Encyclopedia of Lunar Science
DOI 10.1007/978-3-319-05546-6_18-1


# Laboratory Analysis (Reflectance Spectroscopy) of Terrestrial Analogues

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## Theory and Application

The Moon is one of most studied planetary bodies. Silicate minerals, such as orthopyroxene and clinopyroxene, olivine, and plagioclase, are the most important constituents of the lunar surface, associated with oxides and rare apatite (e.g., Papike et al. 1991).

Though olivine and pyroxene show clear spectral signature and well-defined crystal field absorption bands in the visible and near-infrared (Burns 1993), plagioclase is difficult to recognize, due to very low iron content in its crystal structure. In fact, even if it is widely acknowledged that plagioclase is one of the most important constituents of the lunar surface (Heisenger and Head 2006), its presence has been usually related to featureless spectra and interpreted as shocked plagioclase (Spudis et al. 1984; Bussey and Spudis 2000).

Only recently, the spectrometers on board lunar missions (Spectral Profiler (SP), onboard Selene, and Moon Mineralogy Mapper ($M^3$), onboard Chandrayaan), with very high spectral (6–8 and 10 nm, respectively) and spatial (500 and 100 m, respectively) resolution, recognize regions composed of crystalline plagioclase, detecting the plagioclase absorption band in the 1,250 nm spectral region (Ohtake et al. 2009; Pieters et al. 2009; Cheek et al. 2012). Analyzing the plagioclase absorption band depth, Ohtake et al. (2009) recognized areas dominated by plagioclase (plagioclase $>$98 %), defined pure anorthosite (PAN) regions, mostly in crater central peaks.

However, to relate plagioclase absorption band to modal abundance and mineralogical composition can be a difficult task. In fact, on the Moon, several factors such as the mineral chemistry, the presence of different minerals that absorb in a narrow spectral range, the particle size, the space weathering, etc., act in unpredictable ways on the reflectance spectra.

For these reasons, studying terrestrial analogues can be fundamental in order to analyze separately the different factors and then superimpose effects to each other.

## Methodology

For a correct interpretation of reflectance spectra from the lunar surface, but generally from a planetary surface, it is fundamental to analyze terrestrial analogues with compositional and size characteristics similar to the lunar regolith. The lunar regolith consists of mixtures of different rock fragments and minerals at different particle sizes; furthermore, very fine particle sizes, $<$10 μm, enriched in plagioclase have been recognized (McKay et al. 1974).

Consequently, terrestrial analogues will consist of synthetic mixtures of minerals with known composition and known modal abundance and have to be analyzed at different particle sizes, from very fine to coarse ones, to understand the effects of physical properties on reflectance spectra.

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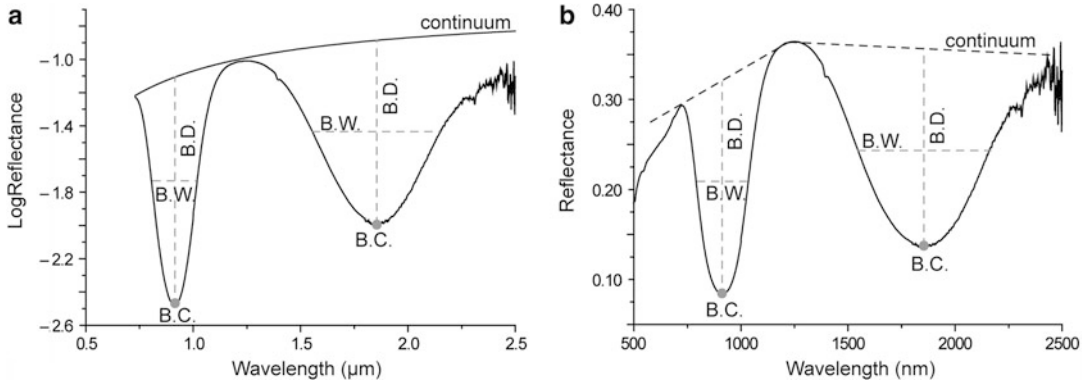


**Fig. 1** The figure shows spectral parameters that describe a reflectance spectrum. B.C.: band center; B.D.: band depth; and B.W.: band width. (**a**) Continuum is a function of wave number and expressed as the logarithm of the reflectance. It is described by two parameters, the intercept c0 and the slope c1; (**b**) continuum is considered as a sum of segments that join reflectance maxima

Here we review the recent knowledge about plagioclase absorption considering terrestrial analogues analyzed by reflectance spectroscopy in the 350–2,500 nm spectral range, generally with the *i*-incidence angle = *30*° and *e*-emission angle = *0*° acquisition geometry. This spectral range is characterized by crystal field absorptions, due to electronic transitions in partly d-filled elements, in particular iron, in mineral crystal structure.

Generally, a reflectance spectrum is characterized by a series of absorption bands superimposed onto a continuum. The continuum that represents the spectrum albedo and reflectance can be described by: (1) a mathematical function described with two parameters, the intercept c0 and the slope c1 (as in the modified Gaussian model, Sunshine et al. 1990, Fig. 1a solid line), and is expressed in the log of the reflectance and as function of the wave number and (2) segments that join the spectrum reflectance maxima (as in Clark and Roush 1984, Fig. 1a dashed line).

An absorption band is described using three spectral parameters: band center (B.C. in Fig. 1), band depth (B.D. in Fig. 1), and band width (B.W. in Fig. 1); band center, the band minimum, represents the energy of the transition; band depth, the distance between band center and continuum, is the probability of the transition; and band width, expressed as the full width at half maximum, is related to vibronic processes (Burns 1993).

Compositional information can be obtained by the band center and band depth: the band center position, related to the energy of the transition, is diagnostic of a particular mineral and of a well-defined crystal site, while band depth gives important information about mineral modal abundance and size.

Figure 2 shows the reflectance spectra of the most abundant lunar minerals: (1) plagioclase (Fig. 1a) is characterized by an absorption band centered at ca. 1,250 nm attributed to iron transition (Adams and Goulland 1978); (2) olivine (Fig. 1b) is characterized by a broad band centered at about 1,050 nm, due to three absorptions due to the iron transition in M1 (900 and 1,200 nm) and M2 (1,050 nm) sites (Burns 1993); and (3) pyroxene (Fig. 1c) is characterized by two absorption bands, at 900–1,100 and 1,800–2,000 nm, respectively, due to the iron transition in M2 site (Burns 1993); increasing Ca content band centers moves toward longer wavelengths.

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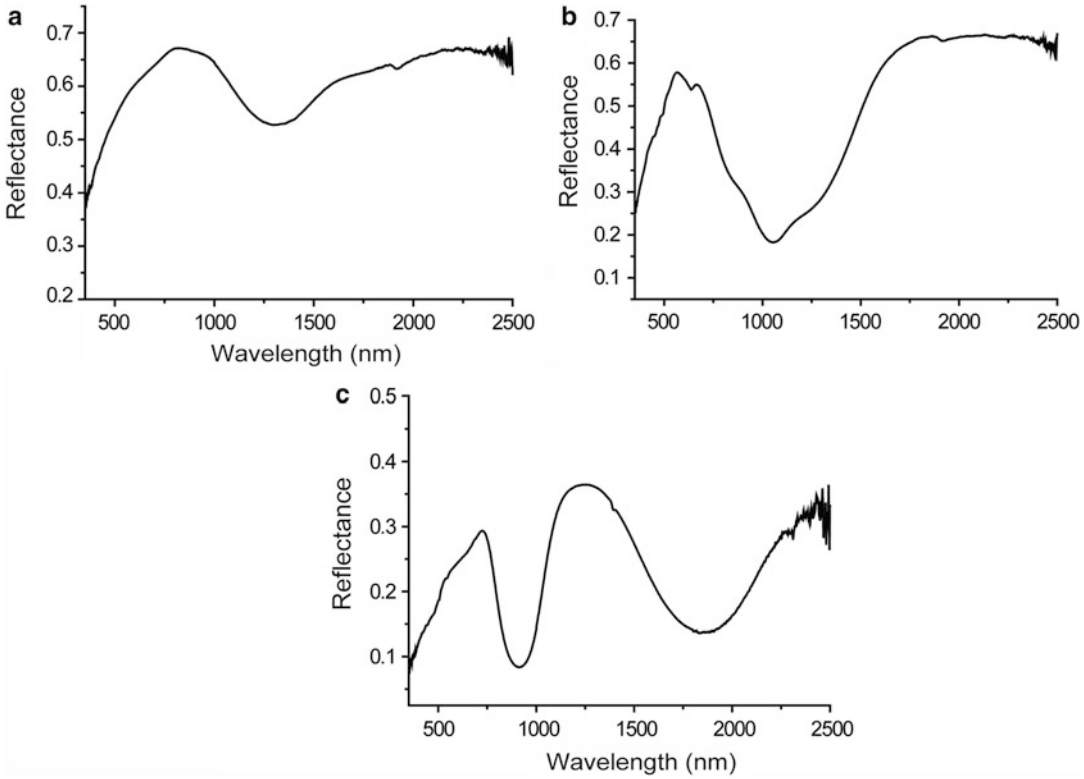


**Fig. 2** (**a**) Reflectance spectrum of plagioclase, characterized by an absorption band centered at ca. 1,250 nm related to iron transition in plagioclase crystal structure; (**b**) reflectance spectrum of an olivine, characterized by three absorption bands, at 900, 1,050, and 1,200 nm, due to iron transition in M1 and M2 sites; (**c**) reflectance spectrum of an orthopyroxene, characterized by two absorption bands at ca. 900 and 1,800 nm due to iron transition in M2 site

## Research Findings

SP and $M^3$ spectrometers detected the crystal field absorption in crystalline plagioclase, associated with mafic minerals, in different lunar regions, e.g., in Tsiolkovsky crater (Ohtake et al. 2009; Cheek et al. 2012), Orientale basin (Pieters et al. 2009; Cheek et al. 2012), and Jackson crater (Ohtake et al. 2009). For this reason, studying the spectral properties of plagioclase and plagioclase-mafic mixtures is fundamental to better understand lunar origin and evolution.

In the following section, we summarize the recent results about the plagioclase reflectance spectroscopy.

### Band Center

As stated before, the band center is directly related to the transition energy (Burns 1993) and is characteristic of well-defined mineral phases. Several papers discussed the band center behavior of mafic minerals, e.g., Sunshine and Pieters (1993, 1998); on the contrary, less is known about the behavior of plagioclase absorption band.

#### Mineral Chemistry: Single Phase

Cheek et al. (2011) evidenced a spectral variation in synthetic plagioclase with increasing the iron content. Serventi et al. (2013b) analyzed three natural plagioclases with different chemical compositions: PL1, $An_{45}$, 0.1 wt.% FeO; PL2, $An_{80}$, 0.36 wt.% FeO; and PL3, $An_{80}$, 0.5 wt.% FeO.

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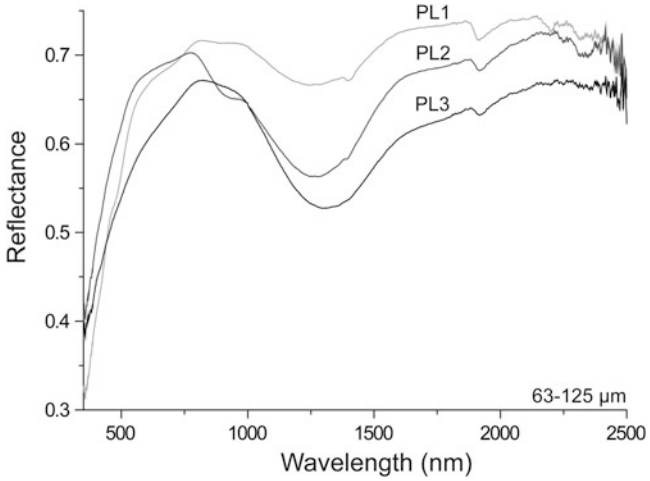


**Fig. 3** Reflectance spectra of three plagioclases with different iron contents at the same particle size, 63–125 μm. Increasing the iron content, from PL1 to PL3, the 1,250 nm band center is shifted toward longer wavelengths

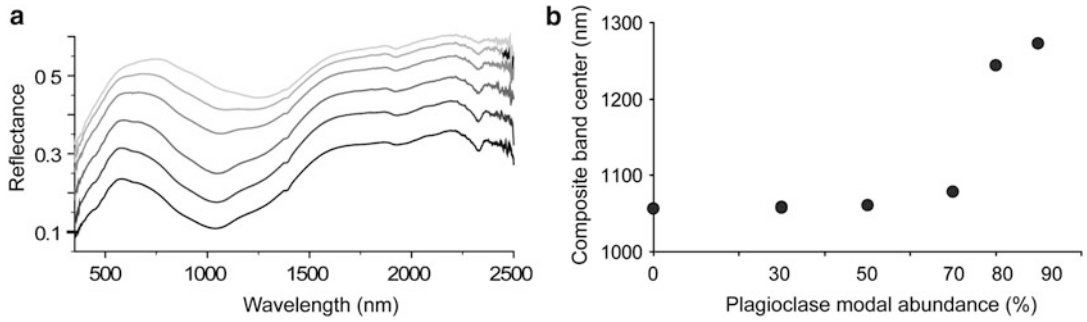


**Fig. 4** (**a**) From black to gray, reflectance spectra of mixtures composed of increasing plagioclase content (30–90 %) and decreasing olivine; (**b**) composite band center, here considered as the absolute reflectance minimum, shifts toward longer wavelength with increasing plagioclase modal abundance in mixtures

Figure 3 (Serventi et al. 2013b) shows the reflectance spectra of PL1, PL2, and PL3 at the 63–125 μm particle size. In particular, increasing the iron content, from PL1 to Pl3, reflectance decreases and the continuum becomes blue (higher reflectance in the near-infrared with respect to the visible region), while the 1,250 nm absorption band shifts toward longer wavelengths.

## Composite Band

Minerals with different chemical composition may produce distinct absorption bands within a narrow spectral range. As shown before, plagioclase absorbs in the 1,250 nm spectral range. On the other hand, olivine is characterized by three absorption bands, due to the iron transition in M1 and M2 sites, at ca. 900, 1,050, and 1,200 nm. Therefore, plagioclase absorption band and the third olivine absorption band occur in 50 nm; this is reflected in a so called composite band (Serventi et al. 2013b), where it is difficult to separate the different minerals. However, spectral parameters and their relative reflectance give useful information on the mineral modal abundance.

Figure 4a shows the reflectance spectra of mixtures composed of different contents of olivine and plagioclase; Figure 4b shows how the composite band center (here considered as the absolute minimum in the reflectance spectra) shifts toward longer wavelength, increasing the plagioclase abundance.

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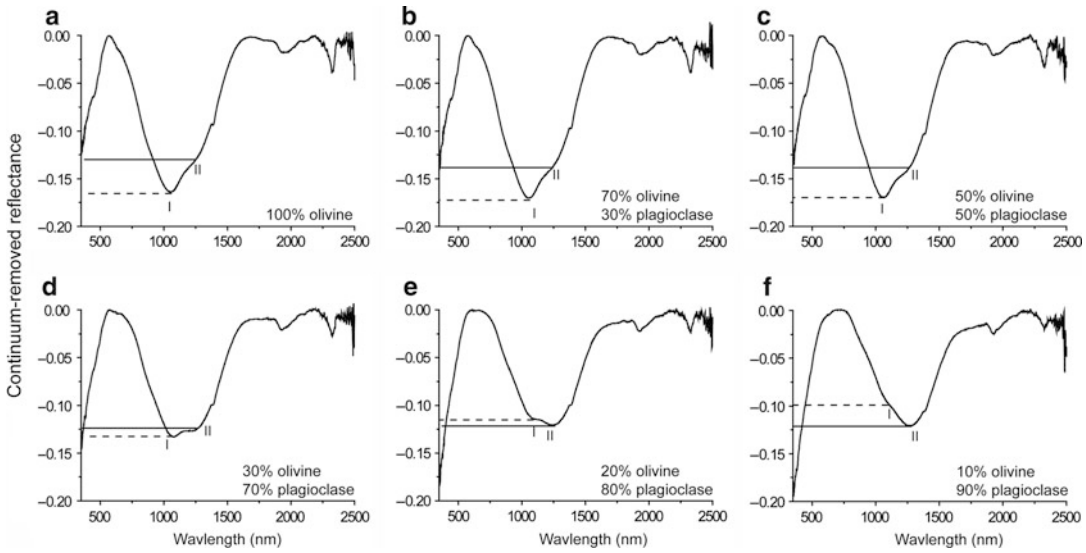


**Fig. 5** Continuum-removed spectra of mixtures shown in Fig. 4. From a to f plagioclase modal abundance increases, from 0 % to 90 %. Increasing plagioclase content, the relative reflectance between band I and band II is reduced, till mixtures with 80 % and 90 % plagioclase where band II is deeper than band I

## Band Depth

Band depth depends on the probability of the light to encounter the spectrally active species (e.g., iron). Thus, it gives important information about the spectral species concentration, both as mineral chemistry and as mineral modal abundance in a rock or in a regolith. In literature, several works discussed the band depth of mafic minerals, as pyroxenes (Sunshine and Pieters 1993) and olivines (Sunshine and Pieters 1998). Few data can be found about the plagioclase band depth.

### Mineral Chemistry

Cheek et al. (2011) and Serventi et al. (2013b) have shown how the iron content controls also the plagioclase absorption band depth. In fact, Fig. 3 shows that increasing iron content, from PL1 to PL2, plagioclase band deepens, while further increasing iron, from PL2 to PL3, the band depth slightly decreases. However, the decrease is associated with an asymmetry of the 1,250 nm band toward the longer wavelengths.

### Mineral Abundance: Composite Band

Figure 5 shows the continuum-removed reflectance spectra of an olivine (Fig. 5a) and of a set of mixtures composed of increasing plagioclase, from 30 % to 90 %. Even if plagioclase and olivine cannot be distinguished, the relative reflectance of absorption bands gives useful information.

In particular, Fig. 5 shows that increasing the plagioclase content in the mixture, the spectral contrast decreases and the reflectance difference between band I (centered at ca. 1,050 nm) and band II (centered at ca. 1,250) is reduced, till the 80 and 90 % PL mixtures where band II is deeper than band I (Fig. 5f).

On the contrary, considering mixtures composed with olivine and very high plagioclase content, more than 90 % (Serventi et al. 2013a), to recognize the olivine spectral signature can be very difficult for olivine content $<5$ %, with important implications for the PAN region definition (Fig. 6).

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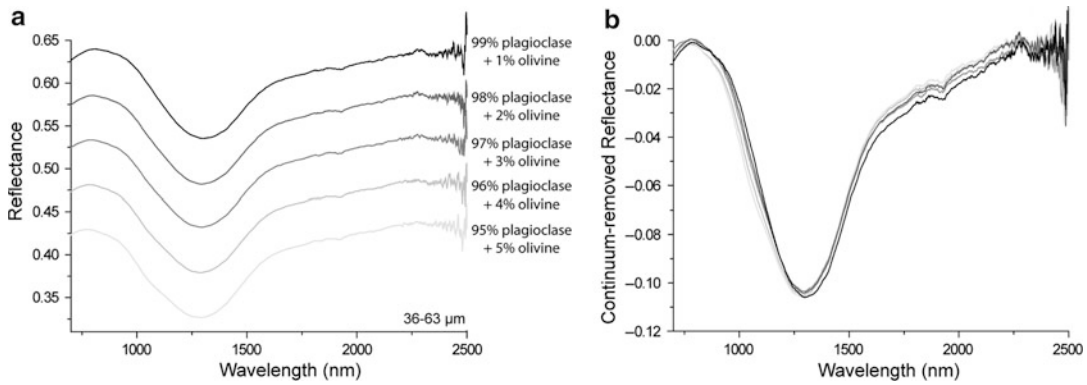


**Fig. 6** Reflectance spectra (**a**) and continuum-removed spectra (**b**) of a set of mixtures composed with more than 95 % plagioclase and olivine. In mixtures composed of less than 5 % olivine, olivine absorption bands are difficult to recognize

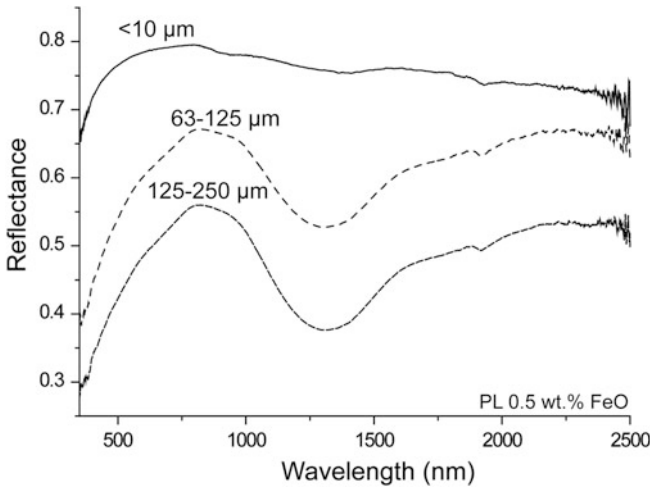


**Fig. 7** Reflectance spectra of a plagioclase with 0.5 wt% FeO at three different particle sizes. Fining the particle size, the reflectance increases and the spectral contrast is reduced

## Particle Size Effect

The size of the mineral grains controls the light path length within the mineral and, therefore, the probability of encountering the spectrally active species. Generally, fining the particle size produces reflectance spectra with high reflectance and reduced spectral contrast; on the other hand, very coarse sizes can saturate the absorption bands (Clark 1999), that is, a flattening of the absorption band bottom.

Figure 7 shows plagioclase reflectance spectra at three different particle sizes, 125–250, 63–125, and <10 µm, sizes present in the lunar regolith (McKay et al. 1974).

The figure shows that fining the particle size, albedo increases and plagioclase absorption band is reduced and almost undetectable for very fine sizes (Serventi et al. 2014), making it very difficult to recognize plagioclase from very fine lunar regolith.

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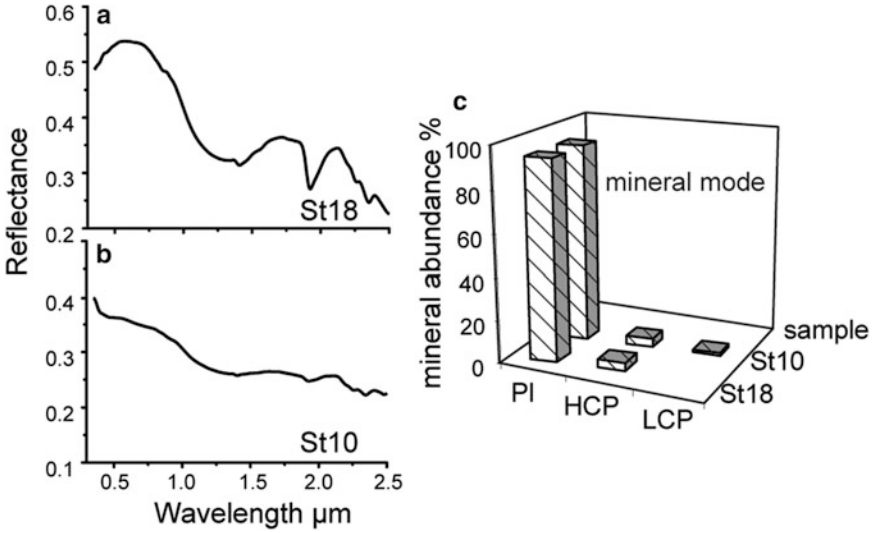


**Fig. 8** (**a**, **b**) Reflectance spectra of two plagioclase-rich mixtures; (**c**) mixture composition and mineral abundance. Increasing the number of spectrally active species in the mixtures, the reflectance spectrum becomes featureless and the plagioclase absorption band is very reduced even if plagioclase is the most abundant mineral

### Critical Mode

Plagioclase, pyroxene, and olivine are spectrally active species with clear absorption bands. However, Carli and Sgavetti (2011) showed how the presence of different active minerals can generate featureless spectra.

Figure 8 displays the reflectance spectra of plagioclase-rich mixtures. In particular, from St18 to St10, the number of different mineralogical phases increases, from two (plagioclase and high-Ca pyroxene) to three (plagioclase, high and low-Ca pyroxene). In particular, increasing the number of minerals, the spectral contrast decreases, masking the plagioclase absorption band, although plagioclase is the most abundant mineral phase (Fig. 8c) and the spectrally active iron as similar concentration in the different minerals.

## Future Directions

Recent missions recognized the plagioclase absorption band at 1,250 nm associated with the presence of crystalline plagioclase on the lunar surface. Knowing plagioclase chemistry and abundance is necessary to understand the origin and the evolution of the Moon. In this work, we have shown that the plagioclase band spectral parameters are controlled by different factors, such as the chemistry and iron content, the presence of other spectrally active minerals, and the particle size. These factors, if not particularly taken into account, can induce errors about the plagioclase estimation. Future analyses will be fundamental in order to have a more detailed knowledge of plagioclase, for example, the application of deconvolution method, such as the modified Gaussian model, and of physical method like the Hapke model (Carli et al. 2014). Furthermore, it would be interesting to introduce reddening factors, e.g., modeling some space weathering processes, in order to understand how they can influence on already reduced spectral contrast.

DOI 10.1007/978-3-319-05546-6_18-1


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