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Application of spectral linear mixing to rock slabs analyses at various scales using Ma_Miss BreadBoard instrument

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12

13

Abstract

15 Focus of this work is the analysis of rock slabs by means of the Ma_Miss BreadBoard
16 instrument. Ma_Miss (Mars Multispectral Imager for Subsurface Studies, Coradini et al., 2010;
17 De Sanctis et al., 2017) is the miniaturized imaging spectrometer onboard the ESA Exomars
18 2020 mission.

19 Here we report the results of the analysis carried out on rock slabs using the Ma_Miss
20 breadboard (BB) (De Angelis et al., 2014; 2015) and a Spectro-Goniometer (SPG). The samples
21 are three volcanic rocks (from the Aeolian Islands and Montiferru volcanoes, Italy) and two
22 carbonate rocks (from Central Apennines, Italy). Visible and near infrared spectroscopic
23 characterization has been first performed on all the samples with a Spectro-goniometer (SPG).
24 Successively, higher spatial resolution spectra were acquired with the Ma_Miss BB setup in
25 each of the areas analyzed with the SPG.

26 We compared the spectra of the same areas of the slabs, acquired with SPG and Ma_Miss BB.
27 Three different analysis approaches have been performed on the spectra: arithmetical
28 averaging of the spectra, linear mixing of reflectances and linear mixing of Single Scattering
29 Albedoes (using Hapke model). The comparison shows that: (i) Ma_Miss instrument has great
30 capabilities for the investigation of rock surfaces with high detail; a large number of different
31 mineralogical phases can be recognized thanks to Ma_Miss high resolution within each
32 millimeter-sized analyzed area; (ii) the agreement with SPG spectra is excellent especially
33 when linear mixing is applied for the convolution of Ma_Miss BB spectra.

34

1. Introduction

36 The Ma_Miss instrument (Coradini et al., 2001, De Sanctis et al., 2017) onboard the ExoMars-
37 2020 Rover mission (Vago et al., 2007; 2013) will perform detailed spectroscopic

38 investigation of the Martian shallow subsurface, in the Visible and Near-Infrared spectral
39 range (0.4-2.2- μ m). Many different mineral classes can be identified by spectral signatures
40 occurring in this range, such as Fe-bearing silicates, OH-bearing phyllosilicates and clays,
41 sulfates and iron-oxides, widely observed on the surface of Mars (see Ehlmann and Edwards
42 2014, for a recent review of Martian mineralogy). The surface of Mars is mainly constituted by
43 mafic silicates (clino- and ortho-pyroxenes and olivine) and plagioclase, as constituents of
44 volcanic rocks of basaltic composition (e.g. Bibring et al., 2005; Poulet et al., 2007; Ehlmann
45 and Edwards 2014). Hydrated minerals (phyllosilicates and sulfates) have been observed by
46 both OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité)/Mars Express
47 and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars)/Mars Reconnaissance
48 Orbiter remote-sensing instruments and also by Mars Science Laboratory onboard Curiosity
49 rover (e.g Bibring et al., 2005; Murchie et al., 2009; Vaniman et al., 2014). Various types of
50 carbonates have been detected from the orbiting instrument CRISM/MRO (e.g Niles et al.,
51 2013). In addition to mineral phases, water and carbon dioxide ice mixtures have been
52 identified in polar caps (e.g Bibring et al., 2004, Langevin et al., 2005, 2007) and water ice is
53 likely to be present in the subsurface (Boynton et al., 2002).

54 Several works in the last decade have focused on spectroscopic analyses of rocks in the form
55 of coarse grains, fragments or slabs, with relevance for planetary surfaces investigations and
56 remote sensing data interpretation. Differences in spectra of powders and rock slabs are well
57 known (see for example Harloff & Arnold, 2001) and mainly concern different spectral slopes,
58 number of absorption features and spectral contrast. Longhi et al. (2001, 2004) analyzed in
59 the VNIR (0.4-2.5 μ m) metamorphic rocks slabs from Madagascar (quartzites, micaschists,
60 marbles, gneisses). They suggested the concept of *spectrofacies*, as a combination of several
61 absorption features; variation of absorption patterns are diagnostic of different types of rocks.
62 In another work Sgavetti et al. (2006) again point to the use of the concept of *spectrofacies* for
63 spectral classification of mafic and metamorphic rocks.

64 Pompilio et al. (2007) investigated bulk mafic cumulate rock samples, separated minerals
65 extracted from the bulk as endmembers and their mixtures. The main difference arising
66 between particulate minerals/synthetic mixtures and bulk rocks slabs is that, in the case of
67 rock slabs, the constituents interact in a complex manner. Spectral trends and correlations
68 with mineral chemistry are strongly influenced by the presence in bulk samples of one or
69 more spectrally active dominant species (Longhi et al., 2004; Sgavetti et al., 2006; Pompilio et
70 al., 2007). Isaacson et al. (2011) also report a similar work concerning combined investigation
71 of both bulk (rock slabs) and extracted mineral separates, focusing on lunar basalts and
72 computing linear mixing of mineral endmembers.

73 Other authors focused on the study of rock slabs of ultramafic to plagioclase cumulates and
74 basalts (Carli, 2009; Carli and Sgavetti, 2011; Carli et al., 2014), analyzing the spectral
75 differences due to intrusive/effusive textural properties. Moreover, an important factor
76 controlling the spectral shape and reducing the albedo and spectral contrast, is given by the
77 number of FeO-bearing constituents within a rock, more than the absolute total FeO content
78 (Carli and Sgavetti, 2011).

79 In a recent work Gurgurewicz et al. (2015) analyzed basaltic rock slabs from cold and hot arid
80 environments, with the aim to investigate spectral effects produced by weathering and
81 application to Mars, and concluding that rock slabs do not fully report spectral information
82 about the alteration history and paleo-environment conditions.

83 In two previous papers we demonstrated how Ma_Miss is able to discriminate between
84 different types of particulate minerals and rocks, discriminating between different grain sizes
85 and retrieving information about spectral parameters (De Angelis et al., 2014; 2015). Ma_Miss
86 will observe with high spatial resolution (120 μm) the borehole excavated by the Drill in the
87 subsurface at different depths, from about 0.3 m down to a maximum of 2 m. This high spatial
88 resolution is comparable with typical grain sizes in the regolith and can be much smaller than
89 the characteristic layer size in a stratigraphic column; Cousin et al. (2015) for example report
90 that coarse grains ($>500 \mu\text{m}$) constitute about half of the soils observed at Gale Crater. Thus
91 Ma_Miss observations will allow reconstructing the stratigraphy of the observed borehole
92 column. Depending on the material strength of the excavated column, powder-like or slab-like
93 surfaces will be observed by the instrument. Assuming a slab-like texture of the excavated
94 borehole, Ma_Miss will allow retrieving information both about differences in the stratigraphy
95 and mineralogical heterogeneity at a sub-millimeter scale level.

96 In order to estimate and validate Ma_Miss setup performances when observing slab-like rocks
97 surfaces, a second instrument, the Spectro-Goniometer, having a much larger spatial
98 resolution (6 mm) has been used. Methodologies and experimental setup are described in
99 section 2. Rock samples used in this work, three volcanic (STR72, FOR5, MFEB1) and two
100 carbonate samples (CAL1, GPR18), are described in section 3; before spectroscopic
101 measurements, the samples were characterized in terms of chemical and mineralogical
102 composition, by means of X-Ray Fluorescence and X-Ray Powder Diffraction techniques
103 (section 3). Several areas have been then observed with the Spectro-Goniometer (SPG) on
104 each rock surface. Each area corresponds to the SPG spatial resolution of 6 mm and thus to a
105 single SPG spectrum. Subsequently, given the much higher spatial resolution of Ma_MISS, 10
106 high-resolution spectra have been acquired with Ma_Miss setup in each of these areas (section
107 4).

108 The comparison of Ma_MISS spectra with measurements performed with the Spectro-
109 Goniometer (SPG), having a much larger spatial resolution, implies the use of statistical
110 methods, especially if we are observing a rock slab with mm-sized surface heterogeneity. A
111 first simple method used to retrieve the SPG spectra is to average all Ma_Miss spectra
112 acquired within a comparable area; this method is used in section 4.4. A second method is
113 based on the linear mixing of reflectance spectra. Three endmembers are extracted among the
114 ten spectra acquired with Ma_Miss within each area, and a linear combination of these ones is
115 computed and optimized to match the corresponding SPG spectrum (section 4.5). The linear
116 mixing of reflectance spectra results in a better final matching with the SPG spectrum;
117 nevertheless this approach is rigorously valid if the mixing scale is macroscopic (Mustard and
118 Pieters, 1987). A third approach concerns the linear mixing of Single-Scattering Albedo (SSA)
119 spectra, for which a linear behavior is expected in case of microscopic mixing scale (Hapke,
120 1981; Mustard and Pieters, 1987); this third method is described in section 4.6.

2. Experimental setup

2.1 Ma_Miss Breadboard setup

The Laboratory BreadBoard setup in use at INAF-IAPS (described in detail in De Angelis et al., 2014) consists of the main optical subsystems of the Ma_Miss instrument (Coradini et al., 2001; Preti et al., 2011) except for the spectrometer. The illumination source is a 5W miniaturized lamp integrated within the instrument. A bundle of optical fibers carries the light from the lamp to the Optical Head, which consists of several miniaturized mirrors and acts to focus the light on the external target. The light is focused through a sapphire window on the target, at a distance of 0.6 mm; then the scattered light is recollected by the same Optical Head, and an optical fiber carries the signal to a spectrometer. In this setup the BreadBoard is coupled with a FieldSpec Pro, which operates in the 0.35-2.5 μm range. The Ma_Miss instrument will nominally operate in the 0.4-2.2 μm range. The illuminated area on the target is 1 mm, while the spatial resolution is about 0.12 mm.

2.2 Spectro-Goniometer setup

This setup (in use at INAF-IAPS) consists of the Spectro-photometer FieldSpec Pro coupled with a mechanical goniometer, which permits to vary phase angles with a minimum of 30°. Illumination and emission angles used with this setup are $i=30^\circ$ and $e=0^\circ$, respectively. The light source is a Quartz Tungsten Halogen (QTH) lamp (power 84W). The illuminated and sensible area onto the target is about 6 mm. The main differences between these two setups have, in terms of spatial resolution, illumination conditions and other factors, have already been described in De Angelis et al. (2014).

2.3 Optical microscopy

All the samples have been analyzed by optical microscopy. The microscope used is a Nikon SMZ 800, equipped with an ED Plan 1.5X WD 45 Nikon objective, C-W10X/22 Nikon oculars, and light source Schott, in use at IAPS-INAf. Microscopy investigation has been carried out inside each single 6-mm sized area observed with the Spectro-Goniometer. Samples have been observed in reflection mode in the form of slabs. Magnifications in the range 1-6.3X have been used among samples depending on particular features (see figs 2 to 6 in section 3). This has been done with the aim of searching and discriminating, within each area observed with the Spectro-Goniometer, grains and features to be successively analyzed with Ma_MISS setup.

2.4 XRF and XRPD analyses

X-Ray Fluorescence (XRF) and X-Ray Powder Diffraction (XRPD) analyses have been carried out at the University of Bari on all samples except the San Bartolo Lava (STR72) volcanic sample, whose analyses were published in Laiolo & Cigolini (2006) (see section 3). Both XRF and XRPD analyses have been performed on powders, obtained from volumes that were representative of whole slabs. XRF analyses have been performed on the two volcanic samples (FOR5 and MFEB1) in order to retrieve major oxide elements composition, while XRD has been performed on the two carbonate samples (CAL1 and GPR18) in order to retrieve mineralogical phases.

Before XRF analyses the samples have been ground with planetary mill Fritsch Pulverisette 7 and ZrO mortars, using four 2-minutes cycles at 300 Hz. Five grams of each sample have been mixed with 2 ml of Elvacite (15% in acetone), and this has been mixed with 5 grams of H₂BO₃ in an aluminum capsule. Pellets have been finally produced pressing this mixture at 25 tons. Analyses have been conducted on pellets using a WDXRF Rigaku Supermini 200 spectrometer with Pd source (50 kV, 4 mA, 200 W) in vacuum. Siliceous rocks standards from CNRS SARM GRPG Paris have been used for calibration. For XRPD analyses an Empyrean Panalytical Diffractometer has been used, with operating conditions 40 kV and 40 mA and CuK α radiation as source. Bragg- Brentano geometry was used. Sample stage was a flat specimen holder. The incident beam path was given by: Soller slits 0.02 rad, fixed incident beam mask 10 mm, anti-scatter slit 1/2°, divergence slits 1/4°. The diffracted beam path was characterized by: anti-scatter slits 7.5 mm; Soller slits 0.02 rad, large beta filter-Nickel detector: PIXcel3D. A phase quantification of mineralogical composition was obtained using the software HighScore Plus™ (Panalytical).

3. Samples characterization

Five samples have been analyzed, in the form of slabs and representative powders. Three of them are volcanic samples, while the other two are carbonates. X-Ray Fluorescence spectroscopy has been performed on two volcanic samples (MFEB1 and FOR5) while X-Ray Diffraction has been performed on the carbonates (CAL1 and GPR18) at the University of Bari (Italy). In the following section the samples are described.

3.1 Macroscopic description and XRF/XRD analyses

3.1.1 San Bartolo lava (STR72)

This sample is a lava from Stromboli (Aeolian arc, Sicily/Italy). The rock is characterized by a very dark groundmass with fine porphyritic texture (fig.1A). Few small vesicles characterize the rock surface. San Bartolo lavas are characterized by a high porphyry index (40-45 %), with plagioclase being the most abundant phase, plus clinopyroxene, olivine and orthopyroxene; accessory phases are constituted by titanomagnetite and apatite (Laiolo and Cigolini, 2006). Phenocrysts of plagioclases (anorthitic to labradoritic), olivine (mainly micro-

phenocrysts), clino- and ortho-pyroxenes and opaque minerals (oxides, titaniferous magnetite) are present. Moreover San Bartolo lavas also contain mafic/ultramafic xenoliths with gabbroic, gabbro-noritic and gabbro-anorthositic compositions. This lava can be classified as porphyritic high-K calc-alkaline basalt (Laiolo and Cigolini, 2006), with SiO₂, 52.60 wt%; Na₂O+K₂O, 3.86 wt% (Peccerillo et al., 2013).

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203 **3.1.2 Lava from Montiferru/Bonarcado (MFEB1)**

204 The rock has been sampled in the Montiferru volcanic region (Abbasanta Plateau,
205 Sardinia/Italy), within a unit that belongs to the Plio-Pleistocene alkaline transitional, and
206 sub-alkaline volcanic cycle (0.14-5.3 Myr) characterized by alkaline
207 basalts/basanites/trachybasalts. It is characterized by fine grey porphyritic texture (fig.1B),
208 with visible phenocrysts of olivine, plagioclase and iron oxides. A great number of large
209 vesicles also characterize the sample, indicating that it is an intermediate volcanic rock which
210 retained large quantity of gas. XRF analyses show that this sample has SiO₂ content of 50.9%
211 and an alkali content of Na₂O+K₂O=8.3% (phonolitic tephrite). Normative calculations suggest
212 that the sample has a mineralogical composition given essentially by feldspar (plagioclase 63
213 wt%, orthoclase 22 wt%) and olivine (8 wt%). Accessory minerals are ilmenite (3 wt%),
214 nepheline and other oxides.

215

216 **3.1.3 Lava from Fordongianus (FOR5)**

217 The sample derives from Montiferru volcanic region (Sardinia/Italy), within a unit defined by
218 intermediate/acidic rocks. The ground mass has a pink coloured, fine and porphyritic texture
219 (fig.1C). Some quartz and feldspar phenocrysts and large lithic fragments are embedded
220 within the groundmass. The sample also shows few small vesicles and signs of weathering and
221 aqueous alteration. XRF analyses show that this sample has an SiO₂ content of 65.1% and an
222 alkali content of Na₂O+K₂O=8.5% (trachy-dacite). Normative mineralogical composition is
223 constituted by feldspar (plagioclase 53 wt%, orthoclase 23 wt%), quartz (16 wt%), pyroxene
224 (hypersthene 6 wt%) plus minor magnetite, ilmenite and corundum.

225

226 **3.1.4 Red micritic limestone (CAL1)**

227 This limestone ("scaglia rossa") derives from Apennines near Gubbio (Umbria/Italy), from a
228 unit at the Cretaceous-Paleogene (K-T) limit (Mesozoic-Cenozoic era transition; Lowrie and
229 Alvarez, 1977; Alvarez 2009); the sample is typical of deep-sea environment and hot-tropical
230 climate. Optical observations show that the rock is characterized by red color likely due to the
231 presence of iron oxides and/or hydroxides (fig.1D); very fine, sub-micron grain size texture
232 and several grey veins. These veins can be due to percolation of fluids from which
233 recrystallized calcite crystals, that intersect the rock matrix. XRPD analyses on powder reveal

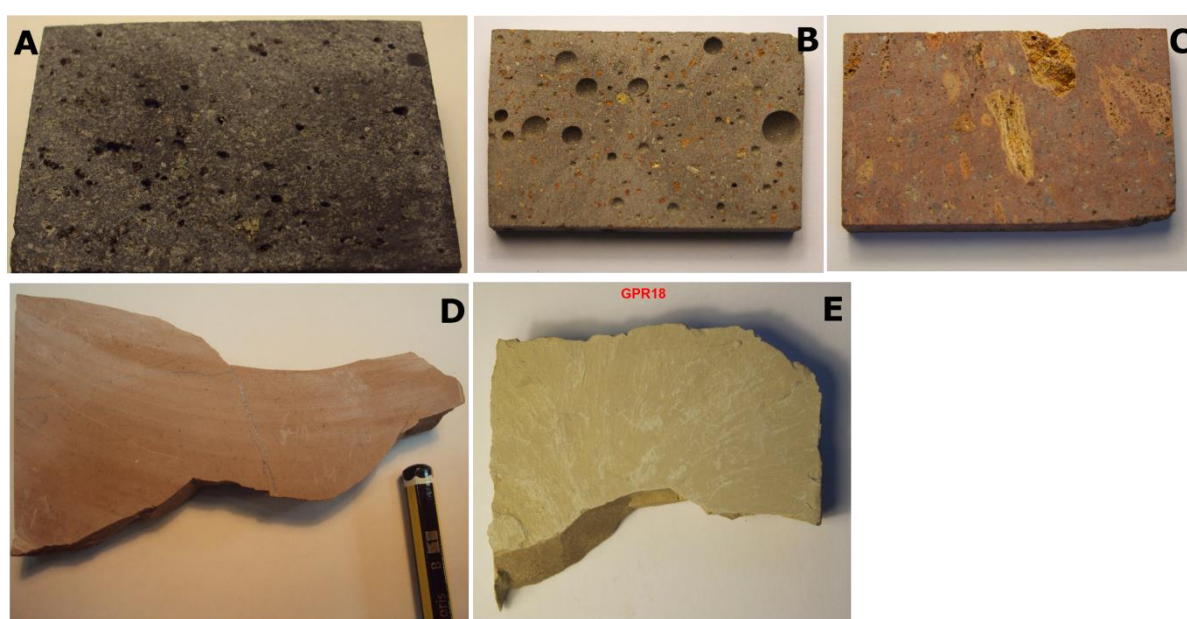
234 that the mineralogical composition consists mainly of calcite (96%) and quartz (4%); the
235 amounts of minerals responsible of reddish color of the studied sample are below the
236 detection limit of diffractometer (1%).

237

238 **3.1.5 Limestone from Mt Ernici (GPR18)**

239 This sample derives from Apennines / Ernici Mountains (Lazio/Italy) (fig.1E). It is
240 characterized by very fine sub-micron grain size matrix, with substantial surface homogeneity
241 and absence of clasts. XRD analysis on this (powdered) sample show that it is composed
242 essentially by 92% dolomite [$\text{CaMg}(\text{CO}_3)_2$] with 8% ankerite [$\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$].

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246 *Fig.1. Analyzed samples. A: San Bartolo Lava (STR72). B: Montiferru/Bonarcado lava (MFEB1). C:*
247 *Fordongianus sample (FOR5). D: Red micritic limestone (CAL1). E: limestone from Mt Ernici*
248 *(GPR18).*

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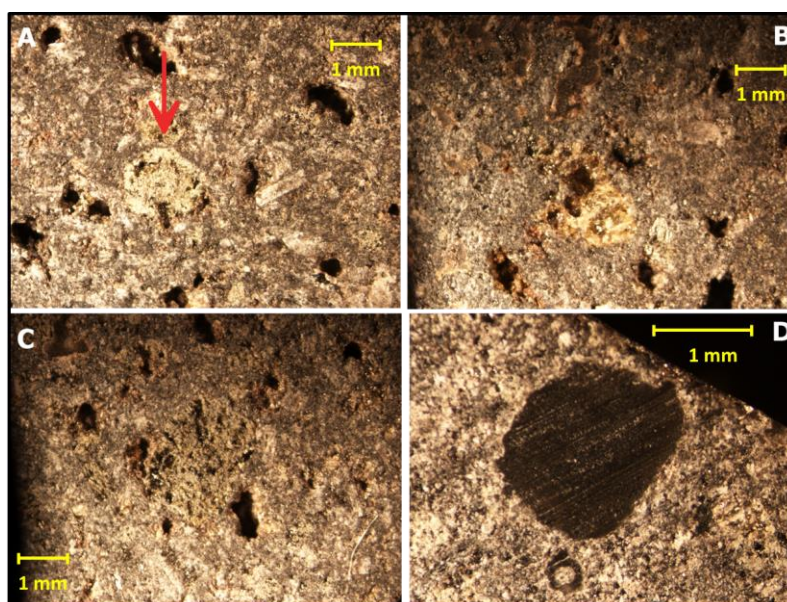
251 **3.2 Analyses by optical microscopy**

252 **3.2.1 San Bartolo lava (STR72)**

253 Some images acquired with the microscope from this sample are in fig.2. In the image of fig.2A
254 a phenocryst of olivine, green hexagonal section, about 1x2 mm in the left center, is evident;
255 plagioclase crystals and vesicles are also visible; plagioclase phenocrysts appear in the form of
256 laths and euhedral-subhedral crystals, sometimes with sieve texture. Pyroxenes, iron oxides

257 and opaques constitute the dark groundmass. In fig. 2B and 2C olivine (green crystal about
 258 1x2 mm in the left center), oxides and plagioclases are embedded within the groundmass. In
 259 fig.2D a black inclusion, about 2x3 mm in size (likely magnetite or ilmenite or a glassy
 260 xenolith) is evident.

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262

263 *Fig.2. Microimages of San Bartolo lava's (STR72) sample. Observations under optical microscope*
 264 *performed on rocks surfaces in reflected light. Magnifications used are: A,B,C = 1X. D = 2X. The red arrow*
 265 *in 2A frame indicates the green hexagonal crystal (likely olivine).*

266

267 **3.2.2 Lava from Montiferru/Bonarcado (MFEB1)**

268 In fig.3 optical microscopy images acquired in reflection mode from the Montiferru lava are
 269 shown. Several vesicles are evident in all frames. Millimeter-sized feldspars and plagioclase
 270 crystals are visible in frames A, B and C. Plagioclases phenocrysts occur in the form of white
 271 laths. Numerous reddish concretions, likely constituted by iron oxides/hydroxides occur on
 272 the rock surface. Alkali basalts occurring in these lava flows (*BD unit* described in Fedele et al.,
 273 2007) are characterized by a porphyry index of 25-30 % and by the common presence of
 274 altered iddingsitised olivine (reddish concretions in Fig.3). The groundmass has a very fine
 275 and dark texture, substantially made of pyroxenes with plagioclase crystals.

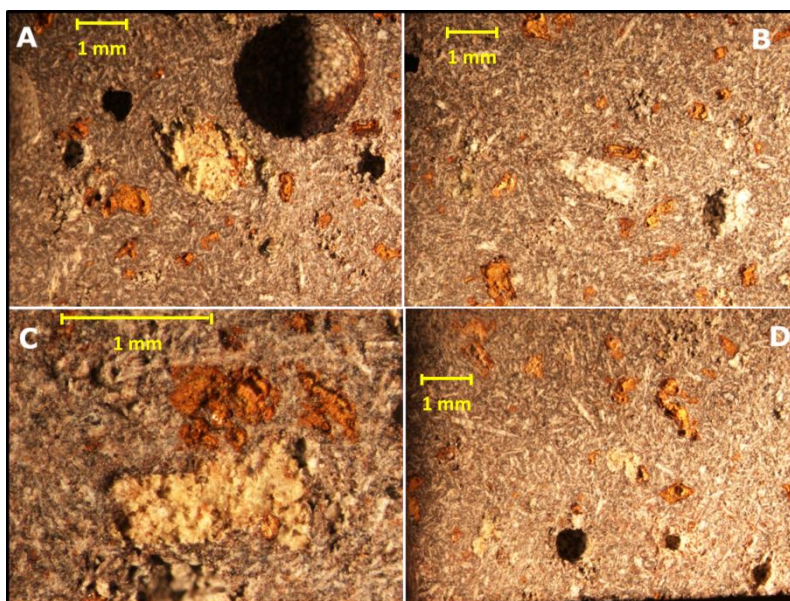
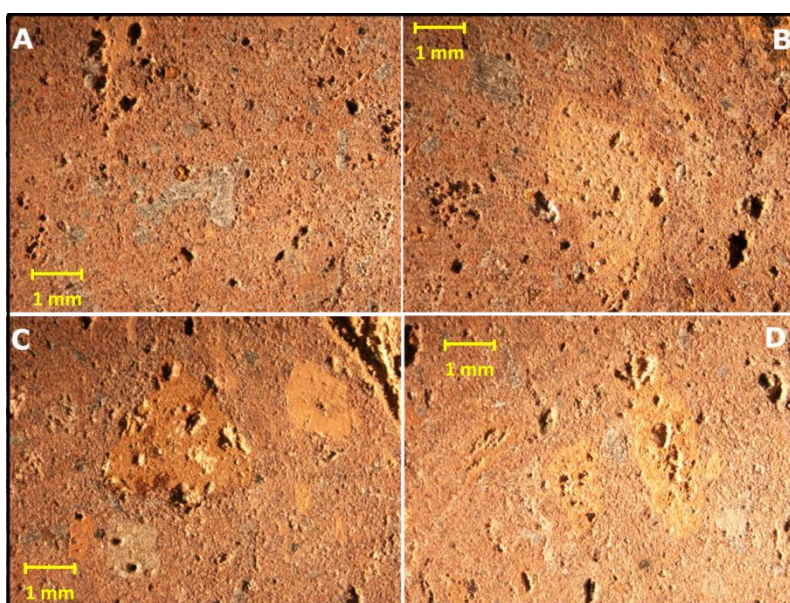


Fig.3. Microimages of Montiferru/Bonarcado (MFEB1) sample. Observations under optical microscope performed on rocks surfaces in reflection light. Magnifications used are: A,B,D = 1X. C = 3X.

3.2.3 Lava from Fordongianus (FOR5)

Optical microscope images relative to volcanic FOR5 sample are in fig.4. The pink-red groundmass is characterized by very fine and vesicular cryptocrystalline texture. Plagioclase and numerous millimetric to sub-millimetric quartz crystals are visible in fig.4A. Embedded in the matrix are also millimetric pink-orange feldspar phenocrysts and iron oxide crystals. Often iron oxides/hydroxides and anhedral quartz crystals have grown and filled inside vesicles.



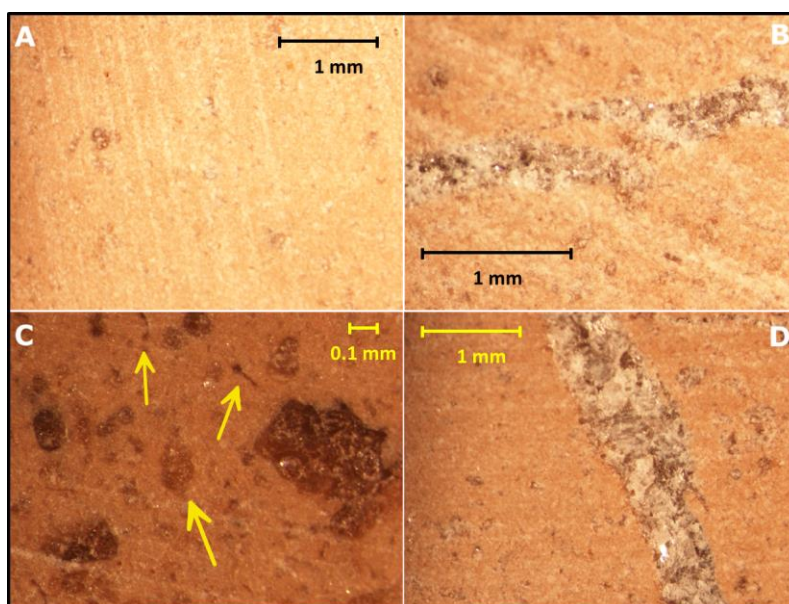
289 Fig.4. Microimages of Montiferru/Fordongianus (FOR5) sample. Observations under optical microscope
290 performed on rocks surfaces in reflection light. Magnifications used are: A,B,C,D = 1X.

291

292 3.2.4 Red micritic limestone (CAL1)

293 In fig.5 images acquired on the red micritic limestone (Scaglia Rossa, Lowrie and Alvarez,
294 1977; Alvarez, 2009) are shown. The typical dimension of the calcite grains is <10 microns.
295 Sub-millimeter hematite and magnetite grains, present in this sample (Lowrie and Alvarez,
296 1977), are visible especially in fig.5B, together with microfossils (about 100 micrometers in
297 size). This *scaglia rossa* sample is a pelagic sediment, and is composed essentially by
298 calcareous plankton (calcareous nannofossils and planktonic foraminifera, Alvarez, 2009; Cita
299 et al., 2005). In fig.5B-D two veins filled with calcite crystals are visible.

300



301

302 Fig.5. Microimages of the sample from Umbria/Apennines (CAL1). Observation under optical microscope
303 performed on rocks surfaces in reflection light. Magnifications used are: A = 2X. B = 3X. C = 5X. D = 2X.
304 Yellow arrows in frame 5C indicate nanofossils.

305

306 3.2.5 Limestone from Mt Ernici (GPR18)

307 A high level of surface homogeneity characterizes the images acquired from this sample,
308 obtained at different values of magnification (fig.6). The dimension of the grains is of the
309 order of 10 micrometers. We note the absence of clasts, inclusions or crystals of size greater
310 than few tens of micrometers.

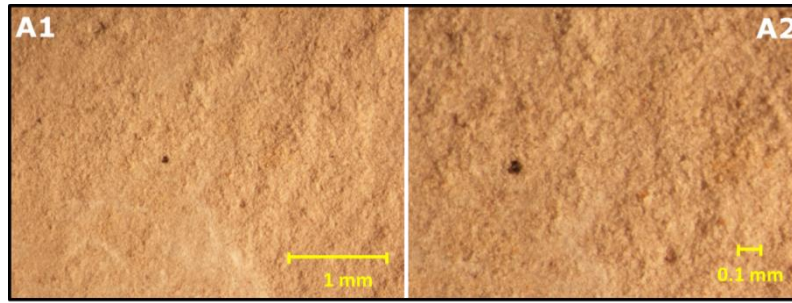


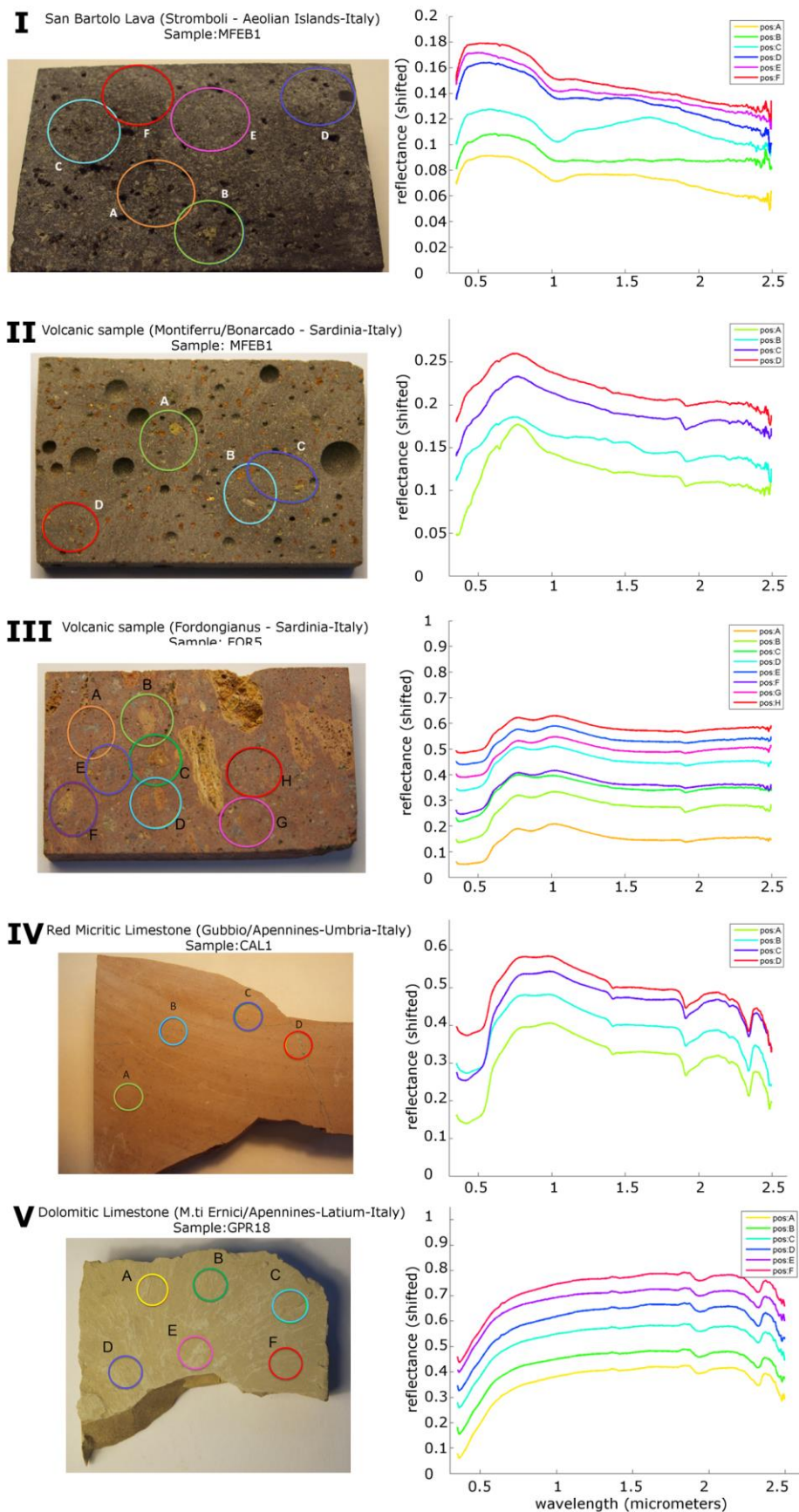
Fig.6. Microimages of the sample from Mt Ernici/Apennines (GPR18). Observations under optical microscope performed on rocks surfaces in reflection light. A1 = 2X. A2 = 4X.

4. Results: spectral analyses

All samples have been first analyzed with the SPG setup, and subsequently with the Ma_MISS BB setup. For each sample, several areas on the surface have been analyzed with the SPG, each area corresponding to the instrumental acquisition area of 6 mm. Then the BB setup has been used to acquire spectra with higher spatial resolution (120 μm of spatial resolution): thus 10 spectra in different positions have been acquired with the BB setup, inside each previous SPG area. In the following sections, the measurements will be described separately and then compared with different methods.

4.1 Measurements with Spectro-Goniometer

Spectra acquired with the Spectro-Goniometer setup are in fig.7 for all samples (I to V). In all cases the area of the spot corresponding to one spectrum is much bigger than the typical size of mineral crystals and grains which are embedded in the surface matrix.



333

334 Fig.7. Spectra acquired with Spectro-Goniometer setup. I: San Bartolo Lava (STR72). II: lava from
335 Montiferru/Bonarcado (MFEB1). III: sample from Montiferru/Fordongianus (FOR5). IV: Red micritic
336 limestone (CAL1). V: limestone from Ernici Mountains (GPR18).

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4.1.1 San Bartolo lava (STR72)

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4.1.2 Lava from Montiferru/Bonarcado (MFEB1)

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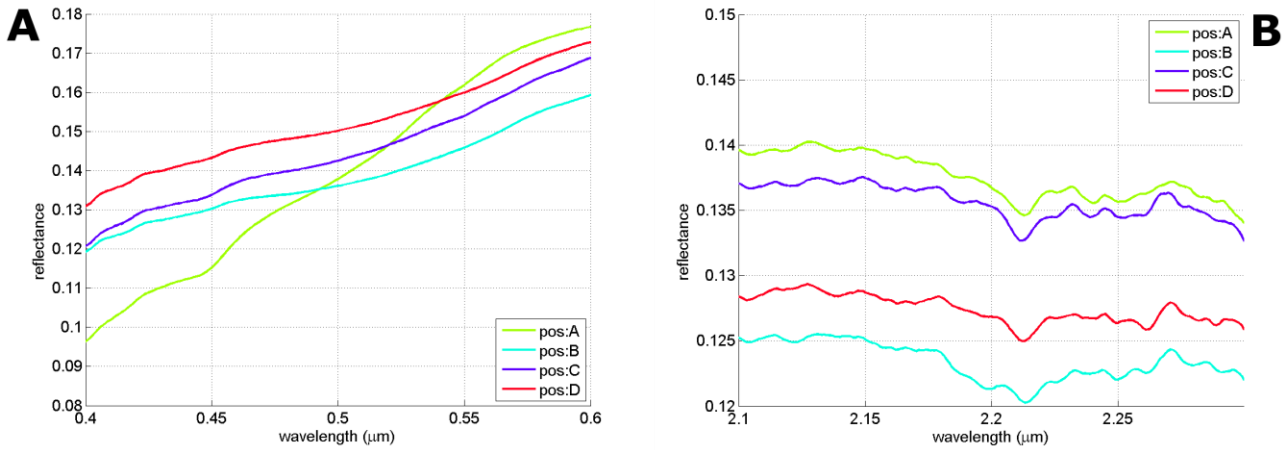
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Six areas have been analyzed with the SPG setup on the surface of the San Bartolo sample (fig.7-I). One single spectrum has been acquired for each area from A to F. All spectra are characterized essentially by the crystal field (CF) absorption within Fe²⁺ at 1 μm (Burns, 1993) and by a net negative (“blue”) slope in the IR. Spectra in positions B, E and F are nearly flat in the NIR range, although E and F show an absorption at 1 μm; the spectrally dominating mineralogy could be pyroxenes with iron oxides/sulfides that are responsible of very low reflectance. Spectra in positions A, C and D also show a 1-μm absorption whose right shoulder extends towards longer wavelengths, up to 1.7 μm: this could be indicative of a mixture of pyroxenes with olivine. Spectra A, C and D moreover show the Fe²⁺ absorption at 2 μm typical of pyroxene. The weak feature appearing at 0.5 μm in spectra A and B is related to spin forbidden transitions in Fe²⁺ in pyroxenes (Klima et al., 2007; Cloutis and Gaffey, 2009). However a continuum removed study would permit more quantitative analyses.

Spectra with SPG setup have been acquired in four areas on the surface of the Montiferru/Bonarcado sample (fig.7-II). They are all characterized by a blue slope in the IR; a weak Fe²⁺ absorption at 1 μm is superimposed onto the negative continuum in spectra A and B. Spectra C and D do not show evident CF absorptions, although a continuum removed investigation could highlight weak absorptions at 1 μm. Spin-forbidden transitions appear in the visible near 0.5 μm (probably Fe²⁺) and in the range 0.44-0.45 μm (Fe²⁺, Cr³⁺ or Ti³⁺) (see Klima et al., 2007) (fig.8A). All spectra show the signs of aqueous alteration, with OH⁻ and H₂O overtone absorptions near 1.4 and 1.9 μm. A weak feature appears near 2.21 μm, that could be attributed to Al-OH vibrational transitions (fig.8B) (see for example Clark et al., 1990). The broad band at 1.7 μm that appears in the spectrum B could also be due to Al-OH (see for example Clark et al., 1990).



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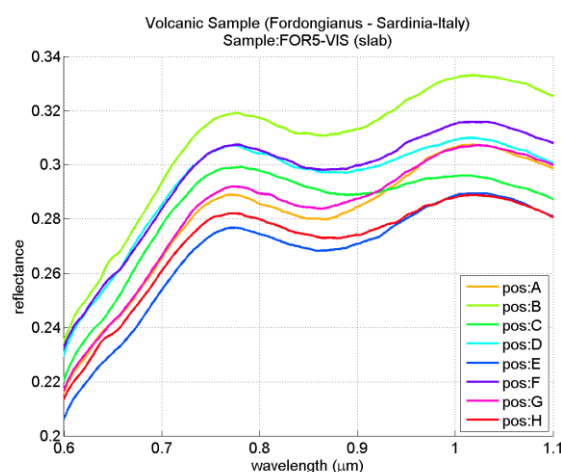
365 Fig.8. Sample from Montiferru/Bonarcado (MFEB1). A: electronic transitions in the VIS range. They are
 366 due to Fe^{2+} ($0.5\ \mu\text{m}$) and other transition elements. B: absorption band at 2.21 micron: it is due to Al-OH
 367 vibrational transition.

368

369 4.1.3 Lava from Fordongianus (FOR5)

370 The eight spectra measured on the surface of FOR5 sample (fig.7-III) have very similar shapes,
 371 although there are substantial differences in the reflectance level. The main absorption
 372 features are the H_2O band at $1.9\ \mu\text{m}$, indicating some water content in the sample, and the
 373 band at $0.86\text{-}0.90\ \mu\text{m}$ due to iron oxides/hydroxides (Laporte-forbidden transition in
 374 hematite/goethite Fe^{3+} ions; fig.9) (Morris et al., 1985; Clark 1999). Both these features could
 375 be indicative of chemical weathering of the sample. All spectra show a net blue slope.

376



377

378 Fig.9. Sample from Montiferru/Fordongianus (FOR5). The absorption feature near $0.87\text{-}0.90\ \mu\text{m}$ is likely
 379 due to Fe^{3+} transition.

380

381 4.1.4 Red micritic limestone (CAL1)

382 The spectra, acquired in four different areas, are similar, although with slightly different levels
 383 of absolute reflectance (range 46-50%), and with a negative slope (fig.7-IV). Spectra are
 384 characterized by CO_3^{2-} absorption bands located at 2.2 and $2.34\ \mu\text{m}$ (Hunt, 1977; Gaffey, 1986;
 385 Clark et al., 1990), OH^- feature at $1.4\ \mu\text{m}$ and the H_2O feature at $1.9\ \mu\text{m}$. Absorptions occurring
 386 at $0.9\ \mu\text{m}$ are likely due to CF transitions within ferric ions (Fe^{3+} , fig.10) (Morris et al., 1985;
 387 Clark 1999).

388

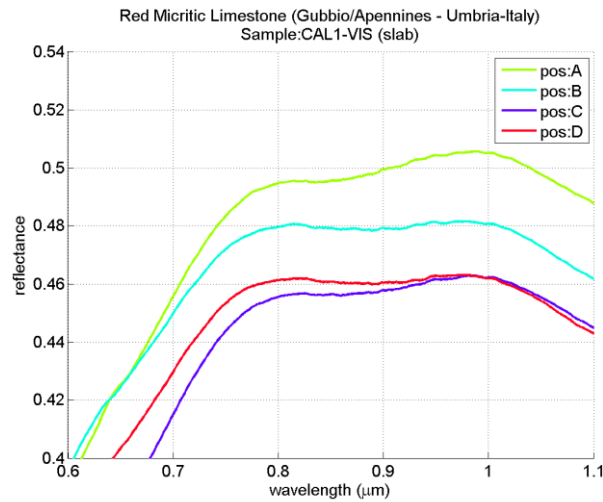


Fig.10. Red Micritic Limestone (CAL1). The absorption feature near 0.87-0.90 μm is likely due to Fe^{3+} transition.

4.1.5 Limestone from Mt Ernici (GPR18)

The spectra of this limestone (fig.7-V; spectra shifted for clarity) are all very similar, both in overall shape and in reflectance value: the maximum reflectance is about 0.55-0.60. Absorption bands diagnostic of carbonate ion CO_3^{2-} appear at 1.75 and 2.34 μm (Gaffey, 1986, 1987); the feature at 2.2 μm is very weak and discernible only in spectrum of position F. Hydroxyl and water absorptions occur at 1.4 and 1.9 μm respectively.

4.2 Measurements with Ma_Miss Breadboard

4.2.1 San Bartolo lava (STR72)

Spectra (fig.12-A) acquired with Ma_Miss BB within area A (fig.7-I area A) show different mineralogical phases. An example of the spots acquired with Ma_Miss within an SPG area is shown in fig.11. Absorptions at $0.9\ \mu\text{m}$ (Fe^{3+}) and $1\ \mu\text{m}$ (Fe^{2+} in pyroxenes) are visible in spectra in positions 1, 3 and 5. Spectra in positions 4 and 7 don't show absorptions, indicating dark/opaque materials. Spectra within area B (fig.12-B) show the presence of olivine, with a broad absorption band centered near $1\ \mu\text{m}$ and extending up to $1.7\ \mu\text{m}$ (positions 1,2,3). Other spectra are indicative of dark materials. In fig.12-C spectra that are indicative of pyroxene are shown, related to area C; they are characterized by pronounced absorptions at 1 and $2\ \mu\text{m}$; spectra in positions 2 and 8 also show a broad feature at $0.8\ \mu\text{m}$ (CF in Fe^{3+}). Spectra acquired within area D are shown in fig.12-D. Some of them are only characterized by a faint absorption band at $1\ \mu\text{m}$, while others are spectrally flat and with variable slope. In particular spectra 1 and 4 in pos.D show a constant positive slope, differently from all other spectra of volcanics. Flat and featureless spectra are related to the black iron oxide inclusion (see fig.7-I area D). A small and narrow feature appearing near $0.6\ \mu\text{m}$ in all STR72 spectra is due to an instrumental artifact.

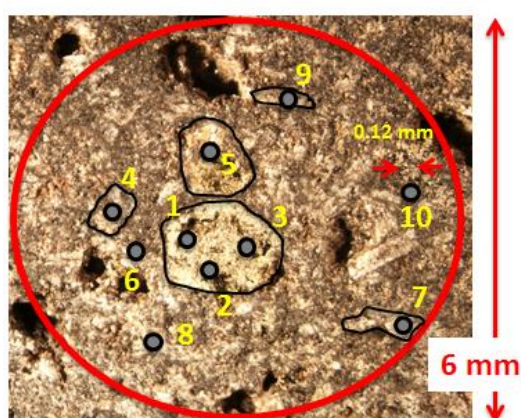


Fig.11. comparison between the spot of the SPG (6 mm, red circle) and the spot of Ma_Miss BB (0.12 mm, black-grey circles, numbered from 1 to 10); the sample is STR72, area A (see spectra in fig.12-A). Black irregular contours are traced to highlight some macroscopic features investigated with Ma_Miss BB.

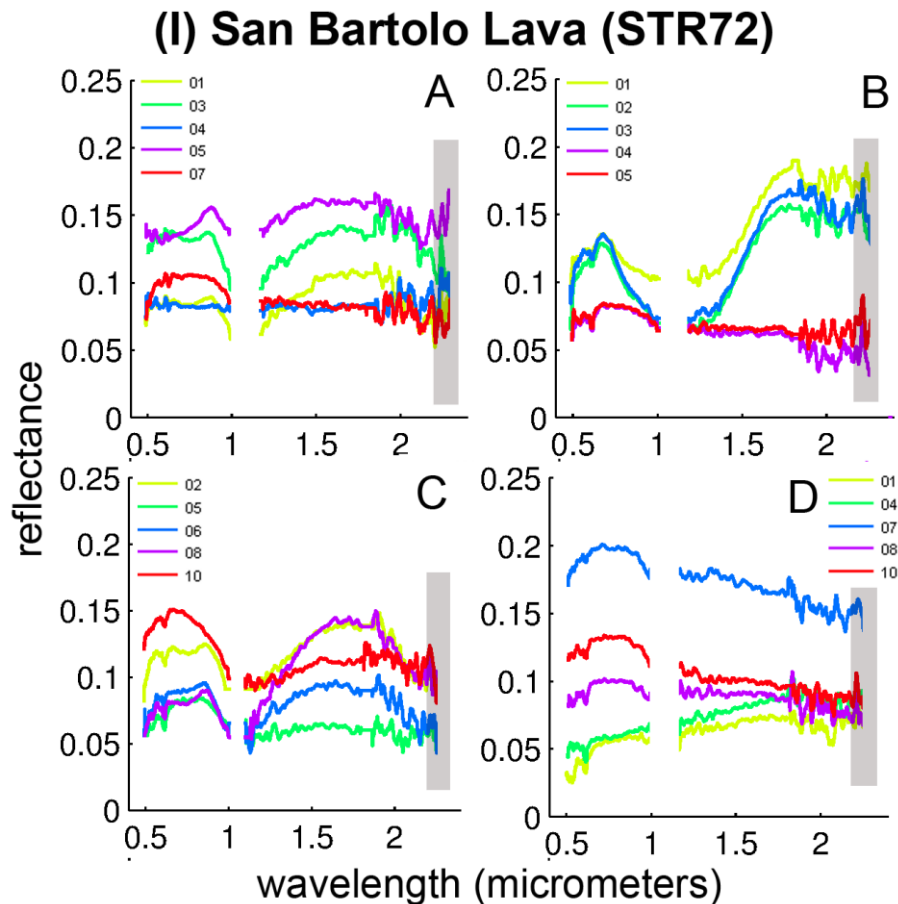


Fig.12. Spectra acquired with Ma_Miss BreadBoard setup. Sample I: San Bartolo Lava (STR72). The letters (A,B,C,D) correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized area, ten spectra in different positions have been acquired with Ma_Miss BB setup; here only five spectra are shown for clarity. Data at 1 μm are not shown in several spectra due to high level of detector noise, as well as data at $\lambda < 0.5 \mu\text{m}$ and $\lambda > 2.3 \mu\text{m}$ in some cases. Gray bars highlight the spectral region which is not accessible for Ma_MISS.

4.2.2 Lava from Montiferru/Bonarcado (MFEB1)

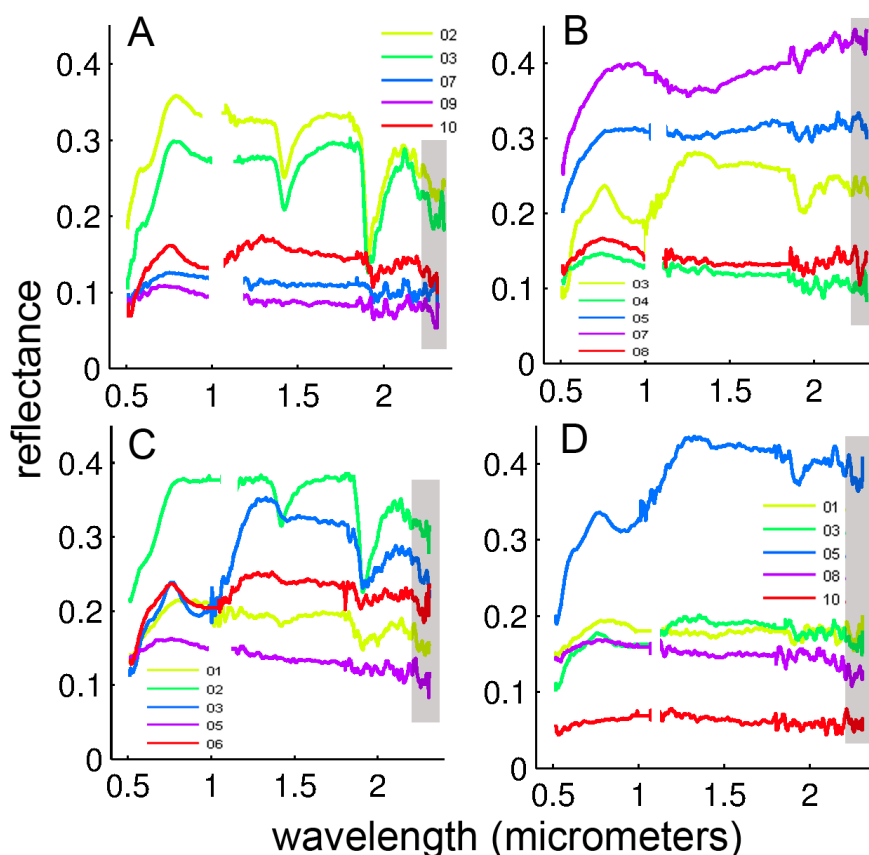
Spectra in fig.13-A (relative to area A in fig.7-II) show a great diversity, indicating several different mineralogical phases within the observed area. Spectra 2 and 3 (blue and green lines), with spin-forbidden absorptions at 0.65 μm ($\text{Fe}^{2+}/\text{Fe}^{3+}$ or Ti^{3+} , see for example Clark et al., 1990, Klima et al., 2007), CF at 1 μm (Fe^{2+}), vibrational overtones at 1.4 μm (OH^-) and 1.9 μm (H_2O) are indicative of hydrated silicate minerals. A feature at 2.2 μm in spectrum 3 could be attributed to Al-OH absorption, suggesting the presence of montmorillonite or other alteration phases associated to plagioclases (see Clark et al., 1990); it must be stressed however that features occurring longward of 2.2 μm are not accessible for Ma_MISS flight instrument. The spectrum 10 is indicative of iron oxides (absorption at 1 μm) with some degree of hydration. Spectra 7 and 9 indicate the presence of dark/opaque minerals (oxides). Spectra of iron hydroxide goethite, characterized by Fe^{3+} absorption at 0.9 μm and OH/ H_2O absorptions at 1.4-1.9 μm , are visible in several positions (fig.13: B, pos.3; C, pos.3,6; D, pos.3,5; see Clark 1999). Plagioclase feldspars are visible in spectra 5 and 7 of fig.13-B, as could be inferred by the CF Fe^{2+} absorption near 1.25-1.3 μm (see Adams and Goullaud, 1978).

456 The presence of silicate minerals with different OH/H₂O band intensities at 1.4-1.9 μm ,
 457 indicative of various degree of hydration is evident in spectra 1,2 of fig.13-C. Dark opaque
 458 minerals are indicated by spectra in fig.13-B (4), fig.13-C (5) and fig.13-D (1, 8 and 10).

459

460

(II) Montiferru/Bonarcado lava (MFEB1)



461

462 *Fig.13. Spectra acquired with Ma_Miss BreadBoard setup. Sample II: Montiferru/Bonarcado Lava (MFEB1). The*
 463 *letters (A,B,C,D) correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized*
 464 *area, ten spectra in different positions have been acquired with Ma_Miss BB setup; here only five spectra are shown*
 465 *for clarity. Data at 1 μm are not shown in several spectra due to high level of detector noise, as well as data at $\lambda < 0.5$*
 466 *μm and $\lambda > 2.3 \mu\text{m}$ in some cases. Gray bars highlight the spectral region which is not accessible for Ma_MISS.*

467

468

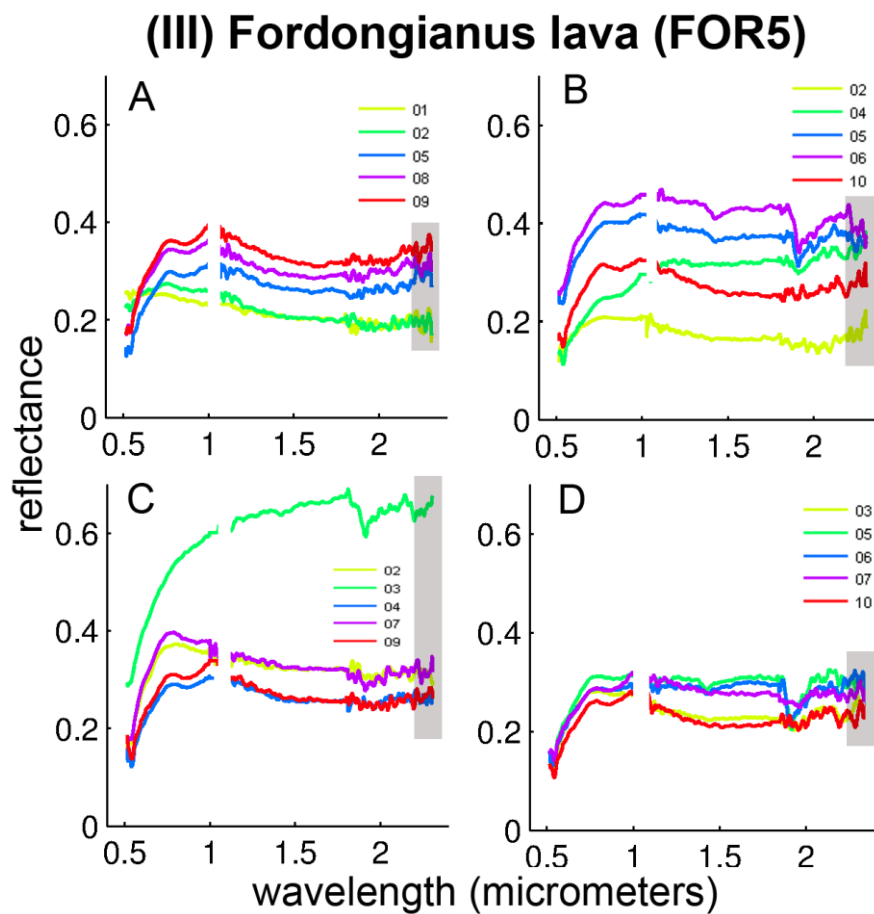
4.2.3 Lava from Fordongianus (FOR5)

470 Spectra are shown in fig.14. Area A (fig.14-A) is characterized by spectra similar to
 471 chert/silica, with some content of dark/opaque minerals; in some positions (spectra 5, 8 and
 472 9) the CF Fe³⁺ absorption feature at 0.9 μm is visible (Clark, 1999). Spectra within area B
 473 (fig.14-B) are similar to chert/hydrated silica with different content of ferric iron and various
 474 degree of hydration (bands at 1.4 and 1.9 μm). Spectra relative to area C (fig.14-C) also are
 475 indicative of high-silica phases with some content of ferric iron (CF absorption in Fe³⁺). We

476 must stress the point that unambiguous detection of chert/hydrated silica can be done with
 477 the diagnostic Si-OH feature located beyond 2.2 μm . Area D (fig.14-D) is characterized by the
 478 presence of hydrated minerals-iron oxide mixture (spectra in position 5,6,7 with intense
 479 OH/H₂O absorptions at 1.4-1.9 μm and CF Fe³⁺ absorptions at 0.9 μm), and by Fe³⁺-bearing
 480 high-silica phases (pos.3,7). Al-OH alteration phases could be present in area C (pos.3) and
 481 area D (pos.3, 10) as suggested by the absorption at 2.2 μm ; also in this case it must be
 482 highlighted that features appearing beyond 2.2 μm will not be observed from Ma_MISS flight
 483 instrument, and Al-OH absorptions occurring at 2.2 μm can be hardly identified.

484

485



486

487 *Fig.14. Spectra acquired with Ma_Miss BreadBoard setup. Sample III: Fordongianus Lava (FOR5). The letters*
 488 *(A,B,C,D) correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized area,*
 489 *ten spectra in different positions have been acquired with Ma_Miss BB setup; here only five spectra are shown for*
 490 *clarity. Data at 1 μm are not shown in several spectra due to high level of detector noise, as well as data at $\lambda < 0.5 \mu\text{m}$*
 491 *and $\lambda > 2.3 \mu\text{m}$ in some cases. Gray bars highlight the spectral region which is not accessible for Ma_MISS.*

492

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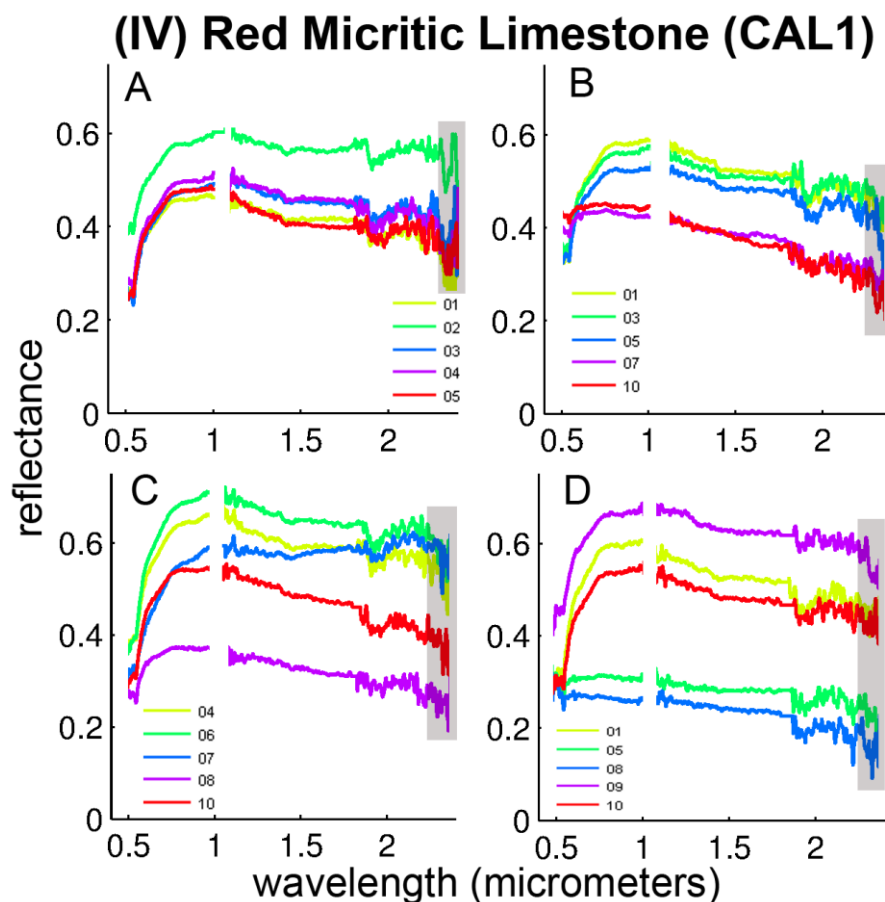
495

4.2.4 Red micritic limestone (CAL1)

496 Spectra acquired in all positions on the micritic limestone sample are quite homogeneous,
 497 with very few differences (fig.15). All spectra are characterized by the CO_3^{2-} absorptions at 2.2
 498 and 2.35 μm , although the noise is high in this spectral region (which is not accessible from
 499 Ma_MISS flight instruments); OH^- and H_2O bands are present at 1.4 and 1.9 μm . Spectra
 500 acquired on grey calcite veins appear relatively flat and with a blue slope (area B, pos.7,10;
 501 area C, pos.8,10; area D, pos.5,8). Spectra acquired in positions corresponding to the red
 502 micritic matrix show the CF Fe^{3+} absorption at 0.9 μm (Clark, 1999), due to some mixing of
 503 calcium carbonate with iron oxide, and a net change in slope at wavelengths shorter than 1.4
 504 μm . It must be noted that eventual carbonates identification by Ma_MISS spectra will not be
 505 based upon features occurring in the 2.2-2.5- μm region. Eventual CO_3^{2-} absorptions appearing
 506 in the 2.16-2.2- μm region could be identified. Nevertheless the identification should be based
 507 also on the comprehensive analysis of other spectral features, such as the reflectance level, the
 508 appearing of hydration features at 1.4-1.9 μm and their shape, the occurrence of CO_3^{2-}
 509 absorptions in the 1.75-2.00- μm range, the spectral behavior in the VIS range.

510

511



512

513 *Fig.15. Spectra acquired with Ma_Miss BreadBoard setup. Sample IV: Red Micritic Limestone (CAL1). The letters*
 514 *(A,B,C,D) correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized area,*
 515 *ten spectra in different positions have been acquired with Ma_Miss BB setup; here only five spectra are shown for*

516 clarity. Data at 1 μm are not shown in several spectra due to high level of detector noise, as well as data at $\lambda < 0.5 \mu\text{m}$
 517 and $\lambda > 2.3 \mu\text{m}$ in some cases. Gray bars highlight the spectral region which is not accessible for Ma_MISS.

518

519

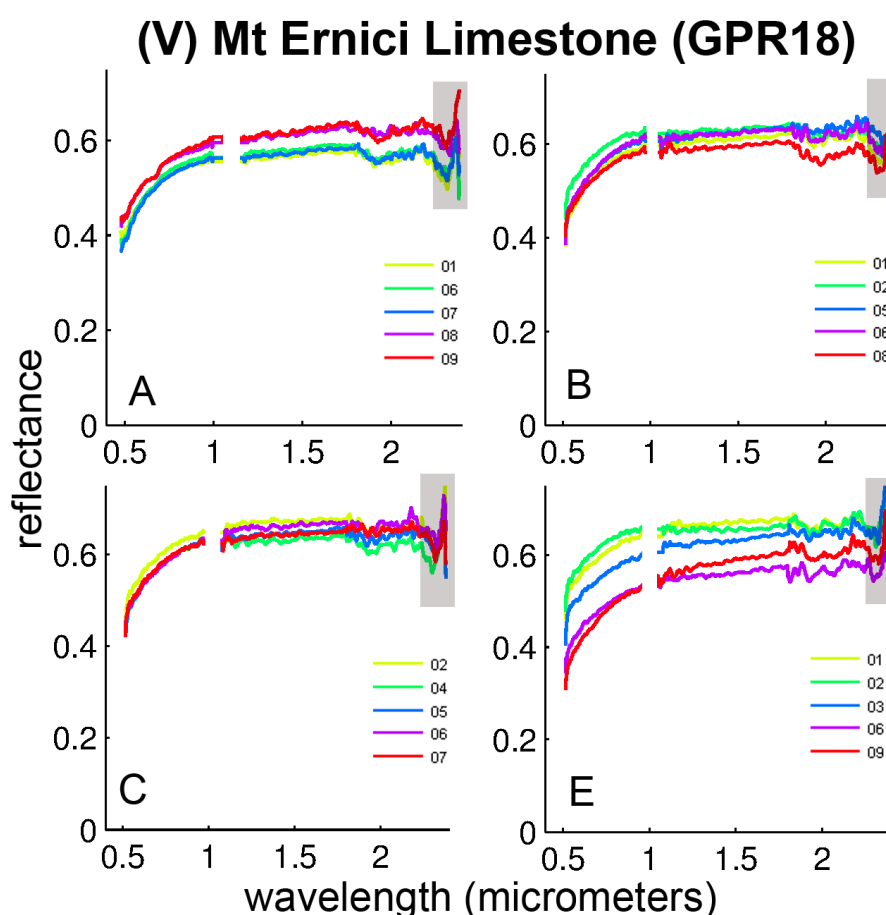
520

521 **4.2.5 Limestone from Mt Ernici (GPR18)**

522 Spectra of the limestone sample GPR18 are shown in fig.16. Spectral profiles are all very
 523 similar, with flat to slightly reddened slopes, and characterized by CO_3^{2-} absorptions near 2.2
 524 and 2.35 μm . The carbonate feature at 2.16-2.2 μm is visible in spectra showed in panel E
 525 (Gaffey, 1986; Clark et al., 1990), while in other spectra it constitutes a unique broadened
 526 band together with the one at 1.9 μm . XRD analyses show that this sample is constituted by
 527 anhydrous dolomite and ankerite, so the 1.9- μm feature can be attributed to some adsorbed
 528 water. Spectra in fig.16-A (pos.8 and 9) also show a weak feature near 0.65 μm , that could be
 529 attributed to an Fe^{3+} spin-forbidden band or to the presence of chlorophyll.

530

531



532

Fig.16. Spectra acquired with Ma_Miss BreadBoard setup. Sample V: Mt Ernici Limestone (GPR18). The letters (A,B,C,E) correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized area, ten spectra in different positions have been acquired with Ma_Miss BB setup; here only five spectra are shown for clarity. Data at $1\ \mu\text{m}$ are not shown in several spectra due to high level of detector noise, as well as data at $\lambda < 0.5\ \mu\text{m}$ and $\lambda > 2.3\ \mu\text{m}$ in some cases. Gray bars highlight the spectral region which is not accessible for Ma_MISS.

5. Comparison between different spatial scales

5.1 Method 1. Average

We used arithmetic average in order to compare spectra obtained with SPG and Ma_Miss BB setup as a first method. For each sample, and for each area (A,...,D) corresponding to a SPG spectrum, the ten spectra S_i acquired with Ma_Miss BB within a zone have been averaged. The resulting mean spectrum S_{avg} is given by:

$$S_{avg} = \sum_{i=1}^{10} S_i$$

In this way all Ma_Miss spectra are considered with the same weight. In fig.17 spectra obtained after averaging Ma_Miss data (S_{avg} , blue lines) are compared with SPG spectra (S_{spg} , green lines), for each analyzed area. Each computed spectrum S_{avg} has been compared with the SPG spectrum determining the sum of residuals (standard deviation):

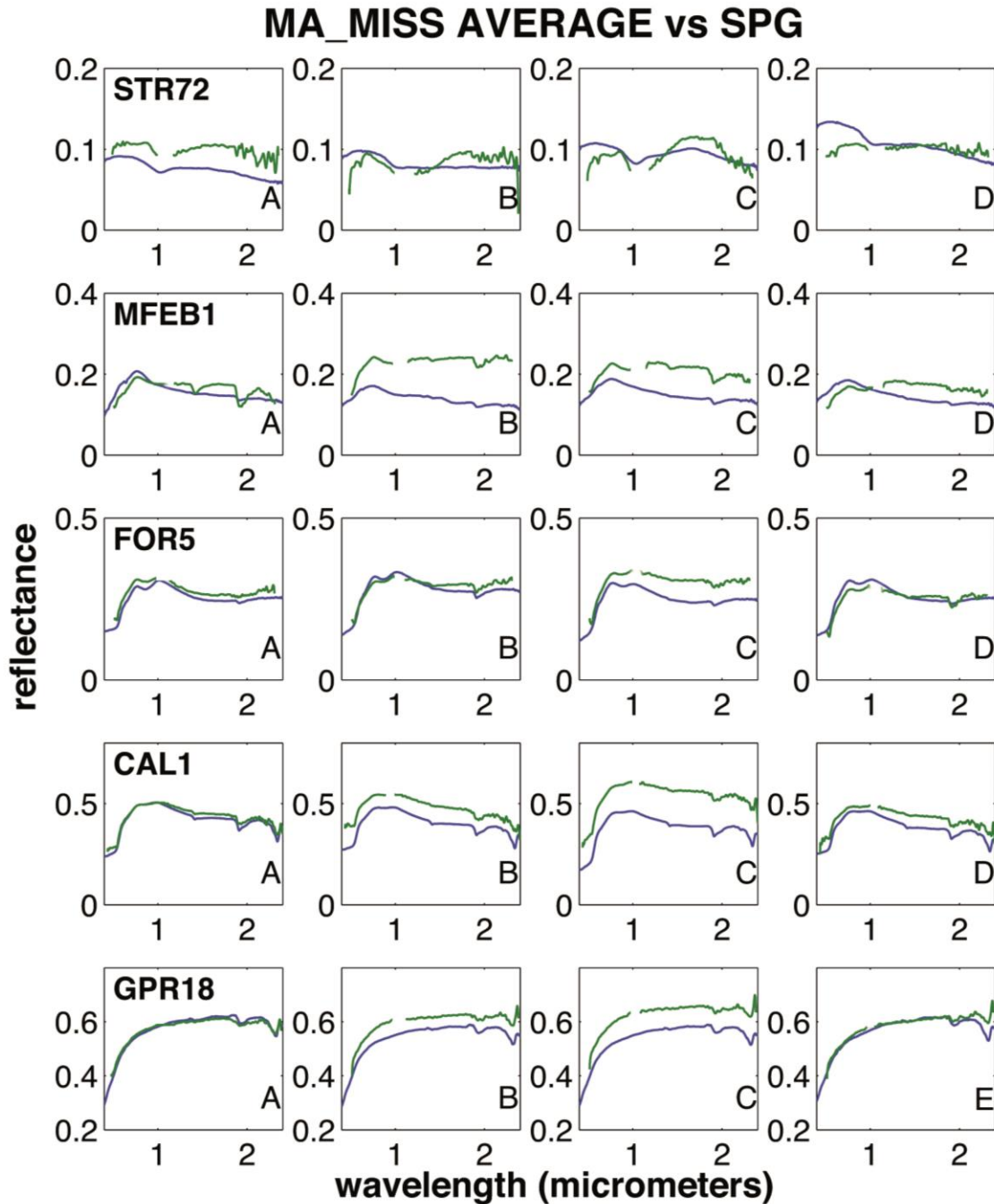
$$R_{avg} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (S_{avg} - S_{spg})^2}$$

Generally averaged Ma_Miss spectra can reproduce quite well SPG spectra of the same areas, although some discrepancies arise. The larger discrepancy between SPG and Average are where the sample is highly heterogeneous. It must be recalled that the ten Ma_MISS spectra acquired within the SPG spot, are selected choosing the points where differences are visible from a visual inspection. The selection effect is clear for the results of the volcanic samples (STR72, MFEB1 and FOR5) that are characterized by high surface heterogeneity.

Concerning the sample STR72 there are some differences in spectral slope and in reflectance, and generally SPG spectra appear more flattened. Ma_Miss spectra in positions B,C show a more prominent and broad absorption at $1\ \mu\text{m}$ than do SPG spectra: in the average spectra, olivine and pyroxene content constitute a major contribute, thus with the arithmetic average method they are overestimated by Ma_Miss. On the contrary SPG spectra of these areas are dominated by dark absorbing phases (magnetite, oxides). Spectral regions better approximated by Ma_Miss average spectra are the VIS ($0.4\text{-}1\ \mu\text{m}$) in area B, and NIR-IR ($1\text{-}2.2\ \mu\text{m}$) in area D (fig.13). SPG spectra of sample MFEB1 also appear more flattened with respect to Ma_Miss average spectra; spectra in positions B,C show greater differences in reflectance.

565 Ma_Miss Average spectra of areas A and D better approximate the SPG spectra, although the
 566 hydrated phases are overestimated in Ma_Miss spectra. Spectra of areas B, C preserve their
 567 spectral shapes in both datasets, but show different overall reflectance levels (fig.13). SPG and
 568 Ma_Miss average spectra of the three other samples (FOR5, CAL1 and GPR18) are very similar
 569 in shape and slope, although some shift in reflectance is evident especially for spectra in
 570 positions B,C (samples CAL1 and GPR18). Nevertheless all absorption features are visible at
 571 the same positions in both set of spectra.

572



573

574 *Fig.17. Comparison between SPG and Ma_Miss measurements: average spectra. Green line: Ma_Miss BB. Blue line:*
 575 *SPG.*

577 5.2 Method 2. Spectral linear mixing of reflectance spectra

578 The second method is linear mixing of reflectance spectra. For each area analyzed on each
 579 sample, in order to compare SPG and Ma_Miss spectra, we started by choosing three
 580 endmember spectra among the ten acquired with Ma_Miss. Endmembers were chosen
 581 following two criteria: a) for the volcanic samples, spectra with marked differences in slope,
 582 shape and absorption features where chosen; b) for the carbonate samples, because no
 583 spectral differences were observed, the spectra with minimum, medium and maximum values
 584 of reflectance were chosen. Calling S_1 , S_2 and S_3 the endmembers, the mixed spectrum S_{mix} is
 585 given by:

$$S_{mix} = a \cdot S_1 + b \cdot S_2 + c \cdot S_3$$

586 The endmembers spectra used for mixing are listed in tab.1. The parameters a , b , c give an
 587 estimate of the percent abundance of the selected components. The condition is that each of
 588 the parameters a , b , c were made to vary in the range 0-1 with steps of 0.1, and the final
 589 spectrum S_{mix} were taken in order to minimize the mean residuals:

$$R_{mix} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (S_{mix} - S_{spg})^2} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (a \cdot S_1 + b \cdot S_2 + c \cdot S_3 - S_{spg})^2}$$

590 In fig.20 the resulting minimum residual R_{mix} (red lines) are shown in comparison with R_{avg} :
 591 the formers (R_{mix}) are generally about one order of magnitude smaller than the latter ones
 592 (R_{avg}), thus indicating the goodness of this method. Looking at the spectra plotted in fig.18 we
 593 can see that the agreement between SPG and Ma_Miss mixed spectra is remarkably improved.

594 Concerning the sample STR72 the Ma_Miss mixed spectra (blue lines) are now characterized
 595 by reflectance values and spectral profiles very similar to SPG data. Spectra in positions B, C
 596 appear now more flattened than average spectra. The Fe^{3+} absorption at 0.9 μm appears in
 597 Ma_Miss spectra in position A, in both cases, while it doesn't appear in SPG spectra. The
 598 narrow feature appearing at about 0.65 μm in Ma_Miss spectra is an instrumental artifact.

599 Regarding the sample MFEB1 the overall spectral profiles are mutually consistent, although
 600 SPG spectra are characterized by a peak in the visible with higher reflectance, and are
 601 generally more flattened. The absorptions at 1.0 and 1.9 μm are well visible in both spectra.

602 Concerning the other three samples (FOR, CAL1 and GPR18) there is a very good agreement
 603 between the two methods (fig.18). SPG and Ma_Miss mixed corresponding spectra overlap
 604 almost entirely, with absorption features also appearing in the same positions. Very minimal
 605 differences in reflectance arise for sample FOR5 (pos.D, below 1.0 μm) and for CAL1 (pos.C,D,
 606 below 1.0 μm). Carbonate CO_3^{2-} features visible in SPG spectra of CAL1 and GPR18 in the 1.9-
 607 2.3- μm region are well approximated by Ma_Miss linear mixing spectra.

608 The linear mixing resulting parameters a , b , c are listed in tab.1. They provide an estimate of
609 the abundances of major components constituting the analyzed samples, although the result
610 depends on the choice of the endmembers. For example, in the sample STR72 area B, the
611 endmember n.3 (olivine; see spectra in fig.12) has an estimated abundance of 10%, while the
612 endmember 6 (dark opaque material) has an estimated abundance of about 80%. The mixed
613 spectrum of area C is instead dominated by pyroxene mineralogy (see for example
614 endmember spectra n.2 and n.10 in fig.12).

615

616

<i>Ma_Miss spectra endmembers</i>					$S_{\text{MIX-REFL}} = a \cdot S_1 + b \cdot S_2 + c \cdot S_3$		
sample:	STR72	<i>Endmember spectrum number</i>			a	b	c
	area A	2	5	10	0.3	0.1	0.3
	area B	3	6	9	0.1	0.8	0.2
	area C	1	2	10	0.2	0.2	0.5
	area D	1	6	7	0.1	0.3	0.4
sample:	MFEB1						
	area A	2	7	10	0.1	1.0	0.1
	area B	1	4	6	0.1	0.6	0.1
	area C	2	3	10	0.1	0.1	0.5
	area D	1	5	7	0.1	0.1	0.7
sample:	FOR5						
	area A	1	2	4	0.1	0.2	0.6
	area B	4	6	10	0.1	0.1	0.8
	area C	2	6	10	0.6	0.1	0.1
	area D	3	5	7	0.5	0.1	0.4
sample:	CAL1						
	area A	1	2	9	0.7	0.1	0.2
	area B	3	4	7	0.6	0.1	0.1
	area C	5	7	8	0.2	0.1	0.6
	area D	8	9	10	0.3	0.2	0.4
sample:	GPR18						
	area A	1	4	9	0.4	0.1	0.5
	area B	6	7	8	0.3	0.5	0.1
	area C	6	8	10	0.1	0.1	0.7
	area E	2	4	8	0.5	0.1	0.4

617

618 *Tab.1. Selected Ma_Miss spectra endmembers for linear mixing; spectra are shown in fig.12-16. Final parameters*
619 *a,b,c of linear mixing are also shown.*

620

621

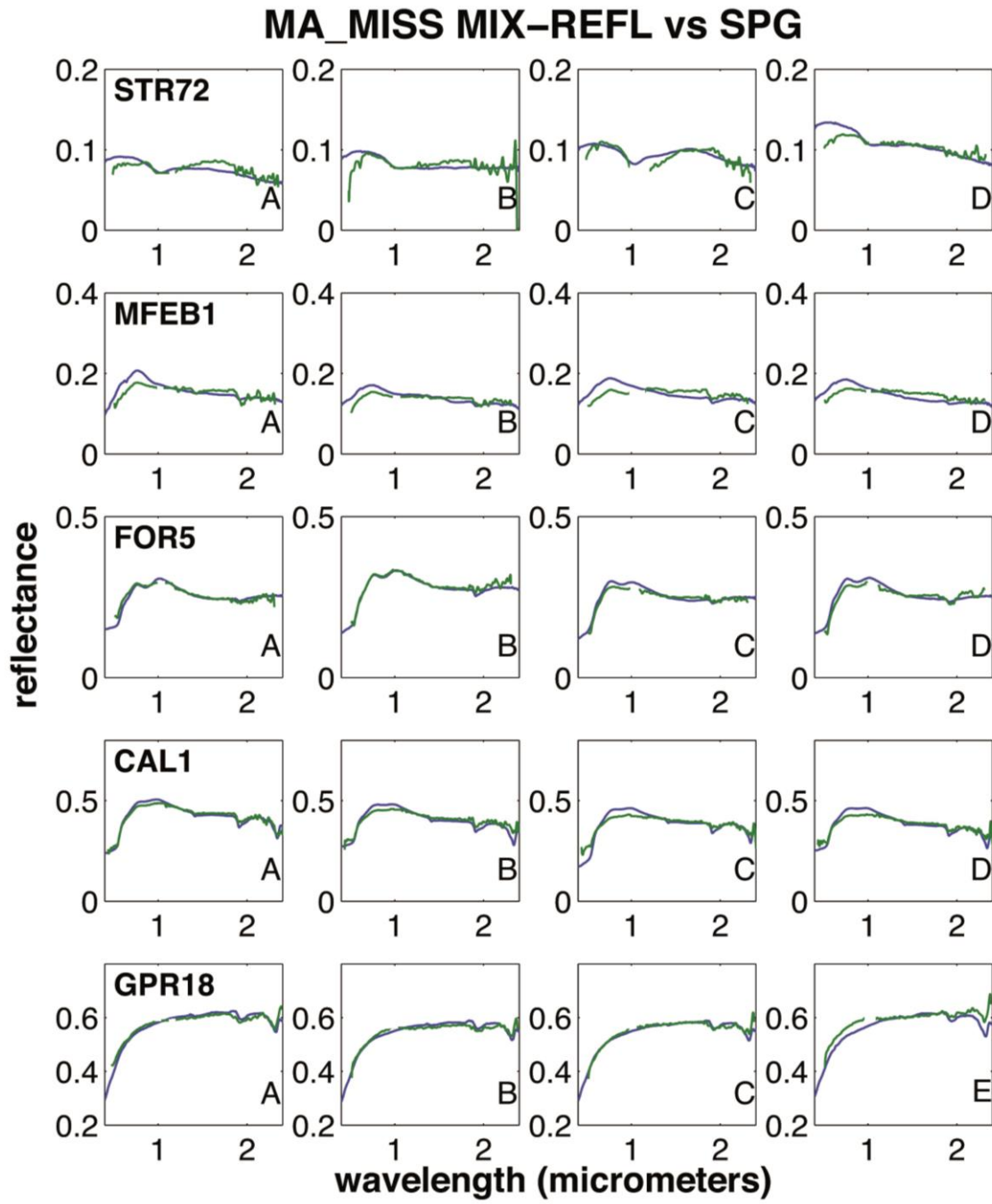


Fig.18. Comparison between SPG and Ma_Miss measurements: spectral linear mixing of reflectance spectra. Green lines: Ma_Miss BB. Blue lines: SPG.

5.3 Method 3. Spectral linear mixing of Single-Scattering Albedo spectra

A third method has been used to compare Ma_Miss and SPG spectra. Single-Scattering Albedo have been computed and then compared from both dataset. The use of SSA-spectra instead of reflectance spectra is valid in the case of microscopic mixing scale, whereas the direct combination of reflectance spectra is correct in the approximation of macroscopic mixing scale.

In this approach the SSA spectrum w corresponding to SPG measurements is first derived, using the relation:

$$R(i, e, g) = \frac{w}{4(\mu + \mu_0)} \times [(1 + B(g)) \cdot P(g) + H(\mu)H(\mu_0) - 1]$$

In which R is the measured reflectance, i and e are the incidence and emission angles respectively, $\mu = \cos(e)$ and $\mu_0 = \cos(i)$ [Mustard and Pieters, 1987 adapted from Hapke, 1981]. Under some assumptions, namely (i) grain sizes $\gg$ wavelengths, (ii) $i, e = 15-40^\circ$, (iii) particles compacted and scattering light isotropically, the above relation can be simplified (Mustard and Pieters, 1987). It must be highlighted that here we apply the Hapke model to slab surfaces, while in previous works, this model is typically applied to particulate minerals measured in laboratory (for example Mustard and Pieters, 1987) or to remote-sensing data (Ciarniello et al., 2011). Details on the calculation are provided in the on-line Supplementary Material. The simplified equation is:

$$R = \frac{w}{4(\mu + \mu_0)} \times \left(\frac{1 + 2\mu}{1 + 2\mu\gamma} \right) \times \left(\frac{1 + 2\mu_0}{1 + 2\mu_0\gamma} \right)$$

Subsequently the SSA spectra of the Ma_Miss endmembers spectra (the same as in section 4.5) have been computed. The linear mixing of Ma_Miss endmembers SSA spectra is given by:

$$w_{mix} = a \cdot w_1 + b \cdot w_2 + c \cdot w_3$$

and the optimal parameters a, b, c have been derived by minimizing the relation:

$$R_{mix} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (w_{mix} - w_{spg})^2}$$

The derived parameters are listed in tab.2, and the Ma_Miss SSA spectra w_{mix} are compared with SPG SSA spectra w_{spg} in fig.19. They show very good agreement for the two carbonate samples (CAL1 and GPR18) and the volcanic sample FOR5. Concerning the CAL1 and GPR18 carbonate samples, the CO_3^{2-} absorptions in the 1.9-2.3- μm region are well represented in the Ma_Miss linear mixing SSA spectra. Absorptions at 0.9 μm related to Fe^{3+} in FOR5 sample are visible in SPG spectra and well approximated by Ma_Miss linear mixing spectra for almost all areas. The albedo values are mutually consistent along the overall spectral range for these three samples. The matching is less good for the other two volcanic samples, MFEB1 and especially STR72. This is due to differences in the albedo of the samples as well as in the

659 spectral shape in the 1.2-2.2- μm region. Deviations between the two methods appear also for
 660 wavelengths $\lambda < 0.7 \mu\text{m}$, especially for STR72. While the two carbonates and FOR5 have
 661 moderately high levels of albedo, the sample MFEB1 has a moderately low level of reflectance,
 662 and STR72 is very dark: the assumptions and approximate equations used here are valid for
 663 albedo $> 10\%$, when materials don't behave like strong absorbers (i.e. in absence of very
 664 strong iron absorptions) (Mustard and Pieters, 1987).

665 This conclusion is further highlighted in fig.20, in which the residuals derived with the three
 666 methods are compared. Regarding the samples CAL1 and GPR18 the residual $R_{\text{mix-SSA}}$ is
 667 generally less than $R_{\text{mix-REFL}}$ and R_{avg} , while for the volcanic samples FOR5 and MFEB1 we have
 668 $R_{\text{mix-REFL}} < R_{\text{mix-SSA}} < R_{\text{avg}}$. Finally the highest values of $R_{\text{mix-SSA}}$ are obtained for the darkest
 669 sample STR72.

670

$W_{\text{MIX-SSA}} = a \cdot w_1 + b \cdot w_2 + c \cdot w_3$				
		a	b	c
sample:	STR72			
	area A	0.2	0.1	0.5
	area B	0.2	0.6	0.2
	area C	0.1	0.3	0.5
	area D	0.1	0.4	0.4
sample:	MFEB1			
	area A	0.1	0.9	0.1
	area B	0.1	0.6	0.2
	area C	0.3	0.1	0.4
	area D	0.1	0.2	0.6
sample:	FOR5			
	area A	0.1	0.5	0.4
	area B	0.1	0.1	0.8
	area C	0.7	0.1	0.1
	area D	0.7	0.1	0.2
sample:	CAL1			
	area A	0.8	0.1	0.1
	area B	0.1	0.1	0.8
	area C	0.1	0.2	0.7
	area D	0.3	0.1	0.6
sample:	GPR18			
	area A	0.6	0.1	0.3
	area B	0.1	0.1	0.8
	area C	0.1	0.1	0.8
	area E	0.5	0.1	0.4

671

672 *Tab.2. Linear mixing of Single-Scattering Albedo spectra, final parameters a, b, c.*

673

MA_MISS MIX-SSA vs SPG

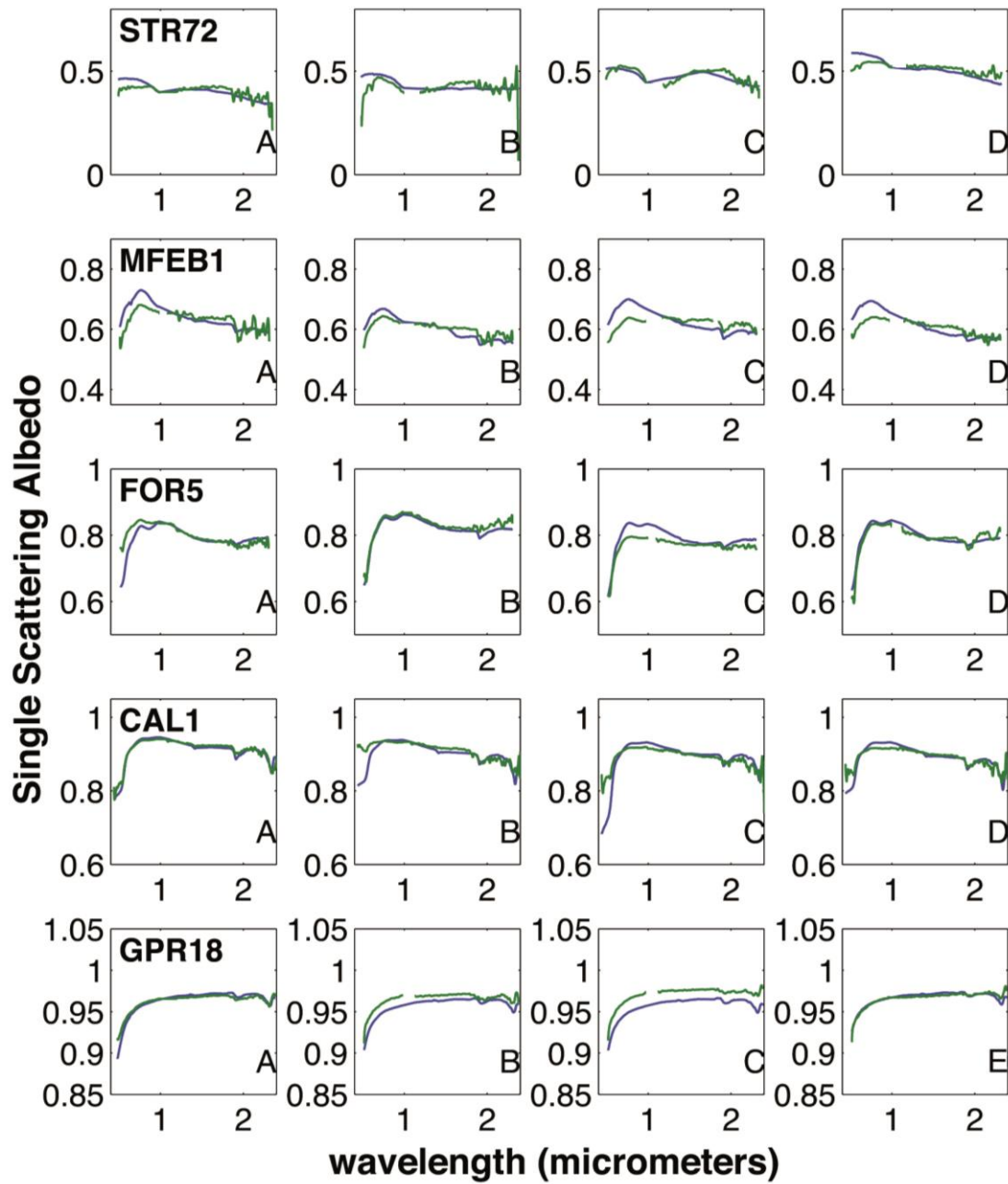


Fig.19. Comparison between SPG (blue lines) and Ma_Miss (green lines) measurements: spectral linear mixing of Single Scattering Albedo (SSA) spectra.

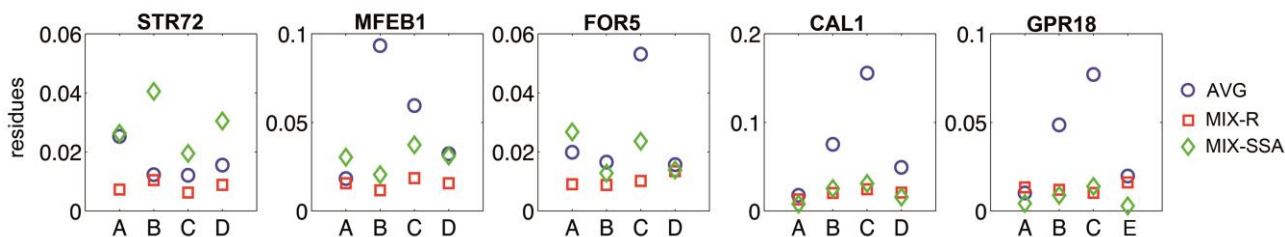


Fig.20. Sum of residuals computed by comparing SPG spectra and Ma_Miss BB spectra, obtained by (i) averaging (blue diamonds), (ii) using linear mixing of reflectance spectra (red squares), (iii) using linear mixing of Single-Scattering Albedo spectra (green diamonds). On X-axes the letters corresponding to analyzed areas are indicated.

6. Discussion

Differences between the two instruments and spatial scales

Analyses of the five rock slabs (three volcanic and two carbonate samples) with Spectro-Goniometer setup permitted to determine their bulk spectral composition at a scale >1 mm, given the SPG spot size of about 6 mm. This analysis allows to obtain an overall information about the average spectral behavior of the samples; it takes advantage in that it is useful in order to provide a first immediate approximate characterization of a rock sample in terms of average absorptions, spectral slopes, reflectance level; in principle this could be helpful in assign a sample to a macro-category of rocks (volcanic, sedimentary, etc.). Nevertheless on the other side the analyses performed with this setup are not able to provide, for example in a volcanic sample, suitable information to discriminate between groundmass and phenocrysts or xenoliths. The large acquisition spot generally includes many different mineralogical phases and cannot help in discriminating among surface heterogeneity at smaller scale.

Analyses performed using the Ma_Miss BreadBoard setup result in a major improvement in the capability of investigate the surface heterogeneity of the rocks. The smaller spot size obtainable thanks to the coupling of Ma_Miss Optical Head and fiber (120 μm) allowed to perform spectral investigation of rocks surfaces at one tenth of millimeter-scale, thus getting information on inclusions and mineral grains of the order of hundred micrometers in size. Analysis of volcanic porphyritic samples with this spatial resolution could in principle permit to spectrally distinguish the rock groundmass from phenocrysts/xenoliths or lithic clasts. Spectral study of igneous holocrystalline plutonic rocks allows to discriminating among the different mineral crystals, thus evaluating the surface heterogeneity in great detail and getting clues about mineralogical diversity.

Ma_MISS high spatial resolution also proves to be able to resolve a greater number of minerals than what resolved by the 6-mm resolution Spectro-Goniometer. A good point is for example the identification of plagioclase grains (fig.13B, spectrum #7) within the lava sample from the Montiferru (MFEB1). Plagioclases are typically difficult to be detected with spectroscopy especially in the VNIR range and when they are embedded in a matrix with more spectroscopically active minerals.

Applicability of Hapke model to bulk rock slabs

The application of Hapke model to bulk rock slabs spectra must be somewhat discussed. The Hapke model (Hapke, 1981, 1993) has been fundamentally developed in order to explain the optical behavior of particulate materials, typically compact/loose powders (i.e. planetary regoliths) or atmospheres, and in that sense has been widely applied by many authors. When this model is applied to bulk rock slabs some differences with respect to particulate must be taken into account.

Widely dispersed particles can be treated as a continuum medium, in which no interferences arise between light rays propagating among particles, and grains don't cast shadows on each other. When particles get more closely packed each other or they are in contact, the medium can no longer be considered as continuum. Interferences arise between portions of waves scattered by adjacent grains; nevertheless for irregular shaped and random oriented particles all coherent effects will be averaged and erased (Hapke, 1981).

Moreover while in a widely dispersed particulate medium, in which particles are $d \gg \lambda$ in size, diffraction cannot be neglected (it's related to forward-scattering), in closely-packed or contact grains the diffraction becomes meaningless and undistinguishable from light scattered by other adjacent particles.

Another aspect is that in a widely disperse particulate medium each single grain is fully illuminated and the scattering/absorption efficiencies are full quantities. In a medium in which interstices are small (compacted powder or bulk rock) the particle cross sections are reduced by other particles' shadows. This implies that scattering and absorption efficiencies are all reduced by the same factor. Anyway their ratios (in w and $P(g)$) in principle remain unchanged.

It is to be considered that within a slab the optical coupling between grains is different with respect to a powder: while relative refraction indexes at grain boundaries in a powder are typically mineral/air or mineral/vacuum, relative refraction indexes within a slab are mineral/mineral (Hapke, 1993). This different optical coupling causes surficial reflections at grain boundaries to be reduced, thus implying a variation in Q_s (*scattering efficiency*) and $p(g)$. Forward scattering dominates in optically thin grains within a slab (Hapke, 1993), which in turn results darker than separate grains. As a consequence optical properties of bulk rock/slabs are somewhat different with respect to properties of separate minerals extracted from the bulk rock: optical parameters obtained are somewhat different in the two cases, nevertheless equations are still applicable.

Comparison of the three methods and endmember retrieval

The first method used to combine Ma_Miss spectra consisted in averaging all measured spectra. Although this results in a good first order approximation to reproduce SPG spectra, nevertheless it is imperfect. The arithmetic average of all measured spectra within

a zone results in all spectra having the same statistical weight. The spectra measured with Ma_Miss within a zone correspond to different mineralogical phases that can show a different spectral behavior and especially can have diverse spectral weights within a mixture: more absorbing phases (e.g. iron oxides) can dominate the mixture (i.e. SPG) spectrum even if they have low abundance.

The other two methods (linear mixing of reflectances and of SSA) results in a substantial improvement and a better matching between combined Ma_Miss spectra and corresponding SPG spectrum. The linear mixing algorithm correctly takes into account the diverse spectral weight of different mineralogical phases. However in the linear mixing procedure a source of error can be manual choice of endmembers. Among the ten Ma_Miss spectra acquired within each SPG zone, three endmember spectra were visually chosen: the choice criterion was that of select the three most diverse spectra among all. Clearly this visual/manual choice of endmembers can be a source of error, because some mineralogical phases can be over/underestimated. A further general source of error can arise from the limited number of Ma_Miss spectra (ten) acquired within each SPG zone. Ma_Miss spectra were collected randomly within each zone after checking that zone both visually and using optical microscope. Clearly a higher number of Ma_Miss spectra acquired within each zone would result in a better matching, when combined and mixed, with SPG spectra. A different collection pattern of the 10 spectra within each SPG zone could give in principle a somewhat different sampling of the same area, although we would expect statistically the same results.

7. Conclusions

In this work we analyzed a set of five rock slabs by mean of VNIR spectroscopy in order to characterize the Ma_Miss instrument capability to accomplish mineral investigations. For this purpose, we used two different instruments: (i) the Spectro-goniometer setup, that is a Fieldspec Pro coupled with a goniometer, with spectral range 0.35-2.5 μm and spatial resolution spot of 6 mm; (ii) the ExoMars/Ma_Miss BreadBoard setup, with analogous spectral range and higher spatial resolution (spot of 0.12 mm).

The rock slabs were first analyzed with the Spectro-goniometer setup (SPG), acquiring spectra from few 6-mm-diameter areas on the rock surfaces; the SPG allows getting an average information on a ten-millimeter scale. Successively the analysis of the same areas by using the Ma_Miss breadboard (BB) setup, acquiring 10 spectra with increased spatial resolution within each SPG area, allowed retrieving spectral information with much greater detail, on sub-millimeter scale. The smaller spot of Ma_Miss (0.12 mm) allows recognizing different mineralogical phases with size down to about one hundred microns.

For each analyzed zone, spectra acquired with Ma_Miss at 120 μm spatial resolution were combined in different ways in order to be compared with the SPG spectrum of the same zone: (i) by arithmetic average of all ten spectra; (ii) by linear mixing of three endmember

refletctances; (iii) by linear mixing of three endmember Single Scattering Albedos (using Hapke Model).

The average method provides good agreement between SPG and Ma_Miss spectra, although linear mixing of endmembers reflectance spectra results in a notable improvement. Further improvement is obtained when combining and comparing Single-Scattering Albedo spectra instead of the reflectance. This approach is more valid and rigorous in the case of microscopic mixing scale of the materials; nevertheless it shows some limitation and mismatching when applied to samples that behave like very strong absorbers, i.e. characterized by reflectance levels less than 10%.

Linear mixing, both of reflectance spectra and of Single-Scattering Albedo, of Ma_Miss BB spectra resulted in an excellent agreement between mixed Ma_Miss spectra and SPG spectra of corresponding areas, better than simply arithmetical averages.

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