

Publication Year	2017
Acceptance in OA@INAF	2020-09-16T11:46:43Z
Title	The role of very fine particle sizes in the reflectance spectroscopy of plagioclase-bearing mixtures: New understanding for the interpretation of the finest sizes of the lunar regolith
Authors	GIOVANNA, SERVENTI; CARLI, CRISTIAN
DOI	10.1016/j.icarus.2017.04.018
Handle	http://hdl.handle.net/20.500.12386/27418
Journal	ICARUS
Number	293

#### 25 Abstract

26 The lunar surface consists of a regolith layer that covers the underlying bedrocks, and is generally

27 characterized by particulates <1 cm. The lunar soil is the fine fraction of the regolith, and is generally

28 between 60 and 80  $\mu$ m. Sizes <10  $\mu$ m, that comprises ca. 5-20% of the soil, were recognized and

29 *petrologically classified.* 

The coarsest sizes of the regolith are chemically and mineralogically similar, while the finest fractions
are more feldspathic, probably due to the easy of fracturing of plagioclase with respect to mafic

32 *minerals*.

33 Due to the more feldspathic nature of the very fine lunar soils, in this paper, we quantitatively

investigate the influence of very fine (<10  $\mu$ m) plagioclase on the absorption bands of mafic minerals

using the Modified Gaussian Model. We considered two plagioclases with different iron content and

36 two mafic end-members (1) 56% orthopyroxene and 44% clinopyroxene, and (2) 30% orthopyroxene

and 70% olivine. We also compared our results with the deconvolution of the same mixtures at coarser

*sizes. Our results mainly show that:* 

39 (1) a fine size acts principally on the reflectance and on the spectral contrast (that increases and

40 *decreases, respectively); (2) a very fine plagioclase has a blue slope in the Near Infrared and very* 

41 shallow 1250 nm band depth, close to zero; (3) consequently, plagioclase band is always shallower

42 than mafic bands; (4) in mixtures with olivine, the composite band center always shows the typical

43 olivine value, differently from coarser mixtures; and (5) mafic material have a blue slope in the Short

44 Wavelength Infrared Region, a more V-shaped 1µm pyroxene absorption and the 1µm mafic band

45 centers are shifted of ca. 40 nm with respect to coarse sizes, reflecting a different weight within the

46 *crystal field absorption of mafic component in very fine size. We also evidenced how a coarse* 

47 plagioclase could be overestimated, while a very fine one could be underestimated if compared to the

48 63-125 $\mu$ m size.

### 49 **1. Introduction**

Very fine sizes dominate many planetary surfaces and their regolith, e.g., Moon, Mars and Mercury.
Different particle size fractions in the regolith (such as soil and dust) affect in different ways the optical
properties of the surface. For this reason, very fine particles and their effects on the reflectance spectra
of the most common planetary minerals have to be investigated in detail to retrieve correct information
about the mineralogical composition and the surface texture.

In particular, the lunar surface consists of a regolith layer that covers the underlying bedrocks, with the 55 56 exception of steep-sided crater walls, central peaks and lava channels (McKay et al., 1970), as shown 57 by the lunar landings and observations. The lunar regolith, due to the absence of atmosphere on the Moon, is the result of different processes, e.g., impact of meteoroids and bombardments of protons 58 from the sun and the stars, and is generally considered to be characterized by material lower than1 cm 59 in size (McKay et al., 1970). The fine fraction of the regolith, deriving from mechanical disintegration 60 of lunar rocks, both basaltic and anorthositic, constitutes the lunar soil. The average lunar soil size is 61 generally between 60 and 80 µm (McKay et al., 1970). The lunar dust describes even finer material 62 than lunar soils (ca. <50 µm). Furthermore, sizes <10 µm, that comprises ca. 5-20% of the soil, have 63 been recognized and petrologically classified (Laul et al., 1978; 1979; 1980). 64 Silicate minerals, such as orthopyroxene (OPX), clinopyroxene (CPX), olivine (OL) and plagioclase 65 (PL) are the most important constituents of the lunar surface, associated with oxides (e.g., Papike et al., 66

67 1991), and can be spectrally identified on the basis of their absorption bands. While the iron-richer

68 mafic minerals have been always easily detected (e.g., Tompkins and Pieters, 1999; Spudis et al.,

69 1984), only recently, and thanks to the improvements on spectrometers onboard the last missions, the

absorption due to the low amount of  $Fe^{2+}$  in PL have been recognized (e.g., Ohtake et al., 2009; Cheek

et al., 2012a,b; Kramer et al., 2014), permitting new evaluation of its modal abundance and

72 composition.

While coarse sizes of the regolith are chemically and mineralogically very similar, the finest fractions, 73 <10 µm, are different and more feldspathic. A possible explanation can be due to simple comminution 74 processes and the easy of fracturing of PL with respect to mafic minerals (Laul et al., 1978; 1979; 75 1980; Devine et al., 1982). 76 According to the more feldspathic nature of the very fine lunar soils, in this paper we present results for 77 a set of PL-bearing mixtures analyzed at the  $<10 \mu m$  particle size, also proposing a comparison with 78 79 coarser mixtures analyzed in Serventi et al. (2013; 2015), to investigate the effects of very fine sizes on the reflectance spectroscopy of lunar-like mineralogies. 80

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82 **2.** Background

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### 2.1 PL and PL-bearing mixtures

84 Only in the last decade, PL and PL-bearing mixtures have been studied in detail, since the

85 improvements in terms of spectral resolution of the spectrometers onboard the lunar missions permitted

to clearly recognize the PL absorption band at ca. 1250 nm due to  $Fe^{2+}$  transition in its crystal structure

87 (Adams and Goulland, 1978; Burns, 1993).

88 Cheek et al. (2011) demonstrated how in a set of synthetic  $An_{85}$  PL with different iron content, the

89 1250 nm band deepens with increasing the iron content, till a maximum value (ca. 0.4 wt.% FeO) after

90 which band depth remains quite constant.

91 Serventi et al. (2013; 2015) showed that PL could be easily recognized in mixtures with pyroxenes

92 (PX) for modal abundance higher than 70%, while in mixtures with OL it can be masked due to the

- narrow spectral range in which both OL and PL absorb creating a complex, composite (COMP)
- absorption. Moreover, spectral parameters, Gaussian modeling and Hapke modeling show how PL can
- spectrally influence the absorption of mafic minerals (Serventi et al., 2013; 2015; Carli et al., 2014a).

Cheek and Pieters (2014) analyzed PL-rich mixtures with varying content and composition of OL, PX 96 and very high-Mg spinels and demonstrated that PL can significantly contribute to reflectance spectra if 97 strongly absorbing minerals are present in low abundances, particularly in mixtures with PX. 98 99 Serventi et al. (2016) concluded that, in PL-dominated mixtures: 1) PL can be an important contributor to reflectance spectroscopy also affecting mafic mineral absorption bands (as also demonstrated by 100 Cheek and Pieters, 2014); 2) PL absorbs in the 1250 nm spectral region but iron-rich PL also affects the 101 longest wavelengths (1600-1800 nm), as also suggested by Pieters (1986) and Hiroi et al. (2012); and 102 103 3) PX are easily recognizable in mixtures with PL even for very low PX concentration (~1%), while 104 OL, if less than 5%, can be masked by iron-rich PL.

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### 2.2 Particle size

Generally, varying the particle size affects albedo, reflectance and spectral contrast; in particular,
decreasing the particle size the albedo increases while the spectral contrast, intended as the strength of
the absorptions, is reduced due to the decrease in the mean optical path length of reflected light
(Adams, 1968; Pieters, 1983). On the other hand, band centers and band widths are almost unaffected
by different particle size (Nash and Conel, 1974), or with shifts that fall in the spectral resolution of the
instruments (Serventi et al., 2013).

113 Crown and Pieters (1987) evaluated the reflectance spectra of mixtures composed with different modal 114 abundance of labradorite (An<sub>80</sub> PL) and enstatite (Mg-OPX) at different particle size. The authors 115 showed that in the spectra of both end-members and mixtures the reflectance increases while the 116 spectral contrast decreases with reducing the size. In addition, they pointed out how the amount of PL 117 detectable in mixtures with mafic minerals is particle size dependable: more PL is required in finer 118 mixtures. Mustard and Hays (1997) investigated the effects of fine particles that are approximately the same size
as the wavelength of light on reflectance spectra of OL and quartz (in the 0.3-25 μm spectral range). In
particular, spectra exhibit a drop in reflectance with the finest sizes. Looking at their Fig. 4, in the 3002500 nm range, OL albedo increases with fining the size, while the spectral contrast is reduced.

Furthermore, the slope in the NIR is less red with decreasing the size. On the contrary, looking at their Fig. 5, quartz's albedo does not change linearly with the particle size; however, the broad absorption at ca. 1000-3000 nm disappears at very fine sizes.

126 Furthermore, the transparency features show several important changes with decreasing particle size:

the spectral contrast increases then decreases, the position of the maximum reflectance of the

transparency features shifts systematically to shorter wavelengths, and the symmetry of the features

129 changes.

130 Cooper and Mustard (1999), analyzing martian analog minerals (e.g., montmorillonite and palagonite), 131 concluded that extremely fine particle sizes generate significant decreases in band strength. In 132 particular, the  $< 5 \mu m$  fractions show vibrational absorption bands that were half the strength of the 133 absorptions from the coarser size fractions. They also concluded that this reduction is due to changes in 134 the ratio of scattering to absorption with particle size, with important implications for the spectroscopic 135 determination of the composition of the extremely fine martian dust.

Craig et al. (2007) evidenced how, increasing particle size, the overall reflectance of OL, OPX and
basalts decreases, while the bands deepen to reach a maximum between 45 and 250 µm to then
decrease. Coarsening the particle size can also produce band saturation effects that complicates the

determination of the absorption band center.

140 Serventi et al. (2013; 2015; 2016) showed how different particle sizes (125-250 μm; 63-125 μm; 36-63

141 μm) of PX, OL and PL spectra does not affect the band center (shifts of few nanometers fall in the

instrumental resolution) but only the band depth, that decreases decreasing the particle size.

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# 3. Experimental procedure: sample preparation and analytical methods

### **3.1 End-member preparation and characteristics**

Separate end-member minerals were obtained from samples belonging to the Stillwater Complex layered intrusion. The samples were accurately investigated under thin section to evidence the rock mineral association and to reduce as much as possible altered samples (Carli et al., 2009). Among the different samples, we selected an anorthosite, a gabbronorite and an ultramafic rock (for the composition refer to Tab. 1). The chemistry of the rock-forming minerals was determined by electron microprobe analyses with a CAMECA SX50 (EMP) at the microprobe laboratory of C.N.R.-IGG

152 (Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse), Padova.

The selected rock samples were first crushed to a coarse size class <2.00 mm, in order to preserve the 153 original rock composition in powdered samples. The powders were then quartered and each fraction 154 was ground to smaller size classes. In particular, we have considered two particle-sizes, <250 µm and 155 156 <125 µm. Each powder particle-size class was then quartered again and half material was then sieved 157 into two size ranges: 63-125 µm and 125-250 µm. The size fractions have been produced by dry sieving; we decided not to perform wet sieving to avoid: 1) possible alteration or contamination; 2) 158 leaching which can settle the size distribution of our samples, differently from what expected in 159 160 atmospherless planetary conditions.

From these samples, two PLs with different iron content and two different mafic, multimineralic compositions were separated using a Frantz Isodynamic Magnetic Separator at the Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma. In Tab. 1, the applied amperage, removed minerals and new samples obtained after magnetic separation are shown. The purity of the end-members has been determined by optical means (X-ray diffraction has been rejected since it is not accurate for phase abundance less than 5%).

The selected PL phases include a medium-iron (PL2) and an iron-rich (PL3) PL (both An<sub>80</sub>, with 0.36
and 0.5 wt. % FeO, respectively), while the Fe, Mg (mafic) compositions consist of two distinct
mineral assemblages, one PX-bearing (E1), and one OL-rich and PX-poor (E3). The Fe, Mg phases
were also analyzed by Mössbauer spectroscopy in order to have a better comprehension of the iron
oxidation state (for further details, please refer to Serventi et al., 2013). Fitting of Mössbauer results
showed the absence of additional phases.

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- **3.2 Mixture preparation**

Mixtures of Fe, Mg (E1, E3) and PL (PL2, PL3) end-members were prepared at two different particle
sizes (63-125 and 125-250 µm). For each particle size, contents ranging between 20-90 wt. % of each
PL end-member was added to each Fe, Mg end-member.

178 For each of the resulting mixtures, we calculated the vol. FeO% due to PL phase with respect to the

179 mixture. The volumetric FeO% is calculated as the FeO wt. % content in PL multiplied by modal PL

180 (%) in each mixture. All the results presented in this work are plotted vs. the vol. FeO in PL.

181 Starting from the 63-125  $\mu$ m mixtures and end-members, very fine sizes (<10  $\mu$ m) were produced

using a micronizer at the Department of Geosciences, Padova. Each powder, with the addition of water

to prevent the heating of the sample, was micronized for 5 minutes; the very fine powder plus water

184 was mixed with ethanol and kept in stove for ca. 2 weeks, until all the water, and ethanol, evaporated.

185 Then, the very fine powders were weighed to check that no loss of material happened during the

186 mechanical grinding.

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### **3.3 Spectral measurements**

Bidirectional reflectance spectra of each mixture were acquired at room temperature and normal
 atmospheric pressure with a Field-Pro Spectrometer <sup>®</sup> mounted on a goniometer (Istituto di Astrofisica

e Planetologia Spaziali, Inaf-IAPS, Roma). The spectra were acquired with a spectral resolution of ~3
nm in the VIS and of ~10-12 nm in the NIR and spectral sampling of 1 nm, with *i=30°* and *e=0°*. The
source used was a QTH (Quartz Tungsten Halogen) lamp and the spot illuminated has an area of ca.
0.5cm<sup>2</sup>. The calibration of the spectrometer was performed with Spectralon<sup>®</sup> optical standard
(registered trademark of Labsphere, Inc.).
Ten spectra were acquired for each powder, emptying and refilling the cup each time, and then only the
mean spectrum was considered for subsequent analyses. In order to avoid problems due to a pressed

surface with a "slab-like behavior" or to coarser powder roughness due to the aggregation of such fineparticles, powders were gently shaken and pressed in the sample holder.

Fig. 1 shows the end-member spectra; mixture spectra are plotted in Fig. 2 and 3, while the continuumremoved spectra of end-members and mixtures are reported in Fig. 4. As a comparison, reflectance
spectra of coarser sizes (63-125 µm and 125-250 µm) are shown in Fig. 2,3.

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#### **3.4 MGM deconvolution**

Each spectrum was analyzed applying the Modified Gaussian Model (MGM) algorithm (Sunshine et al., 1990). Briefly, we considered a fixed continuum tangent to the spectrum reflectance maxima as more reliable in the description of the spectrum shape and for modeling the strength of the absorption bands (approach already followed in Clenet et al., 2011 and Serventi et al., 2015).

209 We first deconvolved the end-members, mafic and PL, as mineralogically unknown end-members,

assigning Gaussians only where either an absorption band or a band asymmetry are visually perceptible
(e.g., 900 nm band in E1 is asymmetric towards the Near Infrared, NIR, region). Then, we deconvolved
the mixtures:

215	1) fixing band center and band width assigned to the mafic end-member absorption bands, with the
214	exception of 1800-2000 nm absoprtion band width that become visually narrower with
215	increasing PL;
216	2) leaving free the mafic band depth, which depends on mineral abundance in a mixture (e.g.
217	Sunshine and Pieters, 1993; Serventi et al., 2015), and Gaussian parameters assigned to the
218	1250 nm absorption band (for further details, interested readers are referred to Serventi et al.,
219	2015).
220	A visual check of the residuals after the fitting, evidenced a pattern in the 700-1100 nm spectral range
221	of the E1-bearing mixtures not detected at coarser sizes. For this reason, starting from values obtained
222	from the fit with the procedure described above, we recomputed MGM leaving free the mafic
223	parameters (see Section 4.3).
224	A number was assigned to each Gaussian, as described in Tab.2.
225	
226	4. Results
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wavelength infrared region (SWIR) with respect to the coarsest size, and (5) E3 (Fig. 1d) shows the
appearance of an evident absorption at 2000 nm.

Both E1 and E3 indicate more influencing OPX reflectance properties with respect to other mafic

239 phases such as OL, CPX. However, the rock sample from which E3 was magnetically separated

contains 2% of chromite. Even if the residual chromite in our sample after separation is very low

241 (<<0.5%), chromite is characterized by a deep absorption at ca. 2000 (e.g. Cloutis et al., 2004), and,

thus, we cannot completely rule out chromite as a contributor to the 2000 nm absorption.

243 PL end-members were magnetically separated from rocks containing PX. The separated PL was

investigated by optical microscope analysis with no detection of residual PX, but we have to consider

that PX inclusions could still be present. For this reason, the 900 nm band showed by PL spectra in Fig.

1a could be indicative of residual PX. Furthermore, Fig. 1b reveals how a fine size emphasizes the

effects of residual PX; the 900 nm band due to  $Fe^{2+}$  in PX becomes more absorbing with decreasing the size (see also the continuum-removed spectrum in Fig. 4b).

Fig. 2, 3 show that a fine particle size (Fig. 2a, b and Fig. 3a, b) increases the reflectance and reduces the spectral contrast compared to the coarsest sizes (Fig. 2c-f and Fig. 3c-f).

251 Considering the 63-125 and 125-250 µm sizes (Fig. 2c-f, 3c-f), a higher PL modal abundance results in

a systematic increase of the reflectance, whereas in the  $<10 \mu m$  size some spectra deviate from this

behavior, such as the 70%PL3-E3 and the PL end-members (see Fig. 2a,b, 3a,b). As explained in

254 Section 3., working with such fine sizes means to deal with problems due to too much pressed surfaces

or to a powder roughness. For this reason, spectra acquired on the same sample have variable

reflectance values, with the mean spectrum showing a standard deviation up to ca. 6% that can explain

the reflectance non-linear behavior with increasing PL modal abundance.

258 PL in very fine E1-bearing mixtures results in a weaker absorption band with respect to the coarse sizes

and is revealed by a flattening in the 1200 nm spectral region for 80% PL-mixture (Fig. 4a,b). A weak

absorption band can be recognize only for more than 90% PL (light-grey spectra in Fig. 4a,b), butalways shallower than PX absorption bands.

262 Serventi et al. (2013) demonstrated how the spectral parameters describing the COMP band, due to the

simultaneous absorptions of OL and PL, give information on the relative minerals' modal abundance.

In particular, considering coarse E3-bearing mixtures, the COMP band center shifts from typical OL

values (1050 nm) to PL values (1250 nm) for PL content >70% (see their Fig.13b). However,

266 investigating the  $< 10 \,\mu\text{m}$  size, the center shifting is not detectable (Fig. 4c,d); this is consistent with 267 the featureless nature of PL.

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- 269

## 4.2 End-member deconvolution

End-members were deconvolved via MGM (see Fig. 5a, 6a; to show the goodness of the fit, RMS is
plotted). E1 residual (Fig. 5a, h) shows a sinusoidal pattern in the 700-1100 nm; comparing our
residuals with those from Klima et al. (2008), which showed the same pattern and the same RMS as
ours, we decided not to add additional Gaussians.

A comparison with the deconvolution of coarser sizes (see Tab. 3) demonstrates how the 900-1000 nm absorptions are fitted with the same number of Gaussians, with the only exception of E1, where an

adjustment Gaussian (G5) centered at ca. 840 nm is not here introduced (in accordance with Klima et

al., 2007). Despite end-member residual seems to indicate a sinusoidal pattern, covariance matrix does

not allow to add more Gaussians. Moreover, a similar residual pattern is present also in Klima et al.

(2007) and Klima et al. (2011). On the contrary, G5 is required for coarser size as discussed in Serventi

et al. (2015; 2016) and in accordance with Sunshine and Pieters (1993).

281 To summarize, Tab. 3 shows how reducing the particle size (i.e., from 250 to  $10 \mu m$ ) of E1:

282 1) As aforementioned, G5 is not needed;

283	2) Bands are shallower, above all G1 and G3, and the Gaussians describing the different
284	absorption bands are very similar in terms of band depth, thus reflecting the general spectral
285	contrast;
286	3) G1 and G2 centers shift towards shorter wavelengths (more than 40 nm);
287	4) The 1850 nm absorption is fitted with only one Gaussian (G3); and
288	5) Band widths do not show significant changes.
289	Considering E3, a reduced size produces shallower bands, and a narrower G8 with respect to coarse
290	ones; G6-G8 centers shift towards longer wavelengths, but with reduced shifts compared to E1.
291	G7 is the deepest one and this is not consistent with the results by Sunshine and Pieters (1998), where
292	G8 is the deepest. However, Buz and Ehlmann (2014) demonstrated how extreme size values may
293	affect the OL spectral parameters that, consequently, deviate from the trend found by Sunshine and
294	Pieters (1998). The authors showed how at very fine sizes (<45 $\mu$ m) G7 is the deepest Gaussian, also in
295	accordance with results from Burns (1993). However, considering E3 (Fig. 6a), G6 is slightly deeper
296	than the results by Buz and Ehlmann (2014), but here we are dealing with even finer sizes.
297	Furthermore, the OPX component may influence G6 depth.
298	The longest wavelengths of E3 are deconvolved with a Gaussian at 1963 nm that can be tentatively
299	assigned either to PX or to chromite (Fig. 6a; Tab. 3).
300	Tab. 4 reports the PL end-member spectral parameters after MGM deconvolution for the different
301	particle sizes. MGM fits are also shown in Fig. 5g,n. In particular, reducing the size, the 1250 nm
302	absorption can still be considered, even if for the finest size the band depth is close to zero. The band
303	center shifts towards longer wavelengths both for PL2 and PL3, even if with shifts less than 10 nm.
304	Tab. 4 shows how a coarse PL2 is deeper than the iron-richer PL3 (also refer to Serventi et al., 2015;
305	2016); however, the <10 $\mu$ m PL3 is deeper than PL2. This can be related to the residual PX in PL2
306	(after magnetic separation is estimated to be less than 1%) that at very fine sizes becomes spectrally

important, thus influencing and reducing the PL band depth. Furthermore, the residual PX produces a 900 nm absorption band that is only slightly less deep than the PL absorption band (0.015 vs. 0.026 -LnRefl, also see Fig. 3a). The 900 nm band depth in PL3, not detectable at the coarser sizes, represents the 30% of the <10  $\mu$ m PL band depth (see Tab. 4), a further demonstration of the featureless behavior of fine PL.

G11, that in literature (e.g., Pieters, 1996; Hiroi, 2012; Serventi et al., 2015; 2016) was tentatively attributed to PL, at the <10  $\mu$ m size is shallower, shifted towards longer wavelengths (1940-1950 nm) and narrower with respect to the coarse sizes. Consequently, in this case, G11 probably adjusts the vibrational processes related to the OH<sup>-</sup> alterations of the natural PL here considered.

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### 317 **4.3 Mixture deconvolution**

Mixtures were deconvolved following the procedure described in Section 3. Fitting results, as well as
RMS, are shown in Fig. 5, 6.

PL band slightly deepens in E1 mixtures (triangles in Fig. 7a), while COMP band decreases in E3
mixtures (stars in Fig. 7a). In Fig. 7b, PL and COMP band center shifts towards longer wavelengths
with increasing the vol. FeO% in PL. Both PL (triangles in Fig. 7c) and COMP (stars in Fig. 7c) band
widen with increasing vol. FeO% values in mixtures.

Fig. 8a,b show that increasing the vol. FeO% in PL, the Gaussians describing the mafic absorptions

become shallower. Fig. 8a displays in detail the behavior described in Section 4.1, with mafic

absorption bands deeper in 60%PL2-E1 and in 80%PL2-E1 than in 50%PL2-E1 and 70% Pl2-E1,

respectively. However, we report the error bar for band depth, calculated in the 95% confidence

interval, and it is clear how 50%PL2-E1 has a much larger error bar than 60%PL2-E1 (±0.05LnRefl

with respect to  $\pm 0.015$  LnRefl). Fig. 7b shows how the depth of Gaussians describing the mafic

absorptions in E3-bearing mixtures decreases more linearly than E1-mixtures.

As stated in Section 3.4, the mafic parameters, with the exception of the depth, has been kept fixed in 331 the first iteration. Basing on the residuals, we decided to leave free those parameters. Their variations 332 have been reported in Fig. 8b, c and in Fig. 8e, for E1 and E3-bearing mixtures, respectively. Fig. 8b 333 shows that G1 and G2 move towards longer wavelengths with increasing PL modal abundances; 334 however, G1 variations for <90% PL and G2 variations for <80% PL are less 10 nm, respectively, and, 335 so within the instrumental spectral resolution. On the contrary, G1 and G2 shift towards longer 336 wavelengths of 12 nm (90% PL), and of 20 nm (80% PL) and 40 nm (90% PL), respectively. These 337 338 values, in particular for G2, cannot be justified by the spectral resolution but must be related to the 339 presence of PL which is not only accommodate by G10 and G11. Fig. 8c reports how G3 becomes narrower with increasing PL modal abundances, while G2 varies slightly only for PL more than 80%. 340 341 G3 variations can be related to PL.

Regarding E3-bearing mixtures (see Fig. 8e), only G3 width varies: G3 becomes narrower with increasing the PL content (with no differences between PL2 and PL3-bearing mixtures, as the values lay on the bisector line), with substantial variations for mixture with more than 70% PL.

Fig. 9 shows a comparison for the spectral parameters after MGM deconvolution for the three different particle sizes:  $<10 \ \mu\text{m}$  (pink and violet symbols, for PL2 and PL3-bearing mixtures, respectively), 63-125  $\mu$ m (light-blue and blue symbols for PL2 and PL3-bearing mixtures, respectively) and 125-250  $\mu$ m (yellow and red symbols for PL2 and PL3-bearing mixtures, respectively). As already stated in section 2.3, the principal difference regards the band depth; Fig. 9a,d evidence how PL and COMP band are shallower compared to coarser sizes , with depth close to zero. In addition, the band width in the fine particle size is strongly reduced (Fig. 9c,f), particularly in E3-bearing mixtures.

352

353 **5. Discussions** 

In this paper we investigated the effects of a very fine particle size on the reflectance spectroscopy of
 PL, mafic end-members and PL-bearing mixtures.

As already stated by Adams (1968) and Pieters (1983), a fine particle size increases the reflectance and
decreases the spectral contrast. Mustard and Hayes (1997) also evidenced how, fining the size, OL
becomes brighter but shallower, and bluer in the NIR (see their Fig. 4A).

In this work, we also showed how the spectra of very fine PL become featureless, with a bluer slope

than a coarse PL in the IR, and how the difference in reflectance between mixtures and end-members is

reduced. Consequently, the general reflectance's increase with increasing the PL abundance

documented at coarser sizes, may not be always respected. This behavior, as well as the bluer slope towards the IR, similar to what happens in bulk surfaces of rocks spectra (as also postulated by Harloff and Arnold, 2001, Pompilio et al., 2007; Carli, 2009), clearly demonstrates how a very fine size could complicate the interpretation of a reflectance spectrum (e.g., slope similar for very fine size and slab of rocks), as well as the evaluation of the minerals' modal abundance.

367 Cheek and Pieters (2014) and Serventi et al. (2015, 2016) demonstrated how, considering PL-

dominated mixtures (PL>70/80%), Fe<sup>2+</sup>-bearing PL can significantly contribute to reflectance spectra, 368 also affecting mafic mineral absorption bands. In fact, in PX-bearing mixtures PL absorption band is 369 even deeper than PX bands for very high PL content, while, in OL-bearing mixtures, the COMP band 370 position shifts towards the typical PL center values (1250-1300 nm) for high PL content. All these 371 372 effects are stronger in the 125-250 µm size than in 63-125 µm one, thus supporting that a coarse PL is spectroscopically more active than a fine one. On the contrary, this work evidences the unpredictable 373 effects of a very fine size on reflectance spectroscopy. For example, the band depth of a very fine PL is 374 very shallow, with a Gaussian depth almost close to zero, and the COMP band center always shows the 375 typical OL values, even for PL>90%. This testifies how a reduced size can mask the contribution of PL 376

on reflectance spectra, with a consequent and possible PL underestimation, that, obviously, leads to
mistakes in the interpretation of reflectance spectra from a Solar System body's surface.

Furthermore, we suppose that the 1800 nm absorption detected at coarse sizes may be not effective at such fine size. In the very fine PL considered in this work, G11 is narrower and shifted towards longer wavelengths (1940-1950 nm) with respect to the coarse sizes and, therefore, probably related to the OH<sup>-</sup> alteration of the terrestrial PL.

383 Here, we introduce an index called Band Depth Ratio (B.D.R.) calculated as follow:

384 
$$B.D.R.(E1) = \frac{B.D.G10}{B.D.G10 + B.D.G1 + B.D.G2}$$
 [1]

385 
$$B.D.R.(E3) = \frac{B.D.G9}{B.D.G9 + B.D.G6 + B.D.G7}$$
 [2]

Where B.D. is the band depth of each Gaussian. This index returns the relative intensity of PL andCOMP bands with respect to all the Gaussians describing the 1000 nm absorption.

We calculated B.D.R. (E1, E3) for <10, and 63-125 and  $125-250 \mu m$  (Serventi et al., 2015) sizes.

389 Results are plotted vs. the 63-125 µm size (Fig. 10); the bisector indicates the ideal conditions that the 390 relative depths do not change with the size. However, symbols do not lay on the bisector: 125-250 µm values (blue symbols) stay in general slightly above the line, while <10 µm values (magenta symbols) 391 are under the line. This demonstrates that, considering the 63-125 µm size as a reference, coarse PL can 392 be slightly overestimated, and very fine PL could be easily underestimated. Moreover, increasing the 393 394 PL abundance generally increases also the difference between B.D.R. for <10 µm and for 63-125 µm. The spectral properties of mafic end-members are affected by very fine sizes too. Regarding E1, the 395 900 nm absorption band is more V-shaped, asymmetric towards the NIR with respect to the coarse 396 sizes and shifted towards shorter wavelengths, thus simulating different mineral content and/or 397 different mineral chemistry (shorter wavelengths correspond to Mg-richer and Ca-poorer PX). The very 398

fine E1 deconvolution does not require G5, on the contrary needed for coarser sizes (see also Pieters et
al., 1993; Serventi et al., 2013).

401 On the other hand, the fine E3 end-member shows two main differences if compared to coarser sizes.

402 The G6-G8 relative depths are not consistent with the trend proposed by Sunshine et al. (1998),

403 confirming the unpredictable effects of very fine sizes; in fact, Buz and Ehlmann (2014) demonstrated
404 how extreme sizes affect the spectral parameters of OL. Furthermore, the fine E3 longest wavelengths

show an absorption not detected at coarser sizes. Since E3 is characterized by 70% of OL and 30% of

406 OPX, it seems plausible that at very fine size the presence of OPX, not detectable at coarser sizes,

407 could become an important spectroscopic contributor.

The spectral properties seen in E1 (band center shifting) together with the behavior seen for E3 in the longest wavelengths, seem to evidence how OPX spectrally dominates at such fine size with respect to other, mafic phases, which present a lower amount of total iron. However, E3 band can be related to residual chromite after magnetic separation.

412 Comparing 63-125 µm and 125-250 µm sizes, Gaussians shift less than 10 nm. The FieldSpec spectral 413 resolution varies between 2 and 12 nm: thus, the band center shifting falls in the instrumental resolution. On the contrary, mafic band centers for <10 µm powders are shifted of ca. 40 nm with 414 respect to the coarser sizes; this is because we are dealing with sizes that are approximately the same 415 size as the wavelength of light and this could lead to unexpected behaviors of the spectral parameters. 416 417 Fig. 11 reports spectra of lunar soils (from the Lunar Soil Characterization Consortium, Pieters et al., 1993; 2000) at three different fine to very fine particle sizes (20-45µm blue spectra, 10-20µm red 418 spectra and  $<10\mu$ m black spectra) acquired from the Apollo missions 14 and 16. In particular, samples 419 #67481 and #67461 are more enriched in PL than samples #14141 and #62231. Generally, reducing the 420 size the reflectance increases. As expected, absorption bands are shallower and, in particular, the 1250 421 nm weak band becomes almost featureless in  $<10 \,\mu m$  spectra. Furthermore, Fig.11 emphasizes the 422

behavior of the  $<10 \ \mu m$  fractions: spectral contrast is extremely reduced if compared to the 10-20  $\mu m$ size. Anyway, we have to take into account that spectra of lunar samples are affected by the presence of npFe° due to the space weathering, which implies a red slope and lower albedo than expected for PLrich fine powders. Nevertheless, the spectra from lunar soils are in accordance with a relative increase in albedo and a strong reduction in absorptions reducing the size and an almost featureless spectrum for  $<10 \ \mu m$  size, loosing information about PL absorption.

Generally, the main feature that discriminates the very fine size is the high albedo, correlated with the decreasing absorption intensity. However, due to the space weathering, this feature may not be so easily recognized on lunar spectra. The low spectral contrast could be evidence of very fine size as well; however, a fine size is not the only reason to explain reduce contrasts (e.g., space weathering, shock effects).

434

# 435 6. Conclusion and implications for the Moon

The Moon regolith, generally <1 cm in size, comprises the lunar soil, which represents the finest fraction of the regolith and derives from mechanical disintegration of lunar rocks, both basaltic and anorthositic, and is generally between 60 and 80  $\mu$ m. Very fine sizes (<10  $\mu$ m) were recognized and thought to represent the 5-20% of the lunar regolith; PL is the dominant phase of this fine regolith (Laul et al., 1978; 1979; 1980).

In this work, we demonstrated how a very reduce size implies a higher albedo and a decrease in the spectral contrast, particularly for the PL spectra that become almost featureless. On the other hand, we showed how the iron-richest mineral in the considered mixtures, OPX, seems to spectrally dominate other mafic and cogenetic minerals, CPX and OL, at the very fine size (e.g., the 900 nm band shift towards shorter wavelengths in E1 and the 2000 nm reflectance decrease in E3). This has important implications for the lunar regolith, where PL is abundant. For example, the presence of PL spectra with a well-defined and deep 1250 nm absorption gives indications not only on the crystallinity of the mineral but also on the particulate size that cannot be too fine in the areas were PL absorption is detected. On the other hand, featureless PL spectra can lead to an erroneous interpretation of the PL abundance, and/or chemistry that can be underestimated. These results evidence that more detailed investigations on such fine sizes should be pursued to better understand how to retrieve composition by modeling remote sensing data.

453

# 454 Acknowledgment

Spectroscopic measurements were carried out at Inaf-IAPS-Istituto Nazionale di Astrofisica, Roma.
EMPA analyses and powder micronization have been performed at Dipartimento di Geoscienze,
Padova. The authors are grateful to prof. Maria Sgavetti for her thoughtful review that greatly
improved the quality of the manuscript. The authors are also grateful to two anonymous reviewer for
their stimulating comments and suggestions.

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546		
547		
548	Figure	captions
549	1)	End-member reflectance spectra at three different particles sizes, 125-250 $\mu$ m (black), 63-125
550		$\mu$ m (dark gray) and <10 $\mu$ m (light gray). Generally, reducing the particle sizes the albedo
551		increases and the spectral contrast is reduced. a,b) Very fine PL are characterized by featureless
552		spectra with a blue slope; c) very fine E1 shows a 900 nm band shifted towards shorter
553		wavelengths and more asymmetric towards the NIR with respect to the coarse sizes; and d) the
554		fine E3 complex 1050 nm band is characterized by three multiple absorptions, but the
555		absorption centered at ca. 1250 nm seems shallower with respect to the coarse sizes and is
556		evident the appearance of an absorption at 2000 nm.
557		
558	2)	Reflectance spectra of E1-PL mixtures at three different particle sizes. a,b) E1+PL2 and
559		E1+PL3, <10 µm; c,d) E1+PL2 and E1+PL3, 63-125 µm; and e,f) E1+PL2 and E1+PL3, 125-
560		250 $\mu$ m. Generally, a fine particle size produces spectra with higher reflectance and reduced
561		spectral contrast compared to the coarsest sizes.

563	3)	Reflectance spectra of E3-PL mixtures at three different particle sizes. a,b) E3+PL2 and
564		E3+PL3, <10 µm; c,d) E3+PL2 and E3+PL3, 63-125 µm; and e,f) E3+PL2 and E3+PL3, 125-
565		$250 \ \mu\text{m}$ . Generally, a fine particle size produces spectra with higher reflectance and reduced
566		spectral contrast compared to the coarsest sizes.
567		
568	4)	End-member and mixture continuum-removed reflectance spectra. Generally, increasing the PL
569		content in mixtures, the mafic absorptions are reduced, while the PL band behavior depends on
570		the mafic end-member. a,b) E1-PL2 and E1-Pl3 mixtures, respectively. PL produces an
571		absorption bands only for very high PL content, more than 80%; c,d) E3-PL2 and E3-Pl3,
572		respectively. The COMP band center shifts from typical OL (1050 nm) values to PL (1250 nm)
573		values is not detectable/noticeable.
574		
575	5)	MGM deconvolution and residuals (expressed in terms of Root Mean Square, RMS) of E1-
576		bearing mixtures. RMS values are consistent with Klima et al. (2011). a-g) E1-PL2 mixtures; h-
577		n) E1-PL3 mixtures. Continuum-removed reflectance is expressed as -LnRefl.
578		
579	6)	MGM deconvolution and residuals (expressed in terms of Root Mean Square, RMS) of E3-
580		bearing mixtures. RMS values are consistent with Klima et al. (2011). a-g) E1-PL2 mixtures; h-
581		n) E1-PL3 mixtures. Continuum-removed reflectance is expressed as -LnRefl.
582		
583	7)	The figure shows the spectral parameter variations in mixtures composed with E1/E3 and PL2,3
584		after MGM deconvolution. In particular, with increasing the volumetric FeO% in PL: a) PL
585		band deepens (triangles), while the COMP band depth decreases (stars); b) PL band center

587

(triangles) and COMP band center (stars) shift towards longer wavelengths (triangles); and c) both PL (triangles) and COMP band (stars) widen.

588

8) The figure shows the spectral parameter variations in mixtures composed with E1/E3 and PL2,3 589 after MGM deconvolution. In particular, with increasing the volumetric FeO% in PL: a,d) the 590 mafic band depth decreases both in E1 and in E3-bearing mixtures. Fig. 8a also shows the 591 vertical error bars for the 50-80% PL2-E1 mixtures; b) G1 and G2 move towards longer 592 593 wavelengths with increasing PL modal abundances. G1 variations and G2 variations for <80% 594 PL are less than 10 nm and, so, explainable by the instrument spectral resolution; G2 shifts for 80% and 90% PL can be related to the presence of PL; c) G3 become narrower with increasing 595 PL modal abundances, while G2 varies only slightly; only G2 variations for more than 70% 596 PL2 can be related to PL, while other variations are, again, explainable with the instrument 597 spectral resolution; and e) G3 becomes narrower with increasing the PL content (with no 598 differences between PL2 and PL3-bearing mixtures, as the values lay on the bisector line), but 599 variations are substantial only for more than 80% PL. 600

601

9) The figure shows a comparison for the spectral parameters after MGM deconvolution for the 602 three different particle sizes: <10 µm (violet symbols), 63-125 µm (pink symbols) and 125-250 603 604 μm (fuchsia symbols). a,d) PL (in E1-bearing mixtures) and COMP (in E3-bearing mixtures) band depths are very reduced compared to the coarse sizes and close to zero; b,e) the PL band 605 center does not show great variations in E1-bearing mixtures, while in E3-PL2 mixtures the 606 COMP band center is shifted towards longer wavelengths. On the contrary, is shifted towards 607 shorter wavelength in E3-PL3 mixtures; and c,f) the band width in the fine particle size is 608 strongly reduced, particularly in the E3-bearing mixtures. 609

611	10) Band Depth Ratio (B.D.R.) for the 125-250 $\mu m$ and <10 $\mu m$ sizes vs. the 63-125 $\mu m$ size. a)
612	E1-bearing mixtures; b) E3-bearing mixtures. The bisector indicates the ideal conditions that
613	the relative depths do not change with the size; however, 125-250 $\mu$ m values (blue symbols)
614	stay above the line, while $\leq 10 \ \mu m$ values (magenta symbols) are under the line.
615	
616	11) Spectra of lunar soils (from the Lunar Soil Characterization Consortium, from Pieters et al.,
617	1993; 2000) at three different, very fine particle sizes (20-45 $\mu$ m blue spectra, 10-20 $\mu$ m red
618	spectra and $<10\mu$ m black spectra). Samples #67481 and #67461 are more enriched in PL than
619	samples #14141 and #62231.Generally, reducing the size the reflectance increases, absorption
620	bands are shallower and, in particular, the 1250 nm band becomes almost featureless in ${<}10~\mu\text{m}$
621	spectra.
622	
623	
624	
625	























Lithology			Mineral <i>∤</i>	Abundanc	9		Amp.	Minerals removed	New samples	Chemistry	FeO wt.%
	0PX %	CPX %	% TO	% Td	Op %	FeO wt. %					
Ultramafic rock	47	ı	19.7	5.1	28.3	FeO wt. %	0.3 1.4	0p PL	CPX+OPX+OL(E3)	OPX(28.2%) En <sub>82</sub> -Wo <sub>4</sub> CPX(3.4%) En <sub>45</sub> -Wo <sub>46</sub> OL(68.4%) Fo <sub>84</sub>	9.03 3.8 14.65
Anorthosite	0.8	4.3	ı	94.2		FeO wt. %	1.4	CPX+OPX+Zois.	PL(PL3)	$PL3 An_{80}$	0.36
Gabbronorite	22.1	17.3	·	9.09		FeO wt. %	1.4	None	CPX+OPX(E1) PL(PL2)	CPX(43.9%) En <sub>45</sub> -Wo <sub>46</sub> PL2 An <sub>80</sub> OPX(56.1%) En <sub>77</sub> -Wo <sub>2</sub>	5.72 0.5 13.45

Tab. 1 Mineral abundances in the starting samples. OPX=orthopyroxene; CPX=clinopyroxene; OL=olivine; PL=plagioclase; Op=opaque minerals; Zois=zoisite. Table also shows the applied amperage (Amp.), the minerals removed and the final samples obtained with the Frantz Isodynamic Magnetic Separator. Chemistry and iron abundance of the new samples are also reported.

Gaussian	Position (nm)	Interpretation
G1	900-950	Fe <sup>2+</sup> in OPX M2 site
G2	1000-1100	Fe <sup>2+</sup> in CPX M2 site
G3	1850-2000	Fe <sup>2+</sup> in OPX M2 site/ chromite
G4	2200-2300	Fe <sup>2+</sup> in CPX M2 site/ Al-OH alterations
G5	840	Adjustment Gaussian
G6	850-950	Fe <sup>2+</sup> in OL M1 site
G7	1000-1100	Fe <sup>2+</sup> in OL M2 site
G8	1200-1250	$Fe^{2+}$ in OL M1 site
G9	1200-1300	COMP band ( $Fe^{2+}$ in OL M1 site+ $Fe^{2+}$ in PL)
G10	1250-1300	Fe <sup>2+</sup> in PL
G11	1600-1800	PL asymmetry/PL alteration

Tab. 2 In the table are reported a list of Gaussians used in the end-member deconvolution, the wavelength position and the mineralogical interpretation.

		RMS						0.06			RMS					0.005		
		Depth		-0.252	-0.217	-0.194	-0.025				Depth	-0.063	-0.139	-0.08	-0.080			
	<10 µm	Width		154	220	509	138			<10 µm	Width	163	241	296	442			
		Center		$903 \pm 10$	$988 \pm 10$	$1894{\pm}10$	2321±40				Center	$881{\pm}10$	$1036\pm 8$	$1262\pm10$	1963±2			
		RMS						0.020			RMS					0.003		
		Depth	-0.370	-0.895	-0.371	-0.631	-0.586			-	Depth	-0.483	-0.722	-0.789				
ΕI	25-250 μm	Width	113	180	191	489	678		E3	125-250 µn	Width	193	218	408				
		Center	837±6	949±30	$1058 \pm 30$	1813±15	2202±50				Center	842±2	$1009\pm 2$	1221±2				
		RMS						0.018			RMS					0.005		
					Depth	-0.400	-0.929	-0.535	-0.766	-0.431				Depth	-0.464	-0.562	-0.655	
	63-125 μm	Width	110	159	199	496	730			63-125 µm	Width	210	204	400				
	-	Center	843±9	934±9	$1028\pm 20$	1851±11	2311±50				Center	861±7	$1028\pm 6$	1221±3				
			G5	G1	G2	G3	G4					G6	G7	G8	G3			

reflectance. RMS represents the Root Mean Square error: the lower the RMS the better the fit. To show the goodness of the fit, for band center, the Tab. 3 In table are reported the spectral parameters obtained by MGM deconvolution of mafic end-members, at the 63-125 µm (on the left), 125-250μm (on the central column) and <10 μm (on the right). Center and width are expressed in nanometers, while depth as the logarithm of the error calculated at 95% level of confidence was reported.

												0.003
		RMS				0.003		RMS				
		Depth	-0.026	-0.016	-0.015			Denth	-0.028	-0.016	-0.01	
	<10 µm	Width	408	250	129		<10m	Width	432	325	205	
		Center	1286±6	$1944 \pm 4$	907±3			Center	1303±5	1957±6	941±4	
		RMS				0.009		RMS				0.007
	n	Depth	-0.3919	-0.06778	-0.0097		5	 Denth	-0.3598	-0.1066		
PL2	l25-250 μr	Width	481	441	54		PL3 125-250 m	Width W	431	636		
		Center	1282±1	1822±6	881±1			Center	1295±2	1711±13		
		RMS				0.005		RMS				0.005
	_	Depth	-0.2439	-0.04704	-0.0395			Denth	-0.2356	-0.06649		
	63-125 μm	Width	505	443	122		3-125 um	Width	438	591		
	-	Center	1271±1	$1837\pm 6$	909±2		¢	Center	1298±2	1734±12		
			G10	G11	G1				G10	G11	Gl	

reflectance. RMS represents the Root Mean Square error: the lower the RMS the better the fit. To show the goodness of the fit, for band center, the Tab. 4 In table are reported the spectral parameters obtained by MGM deconvolution of mafic end-members, at the 63-125 µm (on the left), 125-250μm (on the central column) and <10 μm (on the right). Center and width are expressed in nanometers, while depth as the logarithm of the error calculated at 95% level of confidence was reported.

- 1) 5-20% of lunar regolith is very fine grained (<10 $\mu$ m)
- 2) Very fine sizes increase the albedo but reduce the spectral contrast
- 3) Very fine plagioclase has featureless spectrum
- 4) Mafic materials are affected by fine sizes