procedure based on fitted results by modified Gaussian model is proposed to analyze the spectral curves. Following the new empirical procedure, the end-member abundances can be estimated with a 15% accuracy with some prior mineral absorption features. In addition, the mixture samples configured in our experiments are also irradiated by pulsed lasers to simulate and investigate the space weathering effects. Spectral deconvolution results confirm that low-content olivine on celestial bodies are difficult to measure and estimate. Therefore, the olivine abundance of space weathered materials may be underestimated from remote sensing data. This study may be used to quantify the spectral relationship of olivine-orthopyroxene mixtures and further reveal their correlation between the spectra of ordinary chondrites and silicate asteroids.

Key words: techniques: spectroscopic — instrumentation: spectrographs — methods: data analysis — minor planets, asteroids: general

1 INTroductions

The spectral absorption features provided by hyperspectral remote sensing enable us to investigate the geological and geochemical information over the imaged area (Cloutis 1996; Clark et al. 2003; Zaini et al. 2014). Therefore it is widely used to identify the minerals, rocks, water (ices), and organic materials of the celestial bodies (Adams 1974; Singer 1981; Burbine et al. 2002; Pieters et al. 2009; Basilevsky et al. 2012; Roush et al. 2015; Lauretta et al. 2019), such as terrestrial planets, moon and
asteroids (Cloutis & Bell III 2000; Ohtake et al. 2009; Lindsay et al. 2015; Zhang et al. 2015; Hu et al. 2019; Tsuda et al. 2020). Visible and near-infrared (VNIR) reflectance spectra are susceptible to the mafic minerals (Pieters & Mustard 1988; Lucey 2004; Staid et al. 2011), which contain the characteristics of mineral composition and crystal structure (Hunt 1977; Mustard et al. 2005). As the major group of mafic minerals, olivine and pyroxene are important materials in understanding the geologic evolution, differentiation process and cooling history of terrestrial bodies (Wells 1977; Ishii et al. 1983; Cloutis & Gaffey 1991; Klima et al. 2011). However, many limited factors should be considered when using reflectance spectra to analyze remote sensing data from airless bodies, because most reflectance spectra collected under laboratory are not consistent with the data by remote sensing (Bishop et al. 1998; Cloutis et al. 2008; Shirley & Glotch 2019). One thing that needs to be focused on is space weathering, which can change the chemical compositions and optical properties of the surface materials (Pieters et al. 2000; Brunetto et al. 2006; Fu et al. 2012). It can make the spectral curves redder and dark, and difficult to identify and interpret (Hapke 2001; Chapman 2004; Han et al. 2020). Therefore, many methods for space weathering spectral deconvolution are extensively studied in order to acquire the truth data interpretation (Sunshine & Pieters 1993, 1998; Gallie et al. 2008; Han et al. 2020; Potin et al. 2020).

1.1 Olivine, Pyroxene and Their Mixture Spectroscopy

Olivine is typically the dominant and foremost mineral crystallizing from liquid magma in the Earth’s mantle and bears rich information about the magma ocean (Elthon 1979; Garcia et al. 1995; Danyushevsky et al. 2000; Dyar et al. 2009). Olivines are mafic silicates with the formula (Mg, Fe)$_2$SiO$_4$, solid solutions ranging from fayalite (Fe$_2$SiO$_4$) to forsterite (Mg$_2$SiO$_4$). The olivine structure is nearly hexagonally close-packed and there are two octahedral sites, M1 and M2. Half of the two octahedral interstices occupied by divalent metal ions, usually either Mg$^{2+}$ or Fe$^{2+}$ (Dyar et al. 2009). The color of olivine is mainly determined by the content of Fe$^{2+}$ content. It looks green with lower content of Fe$^{2+}$ but becomes brown at high iron content. In VNIR reflectance spectra, olivine is characterized by its Fe$^{2+}$ electronic transition absorption bands (Burns 1970; Hunt 1977), and forming a wide and superimposed absorption near 1.0 $\mu$m region (Figure 1a). As the Fe$^{2+}$ abundance increases, the 1.0 $\mu$m absorption band center shifts toward longer wavelength and the band width increases (Sunshine & Pieters 1998; Han et al. 2020).

Pyroxenes are crystallized from original magma and forming the primary component of planetary upper mantle and crust, and bear rich magma information (Elkins-Tanton et al. 2005; Elardo et al. 2011; Head & Wilson 2017). Several geothermobarometric tools have focused on pyroxene to study the igneous differentiation in the Earth, asteroids and meteorites (Lindsley 1983; Cloutis & Gaffey 1991; Sunshine et al. 2004; Klima et al. 2008). Pyroxenes are single-chain silicates with the general formula XY$_2$Si$_2$O$_6$, where X and Y are both divalent cations (commonly Ca, Fe, Mg, etc.). The stacking of chains gives rise to two types of cavities, labelled M1 (close to octahedral in shape) and M2 (more irregular in shape) (Burns 1970). Fe$^{2+}$ in the two different crystallographic positions M1 and M2 are responsible for the dominant pyroxene spectra absorptions in the VNIR region, which produce two prominent absorption features near 1.0 $\mu$m (Band 1) and 2.0 $\mu$m (Band 2) bands. While substitutions of other cations such as Ca$^{2+}$ change the crystal structure and make the absorption characteristic to move towards longer wavelength (Adams 1974; Klima et al. 2011). Furthermore, it was found that in the spectra of the pyroxenes (Figure 1b), the wavelengths of the two main absorption bands change as a function of the concentrations of Fe$^{2+}$ and Ca$^{2+}$ (Adams 1974; Klima et al. 2007).

The spectral properties of pyroxenes have been intensively studied in the past (Cloutis & Gaffey 1991; Sunshine & Pieters 1993). The most basic division of pyroxenes is between orthopyroxenes (OPX) and clinopyroxenes (CPX) which is based on differences in chemical composition and crystal structure. According to this scheme, orthopyroxenes essentially contains $<$5 mol% CaSiO$_3$ (wollastonite, Wo) and possess orthorhombic symmetry, while clinopyroxenes can contain 0 $\sim$ 50 mol% Wo and possess monoclinic symmetry (Adams 1974; Cloutis & Gaffey 1991). Therefore, they can form a diagram of pyroxenes quadrilateral, the corners of the quadrilateral are the pyroxene end-members diop-
side (Di, CaMgSi₂O₆), hedenbergite (Hd, CaFeSi₂O₆), Enstatite (En, Mg₂Si₂O₆), and Ferrosilite (Fs, Fe₂Si₂O₆). Example spectra are shown in Figure 1b. The olivines and pyroxenes spectral data are all taken from the Reflectance Experiment Laboratory (RELAB) database support by Brown University.¹

According to the information described above, retrieving the mafic mineral features from the obtained reflectance spectra does seem to be a viable task. It provides an effective method for remote analysis of mafic minerals on the planet’s surface. However, it is still difficult to directly interpret the spectra because spectral analysis are hampered by the overlapping absorption features, especially when dealing with mixture minerals (Clénet et al. 2011). The spectral properties of mineral mixtures do not linearly vary with the relative abundances of different end-members (Adams 1974; Singer 1981; Cloutis & Gaffey 1991).

In this study, we choose the forsterite and low-Fe orthopyroxene as the two end-members. Low-Fe orthopyroxene spectra show a narrow strong absorption near 0.92 μm region and a wide absorption near 1.8 to 1.9 μm region (Klima et al. 2007). Therefore, center position of these two absorption bands will be important information for studying the olivine-orthopyroxene mixture spectra. Figure 2 shows the VNIR reflectance spectra of olivine, orthopyroxene and their mixture (50% OLV + 50% OPX).

### 1.2 Space Weathering Simulations

The spectra of asteroids and lunar regolith are obviously different from those of the laboratory minerals. The former are characterized by distinct red continua slope and weak absorption unlike those of the fresh rocks in the laboratory. Nanophase iron particles (npFe⁰) have been widely observed in lunar soil which is confirmed to be the cause of the difference in these spectra. It is widely thought that the formation of npFe⁰ in lunar soil is the result of space weathering, which include micrometeorite bombardment, energetic particles, as well as cosmic rays (Dybwad 1971; Hapke 1973; Pieters et al. 1993). To understand the physical and chemical mechanisms of space weathering, many simulation experiments were made in the laboratory (e.g., Keller & McKay 1993; Yamada et al. 1999; Hapke 2001; Loeffler et al. 2009; Fu et al. 2012; Jiang et al. 2019). These experiments irradiated pulsed laser beam onto the different samples to simulate the irradiation of micrometeorite bombardments; or implanted proton particles (such as H⁺, He⁺ and Ar⁺) onto the samples to simulate the solar wind implantation; or heated the samples with microwave furnace at high temperature in a vacuum to simulate the space environment. Among these methods, pulsed laser irradiation is effective in generating space weathering effects. Since the pulsed laser can pump energy in a very short time scale, it can be analogous to a high-speed and low-mass dust particle micrometeorite impact (Yamada et al. 1999; Yang et al. 2017). In this study, we utilized the pulsed laser irradiation for space weathering simulations.

Overview of this study, firstly we collected and assembled some olivine-orthopyroxene mixture spectra, the assembled samples are also irradiated with pulsed laser in our experiment. Some calculation methods are utilized to study these spectra. These spectral data, experiments and research methods will be presented in Section 2. While, these methods have limitations and do not work well for some samples. So we developed an empirical procedure to deal with these spectral data. The results and some discussions are presented in Section 3. The conclusions are summarized in Section 4.

### 2 SAMPLES AND EXPERIMENTAL METHODS

#### 2.1 Samples and Reflectance Spectra Measurements

The spectra of synthetic mixtures presented in this study are taken from the RELAB database and our experiment. The end-member components of RELAB synthetic mixture samples are natural olivine (AG-TJM-008) and hypersthene (AG-TJM-009) with grain sizes smaller than 38 μm. The mass mixing ratio of the two minerals are 1/9, 3/7, 5/5, 7/3 and 9/1 respectively. Another part of synthetic mixture samples from RELAB are natural olivine (PO-CMP-017) and enstatite (PE-CMO-012) mixtures and the grain size is 45 ~ 75 μm. The mass mixing ratio of the two minerals are 1/9, 2.5/7.5, 5/5, 7.5/2.5

¹ [http://www.planetary.brown.edu/relab/](http://www.planetary.brown.edu/relab/)
Table 1: Chemical compositions of these olivine and orthopyroxene samples

| Sample ID | AG-TJM-008 | AG-TJM-009 | PO-CMP-017 | PE-CMP-012 | OWN-OLV | OWN-OPX |
|-----------|------------|------------|------------|------------|---------|---------|
| Mineral   | SiO$_2$    | TiO$_2$    | Al$_2$O$_3$ | Cr$_2$O$_3$ | Fe$_2$O$_3$ | FeO |
|           | 40.81      | 0.16       | 0.12       | 0.75        | 0        | 9.55    |
|           |            |            |            |            | 0.13     |          |
|           |            |            |            |            |          | 15.22   |
|           |            |            |            |            |          | 0.01    |
|           |            |            |            |            |          | 0.05    |
|           |            |            |            |            |          | 0.05    |
|           |            |            |            |            |          | 0.01    |
|           |            |            |            |            |          | 0.12    |
|           |            |            |            |            |          | 0.13    |
|           |            |            |            |            |          | 0.34    |
|           |            |            |            |            |          | 1.3     |
|           |            |            |            |            |          | 4.1     |

Notes: The number unit is wt. %.

Table 2: Information summary of the end-member and synthetic mixed samples

| Sample ID | OLIV : OPX | Sample ID | OLIV : OPX | Sample ID | OLIV : OPX (Irradiate) |
|-----------|------------|-----------|------------|-----------|-------------------------|
| AG-TJM-008 | Olivine     | AG-TJM-017 | Olivine     | XT-TXH-030-P | 7.5 : 2.5 (No) |
| AG-TJM-009 | Hypersthene | AG-TJM-018 | 3 : 7       | XT-TXH-031-P | 5 : 5 (No) |
| PO-CMP-017 | Olivine     | AG-TJM-019 | 5 : 5       | XT-TXH-032-P | 7.5 : 2.5 (No) |
| PE-CMP-012 | Enstatite   | AG-TJM-020 | 7 : 3       | XT-TXH-030-P1 | 2.5 : 7.5 (15 mJ) |
| OWN-OLV   | Olivine     | AG-TJM-021 | 9 : 1       | XT-TXH-031-P1 | 5 : 5 (15 mJ) |
| OWN-OPX   | Enstatite   | XO-CMP-015 | 9 : 1       | XT-TXH-032-P1 | 7.5 : 2.5 (15 mJ) |
| OWN-OL1/EN4 | 2 : 8     | XO-CMP-016 | 7.5 : 2.5   | XT-TXH-030-P2 | 2.5 : 7.5 (15 mJ * 2) |
| OWN-OL2/EN3 | 4 : 6     | XO-CMP-017 | 5 : 5       | XT-TXH-031-P2 | 5 : 5 (15 mJ * 2) |
| OWN-OL3/EN2 | 6 : 4     | XO-CMP-018 | 2.5 : 7.5   | XT-TXH-032-P2 | 7.5 : 2.5 (15 mJ * 2) |
| OWN-OL4/EN1 | 8 : 2     | XO-CMP-019 | 1 : 9       | XT-TXH-030-P2 | 2.5 : 7.5 (15 mJ * 2) |

Notes: Six samples with IDs like OWN-xxxx come from our experiment, with grain size less than 75 µm. The others come from RELAB. Seven samples with IDs like AG-TJM-xxx, with grain size < 38 µm. The grain size of the other RELAB samples is 45 ~ 75 µm. Five samples with IDs like XO-CMP-xxx are olivine-enstatite mixture samples. Nine samples with IDs like XT-TXH-xxx are olivine-brownite mixture samples, and six of these nine samples are irradiated with pulsed laser to study space weathering effect. The total amount of each mixture is counted as 10.

and 9/1 respectively. Chemical compositions of these end-member minerals are listed in Table 1. The reflectance spectra of olivine-hypersthene mixtures are shown in Figure 3a. In addition, we also utilize some olivine-brownite mixture samples whose end-member components are not analyzed. The sample IDs and mixture compositions of these samples are listed in Table 2. Measurements of these olivine-orthopyroxene mixtures are conducted using a bidirectional VNIR spectrometer with an incidence angle of 30 and an emission angle of 0 ranging from 0.30 (or 0.32) to 2.55 (or 2.60) µm.

The other part of the samples come from our experiment. We collect some natural pure olivine (OWN-OLV) and enstatite (OWN-OPX) samples as experimental materials. The samples are ground and sieved into grain size less than 75 µm. Chemical compositions of these sample powders are analyzed with wet chemistry method and listed in Table 1. The mass mixing ratios of the two minerals are 1/4, 2/3, 3/2 and 4/1 respectively (Table 2). A Bruker Vertex 70 Fourier transform spectrometer is utilized to get the VNIR reflectance spectra of these samples. Each sample is measured four times with the sample holder rotated 90° every time. The average spectrum is taken as the final spectrum to reduce the effect of any surface inhomogeneity (Jiang et al. 2019). What needs our attention here is that the VNIR reflectance spectra of these materials have an artificial peak near 2.14 µm when Spectralon panel made of polytetrafluoroethylene is used as the calibration plate in the near-infrared (NIR) region (Zhang et al.
Spectral Deconvolution on OL-V-OPX Mixtures

2014), two narrow spectral faint wobbles near 1.41 and 2.33 μm absorption bands presented in some spectra are due to minor alteration. These two small fluctuations do not affect the results of this study, because these artificial wobbles are not on the main band absorption regions (Figure 3b). However, we do need to remove the 2.14 μm artificial peak, as it appears in the orthopyroxene absorption features. Here, we utilize a 4th-order polynomial to fit the data between 1.8 to 2.5 μm. Then the data of the artificial peak (∼2.03 to ∼2.18 μm) are replaced for further study. The modified reflectance spectra are shown in Figure 3b.

2.2 Pulsed Laser Irradiation

The detailed experiment process can be found in Jiang et al. (2019). Here is a brief summary: In order to study the space weathering effects on olivine, orthopyroxene and their mixture spectra, some natural pure olivine and orthopyroxene powders (less than 75 μm) are mixed with a certain fractions. Each time ∼1.0 g of powder samples are uniformly placed in a 2.5 cm × 2.5 cm square in an aluminum holder. These powder samples are baked in a dry oven at 120 for about 12 hours to remove the moisture. The dried samples covered by a thin glass slide to prevent the powders sputtering are placed in a vacuum chamber to cool to room temperature and then subjected to pulsed laser irradiation at a pressure of 10⁻³ Pa.

A nanosecond pulsed laser (1 ∼ 50 mJ incident energy per pulse) is utilized as a micrometeorite bombardment simulation system with pulse frequency of 15 Hz. The laser spot is focused to a circle with a diameter of 0.5 mm using a lens and its moving speed is 1 mm s⁻¹. Researches show that after low-energy laser irradiation, the reflectance of olivine has a much greater change than that of pyroxene. Even after multiple irradiations, the depth of the pyroxene absorption band does not change much (Yamada et al. 1999; Jiang et al. 2019). In order to better simulate the space weathering, we choose the maximum energy density (50 mJ) to irradiate the powder samples twice. The first irradiation is to translate in the vertical direction, and the second time is to translate in the horizontal direction. Each irradiated sample is measured immediately after irradiation. Original and irradiated reflectance spectra with the 2.14 μm artificial peak removed are shown in Figure 4.

The irradiation energy density is set to be 3000 mJ mm⁻² for each sample in our experiments. Due to the reflection and absorption of the glass, the energy transmission rate through the vacuum chamber glass window is about 90%. Considering energy loss as the presence of the glass lens, glass slide and aluminum sample holder, as well as the barrier effect caused by the npFe⁰ vapor deposition and the mineral particles adhered to the inner surface of the glass slide, we assume that 10% of the energy is absorbed by the samples, so the energy deposition is about 300 mJ mm⁻². Total energy deposition rate by dust impacts at 1 AU is estimated to be about 10⁻³ J m⁻² yr⁻¹ based on the calculations of Yamada et al. (1999) and Sasaki et al. (2001). Possibly the irradiation of samples in our experiments corresponds to about 300 Myr in the space.

2.3 The Modified Gaussian Model (MGM)

Originally developed by Sunshine et al. (1990), MGM is a mathematical process based on the absorption of electronic transitions and is a statistical method for studying probability distribution. It is a mathematical procedure for deconvolving the superposed absorption features (Sunshine & Pieters 1993). The MGM program can be obtained from Brown University.² So far, some complex minerals and rock samples have been explored with the MGM approach (e.g., Noble et al. 2006; Clenet et al. 2011; Pinet et al. 2016). However, we need more efforts to improve our spectral modeling and interpretation capability when dealing with the spectra of natural unknown mafic bodies.

To elaborate on this model, four significant characteristics are used for interpreting and exploiting the MGM, which are: band center, FWHM (full width at half maximum), band strength, and continuum, as illustrated in Figure 5. In MGM program, natural logarithm of each spectral curve is modeled in

² http://www.planetary.brown.edu/mgm/
energy domain (wavelength), which means in wavelength domain a natural logarithm spectrum can be deconvolved into multiple Gaussian distributions with a continuum. MGM is modeled as:

$$\ln [R(\lambda)] = C(\lambda) + \sum_{i=1}^{N} S_i \cdot \exp \left[ -\frac{(\lambda^{-1} - \mu_i^{-1})^2}{2\sigma_i^2} \right]$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength, $R(\lambda)$ is the reflectance at wavelength $\lambda$, $S$ is the band strength, $\mu$ is the band center, $\sigma$ is the band width, and $N$ is the number of bands. $C(\lambda)$ is the function of the continuum in wavelength space.

Here the continua are fitted by using the logarithm of second-order polynomial. Continua are modeled close to the inflection regions of each absorption band, and we set an uncertainty within 20% for each parameter:

$$C(\lambda) = \ln \left( c_0 + c_1\lambda + c_2\lambda^2 \right)$$ \hspace{1cm} (2)

$\lambda$= wavelength, $c_0, c_1, c_2$= constants

3 RESULTS AND DISCUSSIONS

3.1 MGM Parameters of Olivine and Orthopyroxene

In VNIR regions, olivine spectra show a broad and complex absorption feature near 1.0 $\mu$m. The Gaussian curves presented in the top panels of Figure 6 indicate that olivine spectra are composed of three individual absorption bands, they are around 0.84 $\mu$m, 1.03 $\mu$m and 1.23 $\mu$m respectively, which are assigned to the M11, M2 and M12 sites in olivine crystal (Burns 1970). The width of each Gaussian absorption band in olivine spectra is related to the iron abundance in olivine crystal and their ratio can be applied to constrain the parameters in MGM (Sunshine & Pieters 1998). Preliminary analyses of band strength derived by the MGM from olivine reflectance spectra show the bandwidths of M1-1 and M2 are similar but the width of M1-2 is about twice as large as M1-1 and M2. Analogously, the absorption strength can also be evaluated as a function of composition. Band strength of M2 and M1-2 are similar and about twice of M1-1.

VNIR reflectance spectra of low-Fe orthopyroxene are dominated by the absorptions near 0.92 $\mu$m and 1.85 $\mu$m (bottom panels in Figure 6). Each absorption is primarily caused by one electronic transition absorption band (Sunshine et al. 1990). The strength of $\sim$0.92 $\mu$m band is stronger than that of $\sim$1.85 $\mu$m band, whereas the band width of $\sim$1.85 $\mu$m absorption is more than twice as large as $\sim$0.92 $\mu$m absorption band.

3.2 MGM Parameters of Olivine-Orthopyroxene Mixtures

The initial MGM parameters of the olivine and orthopyroxene in the two end-member mixture can be used as constraints for further analysis of mixture spectra. We utilize these parameters to initialize the MGM and an intermediate ratio mixture in each group for spectral deconvolution. They are sample IDs: AG-TIM-019 (50% OLV + 50% OPX) in RELAB and OWN-OL3/EN2 (60% OLV + 40% OPX) in our experiment. The starting and final parameters of these two spectra in MGM program are listed in Table 3 and the fitting results are shown in Figure 7.

The results show that when olivine and orthopyroxene are mixed in equal amount, orthopyroxene dominates the spectral absorption features of the mixture. As shown in Figure 6 and Figure 7, the center positions of the orthopyroxene’s absorption bands are relatively stable, the strength is close to half of the pure orthopyroxene and the ratio of FWHM parameters remains the same. While, parameters of the three Gaussian absorption bands in olivine spectra change a lot, the strength of each absorption band is about 1/3 of the pure olivine mineral, and the strongest absorption M1-2 band decrease sharply. When the content of olivine is more than orthopyroxene, the spectral curve of the mixture near 1.0 $\mu$m region...
### Table 3: MGM modelling parameters of mixture samples spectra

| Sample ID     | AG-TJM-019 | OWN-OL3/EN2 |
|---------------|------------|-------------|
| Abundance     | 50% OLV + 50% OPX | 60% OLV + 40% OPX |
| Gaussian Fitting Parameters | | |
| Parameter 1   | 6.00E-01  | 6.17E-01   | 6.60E-01  | 6.57E-01 |
| Continua      | Parameter 2 | 8.50E-05  | 8.49E-05  | 1.10E-05  | 1.10E-05 |
| Parameter 3   | -2.30E-08 | -2.50E-08 | -1.50E-08 | -1.68E-08 |
| M1-1          | Center     | 840        | 836.8     | 840       | 859.1     |
|               | FWHM       | 150        | 102.9     | 150       | 141.7     |
|               | Strength   | -0.08      | -0.802    | -0.07     | -0.069    |
| M2            | Center     | 1035       | 1056.1    | 1030      | 1050.0    |
|               | FWHM       | 150        | 183.6     | 170       | 168.6     |
|               | Strength   | -0.15      | -0.152    | -0.13     | -0.141    |
| M1-2          | Center     | 1245       | 1221.6    | 1220      | 1211.4    |
|               | FWHM       | 300        | 258.3     | 320       | 353.2     |
|               | Strength   | -0.16      | -0.117    | -0.15     | -0.145    |
| Band 1        | Center     | 920        | 919.6     | 920       | 919.1     |
|               | FWHM       | 200        | 176.8     | 200       | 179.5     |
|               | Strength   | -0.65      | -0.686    | -0.20     | -0.203    |
| Band 2        | Center     | 1885       | 1888.5    | 1800      | 1800.1    |
|               | FWHM       | 500        | 541.2     | 450       | 439.5     |
|               | Strength   | -0.40      | -0.422    | -0.12     | -0.114    |

**Notes:** Band center and FWHM are in the unit of nanometers. The final parameters are rounded off to proper precision. Band 1 is for absorption near 1.0 μm in OPX, while Band 2 is for absorption near 2.0 μm in OPX.

We also utilize the band area ratio (BAR) method ([Cloutis et al. 1986](#)) to analyze these spectra. BAR method does not need MGM processing and it is generally considered as a very useful indicator for interpreting the olivine-orthopyroxene mixture spectra, which is nearly independent of mineral composition and mineral grain size ([Cloutis et al. 1986](#)). However, we found that the BAR values of each mixture sample group show a well linear trend, but not all of them follow the trend line given by [Cloutis et al. (1986)](#). In the calculation results of some samples, especially for the BAR values of our newly acquired spectral curves, the deviation between the estimated mineral abundance value and its true value maybe more than 30% (Figure 8).

The deviations are mainly caused by using different spectrometers as stated in [Hapke (2012)](#), band depths and band shapes depend on illumination and viewing geometry. It can cause differences in band shapes between spectra of the same material measured bidirectionally and using an integrating sphere to measure the directionalhemispherical reflectance. Therefore, we should use this trend line with caution, especially when the spectrometers and/or the viewing geometry used for measurement are different and the abundances and/or end-member chemistries are unknown. Fortunately, the well linear trend shown by each BAR parameter group provides a direction for solving this problem. As shown in Figure 6 and Figure 7, M1-2 band (~1.23 μm) in olivine absorption features is able to be distinguished from the absorption band of orthopyroxene. The absorption strength of olivine M1-2 band and overall absorption show a broad asymmetric complex absorption feature, and the absorption features of olivine dominate the spectra curve between 1.0 to 1.5 μm regions.

### 3.3 Modified BAR of Olivine-Orthopyroxene Mixtures

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feature near 1.0 µm contain the information about the relative content of olivine and orthopyroxene. It indicates that we can use the MGM fitting results to estimate the mineral abundance.

Firstly, we utilize MGM to obtain the absorption features of olivine and orthopyroxene in the mixtures. Secondly, a modified band area ratio (MBAR) indicator is obtained by using MGM fitting result parameters. The MBAR is modeled as:

$$\text{MBAR} = \frac{\text{Area}_{2\mu\text{m}}}{\text{Area}_{1\mu\text{m}}}$$

(3)

where, Area is calculated with an approximation and it is defined as:

$$\text{Area} = \sum_{i=1}^{N} 1.065 \times \text{FWHM}_i \times \text{STR}_i$$

(4)

where, 1.065 is the factor to get the integral of Gaussian curve by using FWHM. STR is the absolute value of absorption strength. There are 4 absorption bands in Area$_{1\mu\text{m}}$, which are the three diagnostic absorption features of olivine and one absorption of orthopyroxene (that is Band 1). There is only one orthopyroxene absorption band (Band 2) in Area$_{2\mu\text{m}}$. The illustration in Figure 9 explains these definitions in detail.

Finally, MBAR can be regarded as the absorption intensity coefficient of the two main absorption bands in the olivine-orthopyroxene mixture spectra. As is mentioned above, M1-2 band in olivine spectra are easy to extract from the mixture spectral curves. Dividing MBAR by the olivine M1-2 band absorption strength value (abbreviated as: MBAR/OLV$_{\text{STRM1-2}}$) can get the end-member composition information. The result values show a good pattern on the estimation results, as the orthopyroxene abundance increases, the MBAR value increases, the OLV$_{\text{STRM1-2}}$ value decreases and the ratio data of the two values show an exponential growth trend. In order to show their changing patterns clearly, we use an exponential ordinate to display them. Figure 10 shows the calculation results and the regression equation. The overall error in predicting the mixture composition based on MGM fitting results is less than 15%.

3.4 Fitting Results of Irradiated Samples

Some RELAB samples irradiated with the pulsed laser to simulate the space weathering effect are mentioned in Table 2, but it seems no significant spectral alteration with their spectral curves. However, for our samples, the fresh spectra and irradiation spectra by high energy laser show obviously difference (Figure 12), which are suitable for further study. After irradiation, the spectral features turn weaker and shallower. Absorption intensity and albedo of the visible region decrease faster than the NIR region, whose behaviors redden and darken the irradiated VNIR spectra. In a high-intensity or long-term space weathering environment, the spectra of pyroxene appear more reddening, and olivine spectra appear more darkening. This is consistent with the results presented in Yamada et al. (1999) and Jiang et al. (2019).
Table 4: Comparisons of the absorption band centers before and after irradiations

| Sample ID   | Original (1 µm) | Original (2 µm) | Irradiated (1 µm) | Irradiated (2 µm) |
|-------------|----------------|----------------|-------------------|------------------|
| OWN-OPX     | 912.16         | 1795.26        | 913.45            | 1803.38          |
| OWN-OL1/EN4 | 911.52         | 1801.50        | 912.16            | 1805.26          |
| OWN-OL2/EN3 | 915.38         | 1804.01        | 915.38            | 1809.04          |
| OWN-OL3/EN2 | 931.16         | 1824.32        | 922.55            | 1808.41          |
| OWN-OL4/EN1 | 1037.15        | 1824.32        | 1041.11           | 1824.32          |
| OWN-OLV     | 1056.17        | -              | 1057.03           | -                |

Notes: Band centers are in nm, values listed in this table are approximations.

A widely utilized continuum remove method is employed to compare the spectral absorption features and the band depth of these samples before and after pulsed laser radiation (Clark & Roush 1984). Band center positions of the continuum-removed spectra before and after laser irradiation are compared in Table 4, it is generally believed that continuum-removed band positions are less affected (shift a few nanometers) by space weathering (Pieters et al. 2000; Fu et al. 2012). Figure 13 shows the parameter comparison of these original and irradiated spectral curves. The absorption features near 1.0 µm is the superposition of olivine and orthopyroxene. Obviously, the higher the proportion of olivine is, the more band depth decreases after laser irradiation. While the absorption features near 2.0 µm is only due to the spectral absorption of orthopyroxene, the spectral curves in this region change uniformly. A sub-figure shows the albedo value of these samples and here it uses the average of the spectral reflectance from 0.5 to 0.8 µm (close to visible region). This figure shows that orthopyroxene has stronger resistance to space weathering than olivine. On the whole, the higher content of olivine is in mixture, the weaker absorption features are in its irradiated spectra, which may make these spectra more difficult to identify and interpret.

Also, we deconvolve these space weathered spectra based on the prior mineral knowledge and the constraints mentioned above. After pulsed laser irradiation, the MBAR of these samples all increase (Figure 14a). It can be inferred that the spectra of the short wavelength are more susceptible to space weathering than the longer wavelength in the VNIR region. What is more, as olivine is more susceptible to space weathering, the spectral absorption strength of olivine will reduce significantly. The more olivine content is in the mixtures, the greater ratio decrease of Band M1-2 absorption strength (Figure 14a), which will further increase the deviation in the mixture composition prediction results. MGM deconvolution results of these irradiated mixtures are shown in Figure 14b. The distance between two points in the horizontal direction represents the deviation value of the prediction result. With the increase of olivine (decrease of orthopyroxene) content, the deviation of estimate results also increases.

In addition, an extended calculation shows that it will get a slightly larger MBAR/OLV STR_{M1−2} value than the original spectrum when using MGM to deconvolve the continuum-removed spectrum, that means it will slightly underestimate the olivine abundance. This finding will be used later. All these results remind us that we cannot be too cautious when identifying and interpreting the spectra of space weathered celestial bodies. If the effect of space weathering is not taken into account, MGM deconvolution results will usually underestimate the proportion of olivine in the mixtures.

3.5 Estimating the Composition of Olivine-Orthopyroxene Asteroids

The research results obtained above are very promising and they can be used to study the space weathered celestial bodies, such as asteroids or lunar rocks. Asteroids are considered to be smaller and rotating faster than solid planets, with minimal gravity, these asteroids have thinner regolith (Chapman 2004). Q-type and S-type asteroids are characterized by spectra with moderate silicate absorption features near 1.0 and 2.0 µm (Chapman 2004; DeMeo et al. 2015). Vernazza et al. (2008) and Thomas et al. (2014) analyzed the VNIR spectra of many Q-type and S-type asteroids and reported that most of them have spectral properties similar to LL chondrites, whose main minerals are hypersthene and olivine. Here we
choose some asteroids dominated by olivine-orthopyroxene for further study to estimate their mineral compositions.

3.5.1 Spectral Deconvolution on Olivine-Orthopyroxene Asteroids

The center positions of 2.0 $\mu$m absorption band are useful for determining the compositions of pyroxene. Low-Fe orthopyroxene spectra show that the absorption band center near 2.0 $\mu$m is ranging from 1.80 to 1.95 $\mu$m (Klima et al. 2007). These informations can help us to search the suitable asteroid spectra for studying their mineralogical characterization. Six asteroids with high quality spectra are selected, they are: (4) Vesta, (15) Eunomia, (158) Koronis, (631) Philippina, (2335) James and (4954) Eric. The VNIR spectra of these asteroids are obtained from the Small Main-Belt Asteroid Spectroscopic Survey (SMASS), which are presented on the MIT planetary spectroscopy website.

Absolute spectral albedos are difficult to obtain with accuracy in many remote sensing situations, so all spectra from MIT are normalized to unity at 0.55 $\mu$m. This work smoothed and shifted these asteroids spectra reflectance curves to acclimatize to the MGM. First, the spectra are smoothed using the Savitzky-Golay (SG) filter procedure (order = 3 and framelen = 25) (Savitzky & Golay 1964). Then, the spectral curves should be shifted to the suitable positions: if the maximum value of the asteroid albedo is less than 1.4, the whole spectral curve will be shifted downward by 0.6, while if it is greater than 1.4, it will be shifted downward by 0.7 (Figure 15). The purpose of this shifted operation is to ensure that the spectral curves of these silicate-rich asteroids can be compared with the experiment spectra. Subject to slight space weathering, the slope of the mafic mineral spectra will increase slightly. The steep visible band region and overall inclined spectral curves reveal that these asteroids have suffered space weathering.

It is feasible to use the MGM deconvolution approach to estimate the mineral abundances. MGM with the logarithm of a second-order polynomial continuum removal method is employed to deconvolve these spectra. The deconvolution and estimated results are shown in Figure 16 and Table 5. As shown in Figure 14 and described above, MGM will usually underestimate the proportion of olivine in the mixtures when deconvolution is applied to space weathered spectra, so the olivine content on these asteroids is only conservatively estimated in this paper. It means that the fresh rocks or subsurface materials of these asteroids may contain more olivine.

3.5.2 More Olivine on Asteroid (4) Vesta

Asteroid (4) Vesta is the second most massive and probably the second largest asteroid (Thomas et al. 2005). It has been considered that olivine and hypersthene are likely to be ubiquitous over the whole surface of Vesta (e.g., Hanna & Sprague 2009; Ammannito et al. 2013; Zambon et al. 2014; Le Corre et al. 2015; Poulet et al. 2015). Ammannito et al. (2013) inferred the presence of olivine using two primary methods, which are: Continuum removed spectral curve matching method and Band centers with the BAR parameters. The average spectra of (4) Vesta and olivine-rich site from a bright crater are given in that paper. The spectrum of the bright crater reveals clear olivine signatures, with the band near 1.0 $\mu$m
centered at slightly longer wavelength than the average (4) Vesta spectrum, and the area of the 2.0 \( \mu m \) band is smaller than the average spectrum. The data are shown in Figure 17d.

These data can infer that the surface of the asteroid (4) Vesta contains a high content of olivine. The olivine modeled abundance is about 20%, and the spectra of some fresh rocks from the impact crater are interpreted as having an olivine content of more than 50%, maybe even up to 70% \( \sim 80\% \) (Ammannito et al. 2013; Clénet et al. 2014; Poulet et al. 2015). In order to deconvolve these two continuum removed spectral data, we adjusted the MGM parameters to the study in this work. The deconvolution results (shown in Figure 17) of the spectral data obtained by SM mass and Dawn are very consistent. Remote sensing and orbital average spectral data of the asteroid (4) Vesta show that there are about 30% olivine + 70% orthopyroxene in its surface mafic materials. While the deconvolution results of the bright crater spectrum reveals that there is approximately 70% olivine. Considering that the spectrum of the bright impact crater is continuum removed (as described at the end of Section 3.4) and it has also been slightly weathered in space, we infer that the olivine composition of partial craters on asteroid (4) Vesta are greater than 70%. This result is consistent with the findings of Ammannito et al. (2013) and Poulet et al. (2015). Based on these findings, we can infer that the other asteroids mentioned above also have a high olivine content. However, space weathering prevents the correct deconvolution and interpretation of these spectra.

3.6 Different Orthopyroxenes

The orthopyroxene measured in RELAB and our experiment are both low-Fe orthopyroxenes. To understand whether the mixture of olivine and high-Fe orthopyroxene is also suitable for the method presented here, we carried out the following study. As is shown in Figure 1b, the spectral curve of Ferrosillite, a kind of high-Fe orthopyroxene, shows an obvious absorption characteristic near 1.2 \( \mu m \). This spin-allowed crystal field absorption band is attributed to the presence of Fe\(^{2+}\) in the crystal M1 site, which is on the shoulder of the 1.0 \( \mu m \) band (Klima et al. 2007). This position is very close to olivine’s M1-2 band and thus care must be taken when interpreting the data. In addition, the two main absorption bands centered around 1.0 and 2.0 \( \mu m \) shift towards longer wavelength as the iron content increasing. Here we choose the asteroid (1862) Apollo (Figure 18a) for further study, as its spectral curves show an olivine reflectance peak near 1.6 \( \mu m \) with two high-Fe orthopyroxene absorption bands (Gaffey et al. 1989; Buratti et al. 2004).

Spectral curve matching method is used for this spectrum, and three absorption features near 1.0 \( \mu m \), 1.2 \( \mu m \) and 2.0 \( \mu m \) are compared with systematic mixtures (Figure 18b). It derived olivine abundance is about 80% in the olivine-orthopyroxene mixtures. Two MGM deconvolution procedures are utilized here, one considering the \( \sim 1.2 \mu m \) absorption of the high-Fe orthopyroxene and the other does not considering this band. The deconvolution results are shown in Figure 18c and 18d.

If we ignore the absorption of the \( \sim 1.2 \mu m \) band, the deconvolution result of MGM will get a larger absorption intensity in the olivine M1-2 band than the one who adds the \( \sim 1.2 \mu m \) absorption band. The actual \( \sim 1.2 \mu m \) absorption band will increase the area of 1.0 \( \mu m \) band, which will lead to the MBAR value decreasing. The combination of these two factors will be misinterpreted as the content of olivine in the material is higher than the actual abundance. Figure 18c shows that the surface material of asteroid (1862) Apollo is composed of 96% olivine and 4% orthopyroxene, which does not meet our perception. However, Figure 18d shows it contains about 88% olivine and 12% orthopyroxene (here we have deducted the area of the \( \sim 1.2 \mu m \) absorption band). Although the results of these two estimated values are close, we have proved that the deconvolution result considering the \( \sim 1.2 \mu m \) absorption band is relatively reliable.

4 CONCLUSIONS

In this article, a new empirical procedure based on MGM with some prior mineral absorption bands is presented to estimate the end-members abundance from olivine-orthopyroxene mixture spectra. The accuracy of the end-member abundance can be estimated within 15% by using this new procedure.
Integrated with RELAB database, a new spectral set obtained from olivine-orthopyroxene mixtures assembled at 20% mineral abundance intervals in our experiments is exploited. The VNIR absorption spectra of olivine-orthopyroxene mixtures systematically varied with their various abundances. However, we found the commonly-used BAR does not work well for some mixtures and the BAR of different mixture sets show large deviations. As a powerful tool, MGM is utilized to reveal the composition of mafic mineral assemblages. A modified BAR (namely MBAR) is introduced to describe new-defined band area ratio based on the fitted parameters by MGM. Two parameters of MBAR and olivine M1-2 band absorption strength (as defined in the MGM) are used to estimate the mineral abundances of olivine-orthopyroxene mixtures. The systematic procedure is quite efficient for deconvolution of olivine-orthopyroxene mixture spectra and estimation of the mineral abundances for mafic materials from the VNIR reflectance spectra.

Additionally, space weathering effect on olivine-orthopyroxene mixtures and silicate asteroids is investigated based on the new proposed procedure. Some samples are irradiated by high-energy laser in our experiments and the spectral profiles of these samples vary with irradiation fluxes significantly. After irradiation, we find that mineral diagnostic spectral features (∼1.0 and ∼2.0 µm bands) become weaker and shallower. The intensities of absorption bands and albedos of these spectra in the visible region decrease faster than that in the NIR region. The MGM deconvolution results of these irradiated mixtures indicate that orthopyroxene has stronger resistance to space weathering than olivine. Among the results, MBAR increases, while olivine M1-2 band absorption strength decreases, which makes these irradiated spectra more difficult to identify and interpret. This usually leads to an underestimate of olivine abundance. The VNIR spectra of main-belt asteroid (4) Vesta from SMASS catalog and Dawn mission are investigated by applying the new procedure and the results are consistent with the others’ studies.

Besides, the influence of absorption band strength of high-Fe orthopyroxene at ∼1.2 µm is also discussed in this study and we claim that this band should not be ignored in the analysis of olivine and high-Fe orthopyroxene mixtures. In the future, more experiments for spectral deconvolution of different mafic mixtures and studies for various space weathering effects will be implemented to extend the applications of the new proposed procedure and MGM.

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Fig. 1: Reflectance spectra of olivine with varied Mg-number (Fo#) and the ones with pyroxene quadrilateral end-members. (a). Spectra of olivine with varied Fo#. (b). The comparison of the spectra with various pyroxene quadrilateral end-members: Di (diopside; shown as green), Hd (hedenbergite; orange), En (Enstatite; red) and Fs (Ferrosillite; blue)
Fig. 2: VNIR reflectance spectra of three mineral components with orthopyroxene (shown as blue), olivine (green), and olivine-orthopyroxene mixture (red). The RELAB IDs of these spectra are AG-TJM-008 (OLV), AG-TJM-009 (OPX) and AG-TJM-019 (MIX) respectively.
Fig. 3: VNIR reflectance spectra of mixtures composed of olivine and orthopyroxene mixed with different proportions. (a). The spectra are obtained from RELAB database. (b). Spectral profiles are taken from our experiments (2.14 µm artificial peaks are removed, narrow ~1.41 and ~2.33 µm absorption bands presented in some spectra are due to minor alteration). For the sake of clarity, with the increase of olivine content, the reflection spectra are superimposed and moved multiple +0.1 on the ordinate.
Fig. 4: VNIR reflectance spectra of mixtures composed of olivine and orthopyroxene mixed with different proportions before (solid lines) and after (dashed lines) 50 mJ*2 laser irradiation. Narrow ∼1.41 and ∼2.33 µm absorption bands present in some spectra are due to minor alteration. The colors of spectral curves are the same as Figure 3b.
Fig. 5: Four significant characteristic parameters for MGM fitting. For the sake of clarity, the residuals (pink line) are shifted by +0.1 on the ordinate.
Fig. 6: The comparison of MGM fitting results for the spectral curves with olivine and orthopyroxene obtained from RELAB database (panel (a): RELAB olivine and panel (c): RELAB orthopyroxene) and our experiments (panel (b): OWN olivine and panel (d): OWN orthopyroxene).

Fig. 7: MGM fitting results for the samples composed of olivine and orthopyroxene mixed with different proportions. The fitting curves with the OPX absorption features are plotted as the blue curve. The red curve represents the olivine absorption bands fitting by using the Gaussian function.
Fig. 8: BAR values derived from the spectra with olivine-orthopyroxene mixtures utilized in this study. The solid line represents the trend line given by Cloutis et al. (1986). Black dots and triangles denote the results estimated from RELAB and our original experiment samples respectively.
Fig. 9: The spectral diagnostic feature of modified band area ratio (MBAR) derived from MGM fittings. For the obvious absorption feature close to 1.0 µm, the area of this band composed of four Gaussian curves (shown as blue) is defined as Area$_{1\mu m}$. For the band at around 2.0 µm, this feature is made by single Gaussian curve with orthopyroxene (orange line) and then defined as Area$_{2\mu m}$. 
Fig. 10: A plot of MBAR/OLV,,,,STR M1–2 ratio versus orthopyroxene abundance. The solid line represents a linear least-square fit for all data with the orthopyroxene abundance between 10% and 90%. The notations of data points are the same as Figure 8.

Fig. 11: Spectral reflectance of two RELAB olivineorthopyroxene mixture samples and mineral abundance estimation results obtained by MGM. Dot represents the true value and square represents the estimated value.
Fig. 12: Comparison of the spectral curves composed of olivine-orthopyroxene admixtures mixed with different proportions and their irradiated results.
Spectral Deconvolution on OLV-OPX Mixtures

Fig. 13: Variations of band-depths and albedos (average of the spectral reflectance ranging from 0.5 to 0.8 μm) of olivine-orthopyroxene mixtures before and after pulsed-laser irradiation.

Fig. 14: Deconvolution results of the olivine-orthopyroxene mixtures derived from MGM fittings. (a). The evolution of MBAR ratios (Band M1-2 absorption strengths) of olivine-orthopyroxene mixtures with different proportions before and after pulsed-laser irradiation. (b). Correlation of truthful and estimation abundances of the mixtures with pulsed-laser irradiation, the blue circles and orange squares represent the truthful and estimation abundances of these mixtures respectively.
Fig. 15: VNIR spectra of six asteroids (4) Vesta, (15) Eunomia, (158) Koronis, (631) Philippina, (2335) James and (4954) Eric. These spectra are normalized at 0.55 µm and shifted downward to suitable positions.
Fig. 16: Decomposition of the components of 1.0 and 2.0 µm features for six asteroids (4) Vesta, (15) Eunomia, (158) Koronis, (631) Philippina, (2335) James and (4954) Eric. The OPX absorption bands fitted by MGM method are plotted as blue curves and red lines represent the absorption features with olivine. The black curves are the sum of all band profiles plus the continuum.
Fig. 17: Decomposition of the components of absorption features for main-belt asteroid (4) Vesta. (a). Modeled spectral fitting of the crater area with olivine-rich. (b). Modeled spectral fitting of average Vesta spectrum. (c). The estimations of mineral abundances derived from the SMASS and Dawn spectral data. (d). Comparison of the continuum-removed spectra obtained from various areas of (4) Vesta (Data from Ammannito et al. (2013) and olivine-orthopyroxene systematic mixtures with different proportions.)
Fig. 18: VIR Spectral curve of asteroid (1862) Apollo and decomposition of the components of 1.0 and 2.0 μm features. (a). The observed and smoothed spectra are normalized at 0.55 μm and shifted downward to the suitable positions. (b). Comparison of the continuum-removed spectral curves and olivine-orthopyroxene mixtures with different proportions. (c). Decomposition of the components of absorption features without considering ∼1.2 μm sub-band composed of high-Fe orthopyroxene. (d). The curve is fitted by using same method as (c) panel, but considering ∼1.2 μm absorption band (marked as green line).