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2 ***using Ma\_Miss BreadBoard instrument***

3

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10

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12

13

14 **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

35 **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- $\mu\text{m}$ ). 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  $\mu\text{m}$ ) 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  $\mu\text{m}$ ) 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.

121

## 122 **2. Experimental setup**

### 123 **2.1 Ma\_Miss Breadboard setup**

124 The Laboratory BreadBoard setup in use at INAF-IAPS (described in detail in De Angelis et al.,  
125 2014) consists of the main optical subsystems of the Ma\_Miss instrument (Coradini et al.,  
126 2001; Preti et al., 2011) except for the spectrometer. The illumination source is a 5W  
127 miniaturized lamp integrated within the instrument. A bundle of optical fibers carries the  
128 light from the lamp to the Optical Head, which consists of several miniaturized mirrors and  
129 acts to focus the light on the external target. The light is focused through a sapphire window  
130 on the target, at a distance of 0.6 mm; then the scattered light is recollected by the same  
131 Optical Head, and an optical fiber carries the signal to a spectrometer. In this setup the  
132 BreadBoard is coupled with a FieldSpec Pro, which operates in the 0.35-2.5  $\mu\text{m}$  range. The  
133 Ma\_Miss instrument will nominally operate in the 0.4-2.2  $\mu\text{m}$  range. The illuminated area on  
134 the target is 1 mm, while the spatial resolution is about 0.12 mm.

135

### 136 **2.2 Spectro-Goniometer setup**

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

144

### 145 **2.3 Optical microscopy**

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

154

155

156

## 157            2.4    XRF and XRPD analyses

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

166 Before XRF analyses the samples have been ground with planetary mill Fritsch Pulverisette 7  
167 and ZrO mortars, using four 2-minutes cycles at 300 Hz. Five grams of each sample have been  
168 mixed with 2 ml of Elvacite (15% in acetone), and this has been mixed with 5 grams of H<sub>2</sub>BO<sub>3</sub>  
169 in an aluminum capsule. Pellets have been finally produced pressing this mixture at 25 tons.  
170 Analyses have been conducted on pellets using a WDXRF Rigaku Supermini 200 spectrometer  
171 with Pd source (50 kV, 4 mA, 200 W) in vacuum. Siliceous rocks standards from CNRS SARM  
172 GRPG Paris have been used for calibration. For XRPD analyses an Empyrean Panalytical  
173 Diffractometer has been used, with operating conditions 40 kV and 40 mA and CuK $\alpha$  radiation  
174 as source. Bragg- Brentano geometry was used. Sample stage was a flat specimen holder. The  
175 incident beam path was given by: Soller slits 0.02 rad, fixed incident beam mask 10 mm, anti-  
176 scatter slit 1/2°, divergence slits 1/4°. The diffracted beam path was characterized by: anti-  
177 scatter slits 7.5 mm; Soller slits 0.02 rad, large beta filter-Nickel detector: PIXcel3D. A phase  
178 quantification of mineralogical composition was obtained using the software HighScore  
179 Plus™ (Panalytical).

180

## 181            3. Samples characterization

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

187

### 188            3.1    Macroscopic description and XRF/XRD analyses

#### 189            3.1.1   *San Bartolo lava (STR72)*

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

196 phenocrysts), clino- and ortho-pyroxenes and opaque minerals (oxides, titaniferous  
197 magnetite) are present. Moreover San Bartolo lavas also contain mafic/ultramafic xenoliths  
198 with gabbroic, gabbro-noritic and gabbro-anorthositic compositions. This lava can be  
199 classified as porphyritic high-K calc-alkaline basalt (Laiolo and Cigolini, 2006), with SiO<sub>2</sub>,  
200 52.60 wt%; Na<sub>2</sub>O+K<sub>2</sub>O, 3.86 wt% (Peccerillo et al., 2013).

201

202

### 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 SiO<sub>2</sub> content of 50.9%  
211 and an alkali content of Na<sub>2</sub>O+K<sub>2</sub>O=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 SiO<sub>2</sub> content of 65.1% and an  
222 alkali content of Na<sub>2</sub>O+K<sub>2</sub>O=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

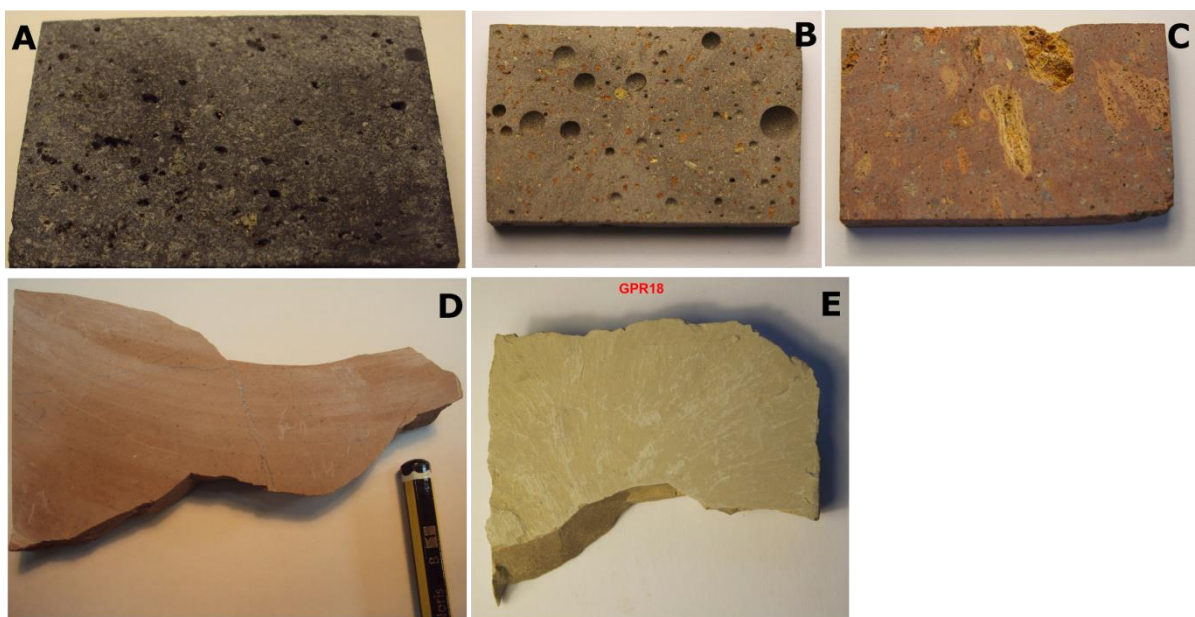
234 that the mineralogical composition consists mainly of calcite (96%) and quartz (4%); the  
235 amounts of minerals responsible of reddish color of the studied sample are below the  
236 detection limit of diffractometer (1%).

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 [ $\text{Ca}(\text{Fe}^{2+},\text{Mg},\text{Mn})(\text{CO}_3)_2$ ].

243



244

245

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).*

249

250

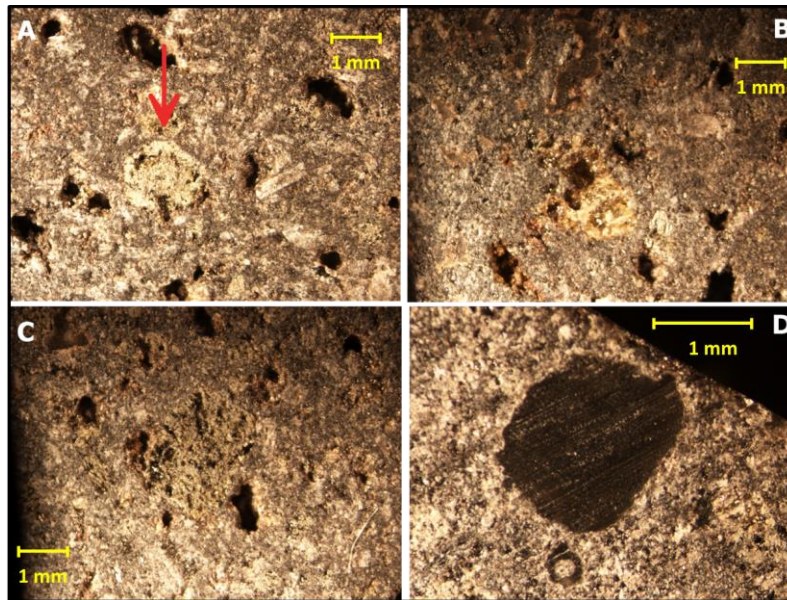
## 251 **3.2 Analyses by optical microscopy**

### 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.

261



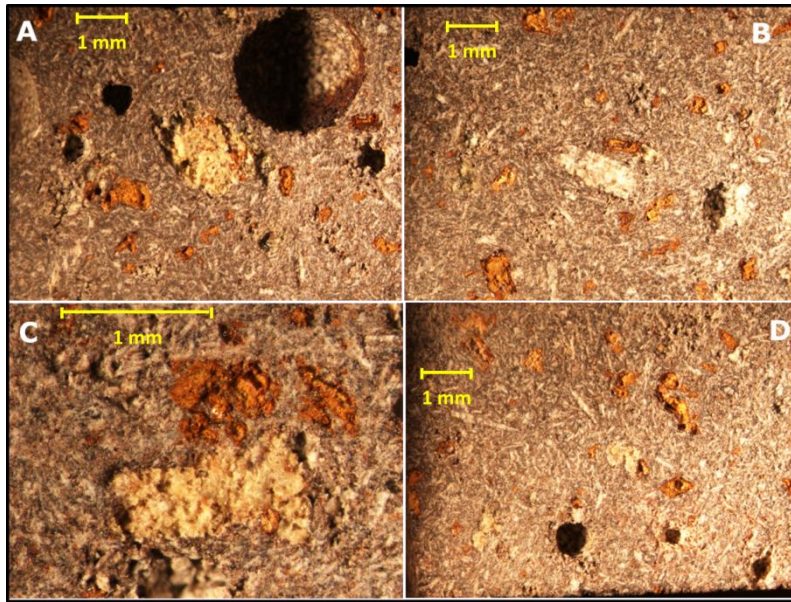
262

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.



276

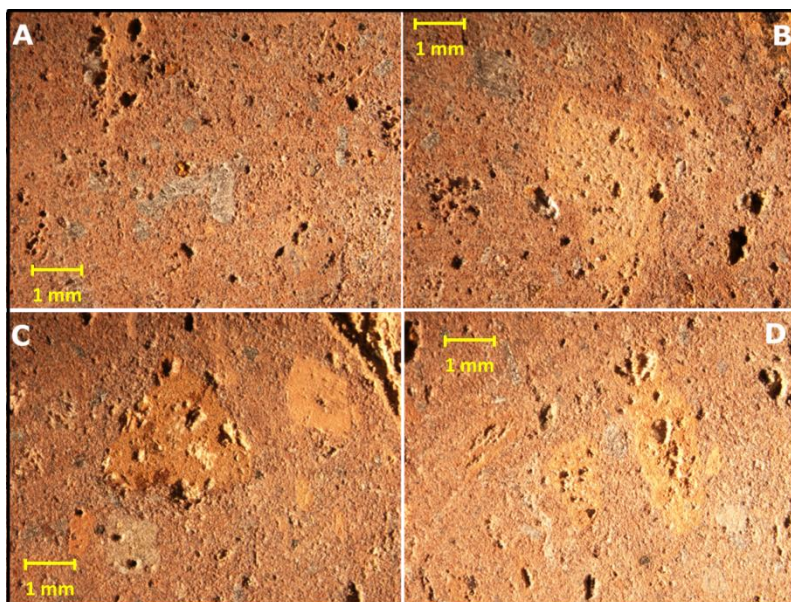
277 *Fig.3. Microimages of Montiferru/Bonarcado (MFEB1) sample. Observations under optical microscope*  
 278 *performed on rocks surfaces in reflection light. Magnifications used are: A,B,D = 1X. C = 3X.*

279

### 280 **3.2.3 Lava from Fordongianus (FOR5)**

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

287



288

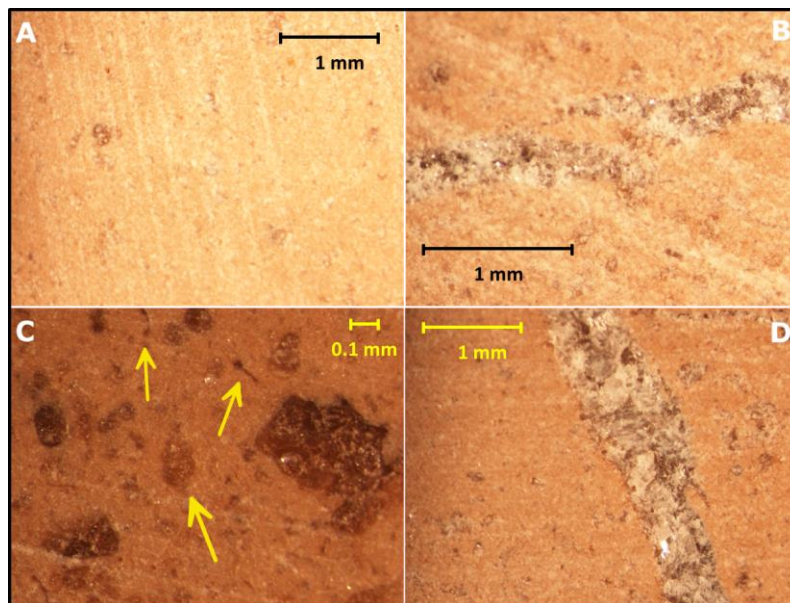
289 Fig.4. Microimages of Montiferru/Fordongianus (FOR5) sample. Observations under optical microscope  
290 performed on rocks surfaces in reflection light. Magnifications used are: A,B,C,D = 1X.

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



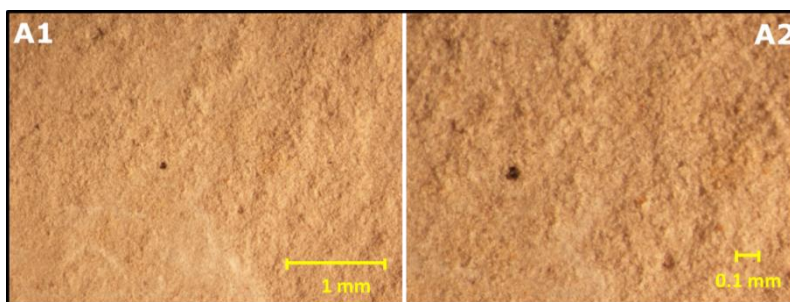
301

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.



311

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

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#### 319 **4. Results: spectral analyses**

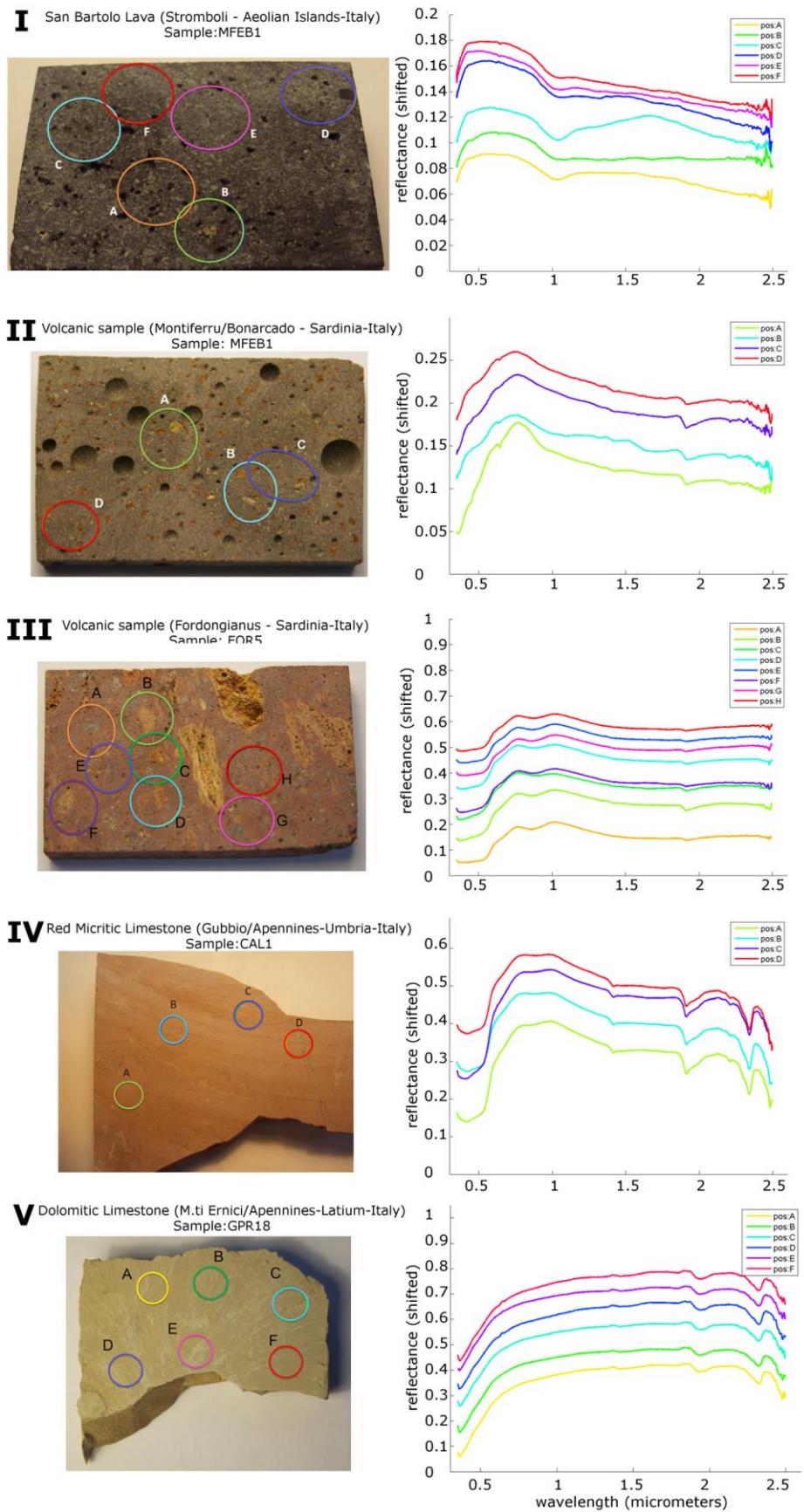
320 All samples have been first analyzed with the SPG setup, and subsequently with the Ma\_MISS  
321 BB setup. For each sample, several areas on the surface have been analyzed with the SPG, each  
322 area corresponding to the instrumental acquisition area of 6 mm. Then the BB setup has been  
323 used to acquire spectra with higher spatial resolution (120  $\mu\text{m}$  of spatial resolution): thus 10  
324 spectra in different positions have been acquired with the BB setup, inside each previous SPG  
325 area. In the following sections, the measurements will be described separately and then  
326 compared with different methods.

327

##### 328 **4.1 Measurements with Spectro-Goniometer**

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

332



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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338

#### 4.1.1 San Bartolo lava (STR72)

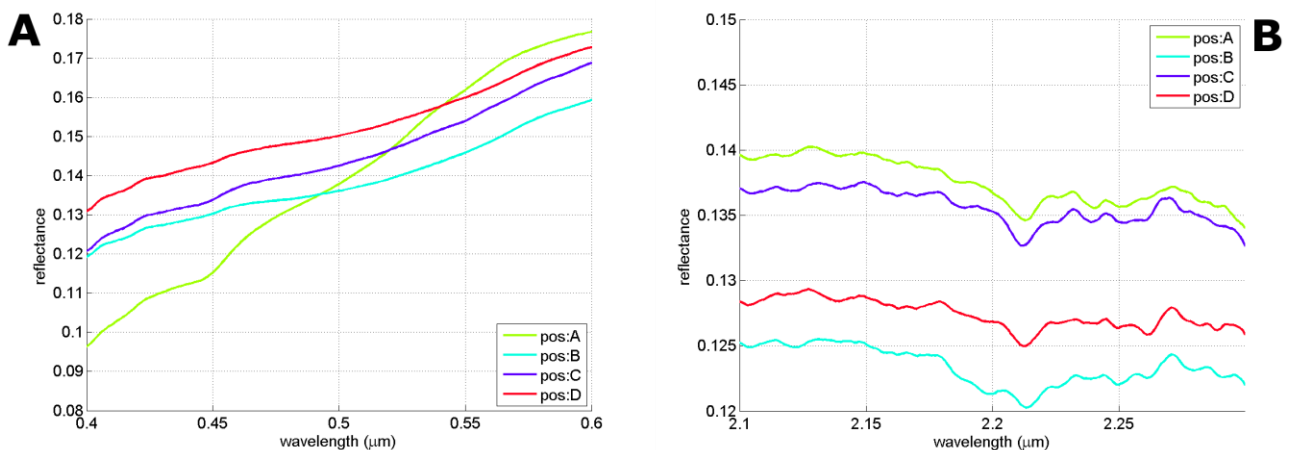
339 Six areas have been analyzed with the SPG setup on the surface of the San Bartolo sample  
340 (fig.7-I). One single spectrum has been acquired for each area from A to F. All spectra are  
341 characterized essentially by the crystal field (CF) absorption within Fe<sup>2+</sup> at 1 μm (Burns,  
342 1993) and by a net negative (“blue”) slope in the IR. Spectra in positions B, E and F are nearly  
343 flat in the NIR range, although E and F show an absorption at 1 μm; the spectrally dominating  
344 mineralogy could be pyroxenes with iron oxides/sulfides that are responsible of very low  
345 reflectance. Spectra in positions A, C and D also show a 1-μm absorption whose right shoulder  
346 extends towards longer wavelengths, up to 1.7 μm: this could be indicative of a mixture of  
347 pyroxenes with olivine. Spectra A, C and D moreover show the Fe<sup>2+</sup> absorption at 2 μm typical  
348 of pyroxene. The weak feature appearing at 0.5 μm in spectra A and B is related to spin  
349 forbidden transitions in Fe<sup>2+</sup> in pyroxenes (Klima et al., 2007; Cloutis and Gaffey, 2009).  
350 However a continuum removed study would permit more quantitative analyses.

351

352

#### 4.1.2 Lava from Montiferru/Bonarcado (MFEB1)

353 Spectra with SPG setup have been acquired in four areas on the surface of the  
354 Montiferru/Bonarcado sample (fig.7-II). They are all characterized by a blue slope in the IR; a  
355 weak Fe<sup>2+</sup> absorption at 1 μm is superimposed onto the negative continuum in spectra A and  
356 B. Spectra C and D do not show evident CF absorptions, although a continuum removed  
357 investigation could highlight weak absorptions at 1 μm. Spin-forbidden transitions appear in  
358 the visible near 0.5 μm (probably Fe<sup>2+</sup>) and in the range 0.44-0.45 μm (Fe<sup>2+</sup>, Cr<sup>3+</sup> or Ti<sup>3+</sup>) (see  
359 Klima et al., 2007) (fig.8A). All spectra show the signs of aqueous alteration, with OH<sup>-</sup> and H<sub>2</sub>O  
360 overtone absorptions near 1.4 and 1.9 μm. A weak feature appears near 2.21 μm, that could  
361 be attributed to Al-OH vibrational transitions (fig.8B) (see for example Clark et al., 1990). The  
362 broad band at 1.7 μm that appears in the spectrum B could also be due to Al-OH (see for  
363 example Clark et al., 1990).



364

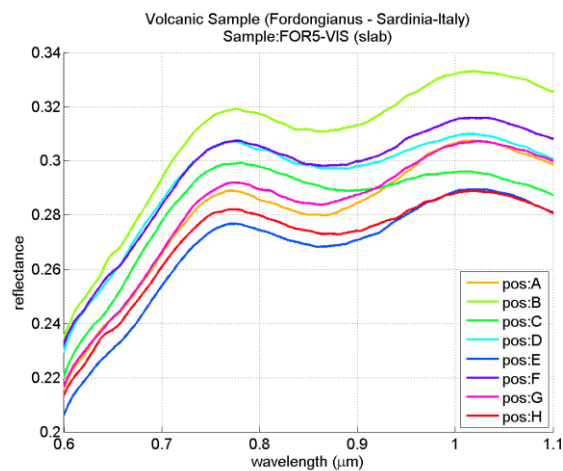
365 Fig.8. Sample from Montiferru/Bonarcado (MFEB1). A: electronic transitions in the VIS range. They are  
366 due to  $Fe^{2+}$  ( $0.5 \mu m$ ) and other transition elements. B: absorption band at 2.21 micron: it is due to Al-OH  
367 vibrational transition.

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  $1.9 \mu m$ , indicating some water content in the sample, and the  
373 band at  $0.86-0.90 \mu m$  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.

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377

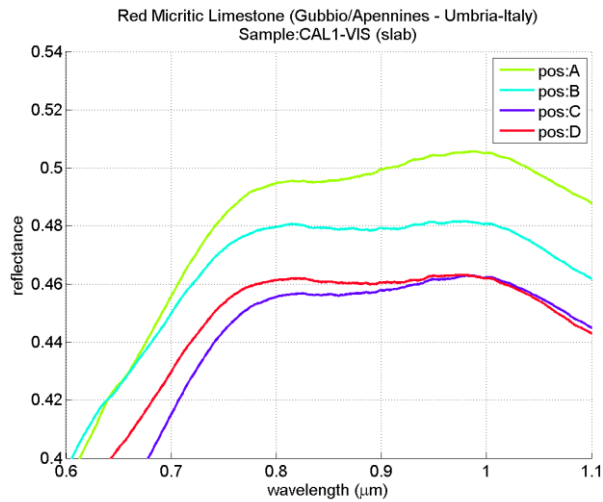
378 Fig.9. Sample from Montiferru/Fordongianus (FOR5). The absorption feature near  $0.87-0.90 \mu m$  is likely  
379 due to  $Fe^{3+}$  transition.

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  $2.34 \mu m$  (Hunt, 1977; Gaffey, 1986;  
385 Clark et al., 1990),  $OH^-$  feature at  $1.4 \mu m$  and the  $H_2O$  feature at  $1.9 \mu m$ . Absorptions occurring  
386 at  $0.9 \mu m$  are likely due to CF transitions within ferric ions ( $Fe^{3+}$ , fig.10) (Morris et al., 1985;  
387 Clark 1999).

388



389

390 *Fig.10. Red Micritic Limestone (CAL1). The absorption feature near 0.87-0.90 μm is likely due to Fe<sup>3+</sup>*  
 391 *transition.*

392

393 **4.1.5 Limestone from Mt Ernici (GPR18)**

394 The spectra of this limestone (fig.7-V; spectra shifted for clarity) are all very similar, both in  
 395 overall shape and in reflectance value: the maximum reflectance is about 0.55-0.60.  
 396 Absorption bands diagnostic of carbonate ion CO<sub>3</sub><sup>2-</sup> appear at 1.75 and 2.34 μm (Gaffey, 1986,  
 397 1987); the feature at 2.2 μm is very weak and discernible only in spectrum of position F.  
 398 Hydroxyl and water absorptions occur at 1.4 and 1.9 μm respectively.

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## 4.2 Measurements with Ma\_Miss Breadboard

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### 4.2.1 San Bartolo lava (STR72)

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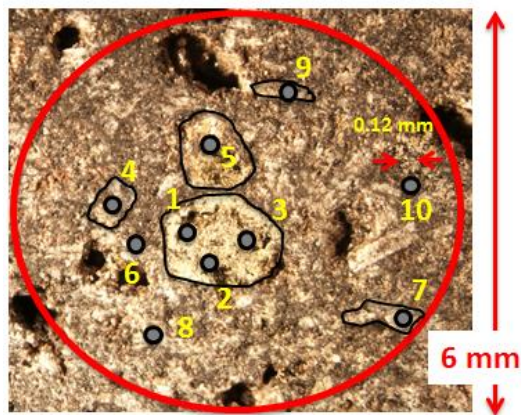
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427

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  $0.9\ \mu\text{m}$  ( $\text{Fe}^{3+}$ ) and  $1\ \mu\text{m}$  ( $\text{Fe}^{2+}$  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  $\text{Fe}^{3+}$ ). 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.



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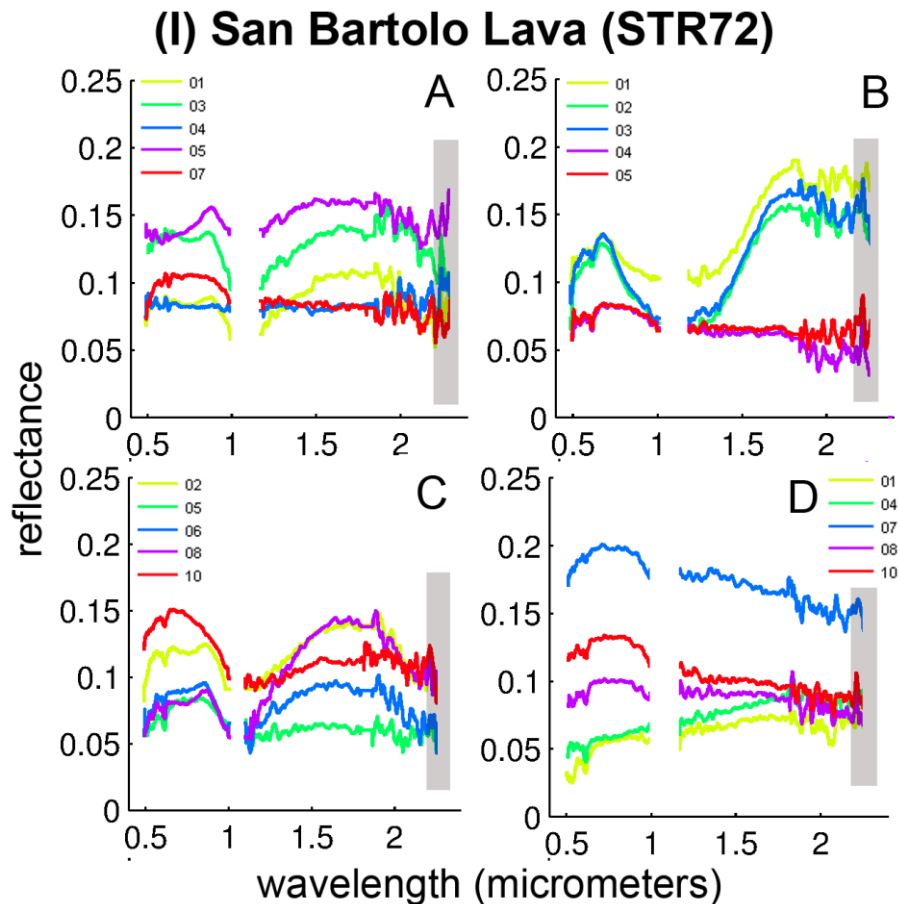
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*Fig.11. comparison between the spot of the SPG (6 mm, red circle) and the spot of Ma\_Miss BB (0.12 mm, black-grey circles, numbered from 1 to 10); the sample is STR72, area A (see spectra in fig.12-A). Black irregular contours are traced to highlight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



434

435 *Fig.12. Spectra acquired with Ma\_Miss BreadBoard setup. Sample I: San Bartolo Lava (STR72). The letters (A,B,C,D)*  
 436 *correspond to the areas analysed with Spectro-goniometer setup (fig.2). In each single 6-mm-sized area, ten spectra*  
 437 *in different positions have been acquired with Ma\_Miss BB setup; here only five spectra are shown for clarity. Data*  
 438 *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  $\lambda > 2.3$*   
 439  *$\mu\text{m}$  in some cases. Gray bars highlight the spectral region which is not accessible for Ma\_MISS.*

440

#### 441 **4.2.2 Lava from Montiferru/Bonarcado (MFEB1)**

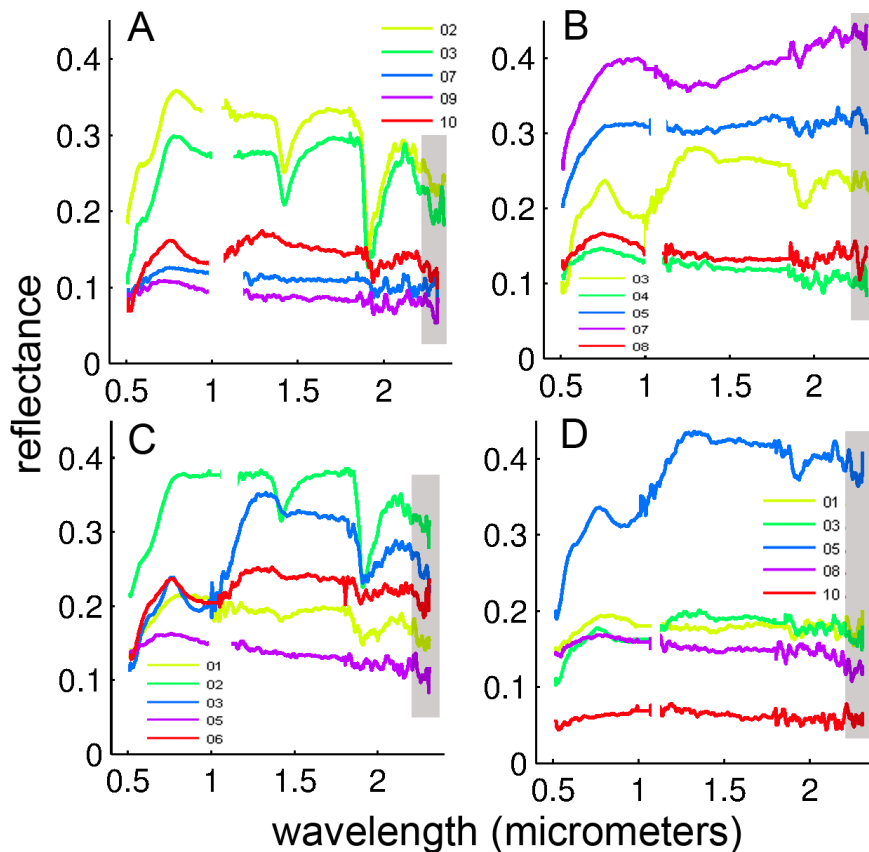
442 Spectra in fig.13-A (relative to area A in fig.7-II) show a great diversity, indicating several  
 443 different mineralogical phases within the observed area. Spectra 2 and 3 (blue and green  
 444 lines), with spin-forbidden absorptions at  $0.65 \mu\text{m}$  ( $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{Ti}^{3+}$ , see for example Clark et  
 445 al., 1990, Klima et al., 2007), CF at  $1 \mu\text{m}$  ( $\text{Fe}^{2+}$ ), vibrational overtones at  $1.4 \mu\text{m}$  ( $\text{OH}^-$ ) and  $1.9$   
 446  $\mu\text{m}$  ( $\text{H}_2\text{O}$ ) are indicative of hydrated silicate minerals. A feature at  $2.2 \mu\text{m}$  in spectrum 3 could  
 447 be attributed to Al-OH absorption, suggesting the presence of montmorillonite or other  
 448 alteration phases associated to plagioclases (see Clark et al., 1990); it must be stressed  
 449 however that features occurring longward of  $2.2 \mu\text{m}$  are not accessible for Ma\_MISS flight  
 450 instrument. The spectrum 10 is indicative of iron oxides (absorption at  $1 \mu\text{m}$ ) with some  
 451 degree of hydration. Spectra 7 and 9 indicate the presence of dark/opaque minerals (oxides).  
 452 Spectra of iron hydroxide goethite, characterized by  $\text{Fe}^{3+}$  absorption at  $0.9 \mu\text{m}$  and OH/ $\text{H}_2\text{O}$   
 453 absorptions at  $1.4\text{-}1.9 \mu\text{m}$ , are visible in several positions (fig.13: B, pos.3; C, pos.3,6; D,  
 454 pos.3,5; see Clark 1999). Plagioclase feldspars are visible in spectra 5 and 7 of fig.13-B, as  
 455 could be inferred by the CF  $\text{Fe}^{2+}$  absorption near  $1.25\text{-}1.3 \mu\text{m}$  (see Adams and Goullaud, 1978).

456 The presence of silicate minerals with different OH/H<sub>2</sub>O 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 λ<0.5*  
 466 *μm and λ>2.3 μm in some cases. Gray bars highlight the spectral region which is not accessible for Ma\_MISS.*

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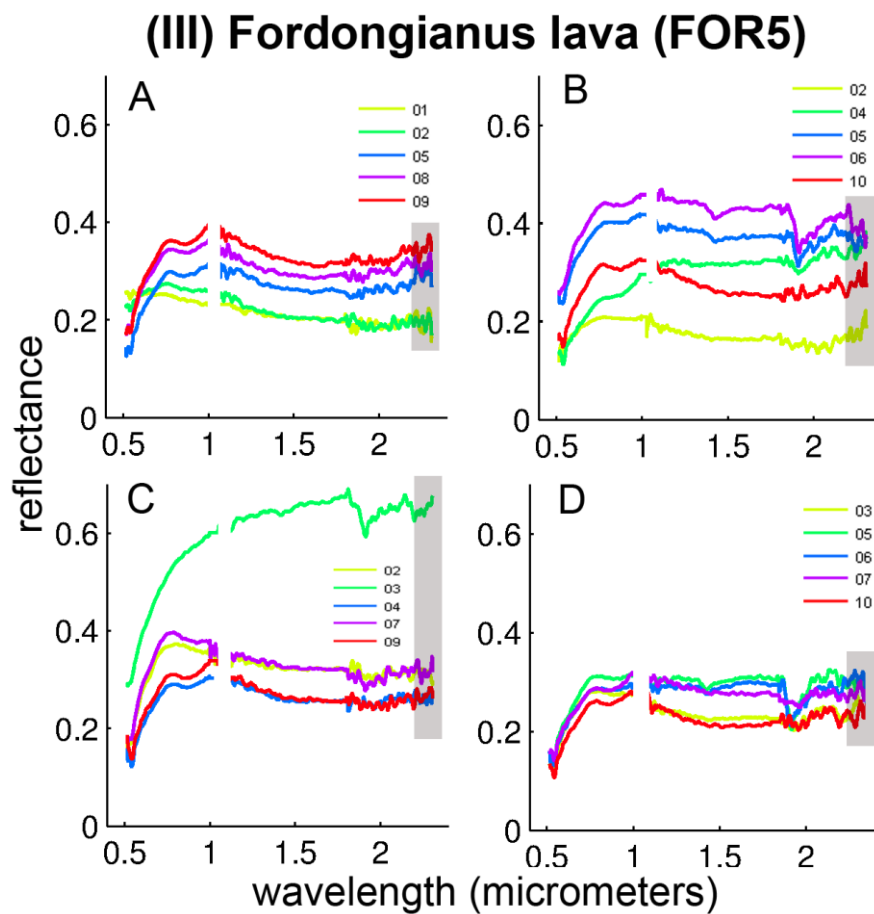
### 4.2.3 Lava from Fordongianus (FOR5)

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 Fe<sup>3+</sup> 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 Fe<sup>3+</sup>). 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  $\mu\text{m}$ . 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/H<sub>2</sub>O absorptions at 1.4-1.9  $\mu\text{m}$  and CF Fe<sup>3+</sup> absorptions at 0.9  $\mu\text{m}$ ), and by Fe<sup>3+</sup>-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  $\mu\text{m}$ ; also in this case it must be  
 482 highlighted that features appearing beyond 2.2  $\mu\text{m}$  will not be observed from Ma\_MISS flight  
 483 instrument, and Al-OH absorptions occurring at 2.2  $\mu\text{m}$  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  $\mu\text{m}$  are not shown in several spectra due to high level of detector noise, as well as data at  $\lambda < 0.5 \mu\text{m}$*   
 491 *and  $\lambda > 2.3 \mu\text{m}$  in some cases. Gray bars highlight the spectral region which is not accessible for Ma\_MISS.*

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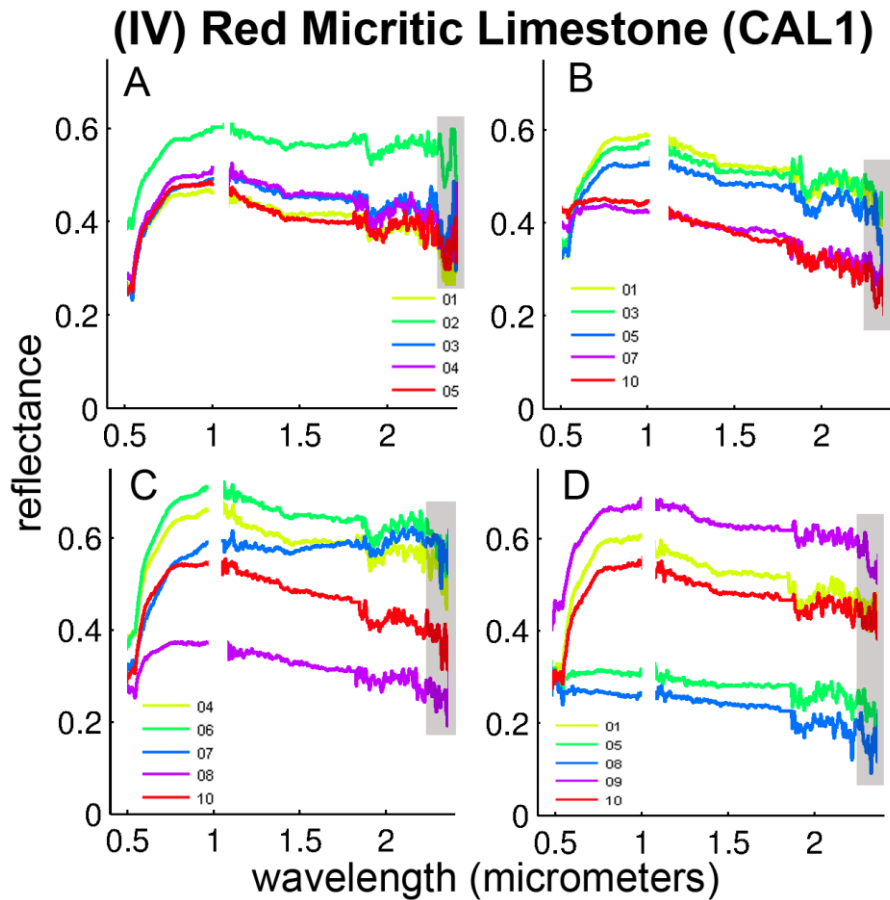
495

#### 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  $\text{CO}_3^{2-}$  absorptions at 2.2  
 498 and 2.35  $\mu\text{m}$ , although the noise is high in this spectral region (which is not accessible from  
 499 Ma\_MISS flight instruments);  $\text{OH}^-$  and  $\text{H}_2\text{O}$  bands are present at 1.4 and 1.9  $\mu\text{m}$ . 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  $\text{Fe}^{3+}$  absorption at 0.9  $\mu\text{m}$  (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  $\mu\text{m}$ . 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- $\mu\text{m}$  region. Eventual  $\text{CO}_3^{2-}$  absorptions appearing  
 506 in the 2.16-2.2- $\mu\text{m}$  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  $\mu\text{m}$  and their shape, the occurrence of  $\text{CO}_3^{2-}$   
 509 absorptions in the 1.75-2.00- $\mu\text{m}$  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  $\mu\text{m}$  are not shown in several spectra due to high level of detector noise, as well as data at  $\lambda < 0.5 \mu\text{m}$   
517 and  $\lambda > 2.3 \mu\text{m}$  in some cases. Gray bars highlight the spectral region which is not accessible for Ma\_MISS.

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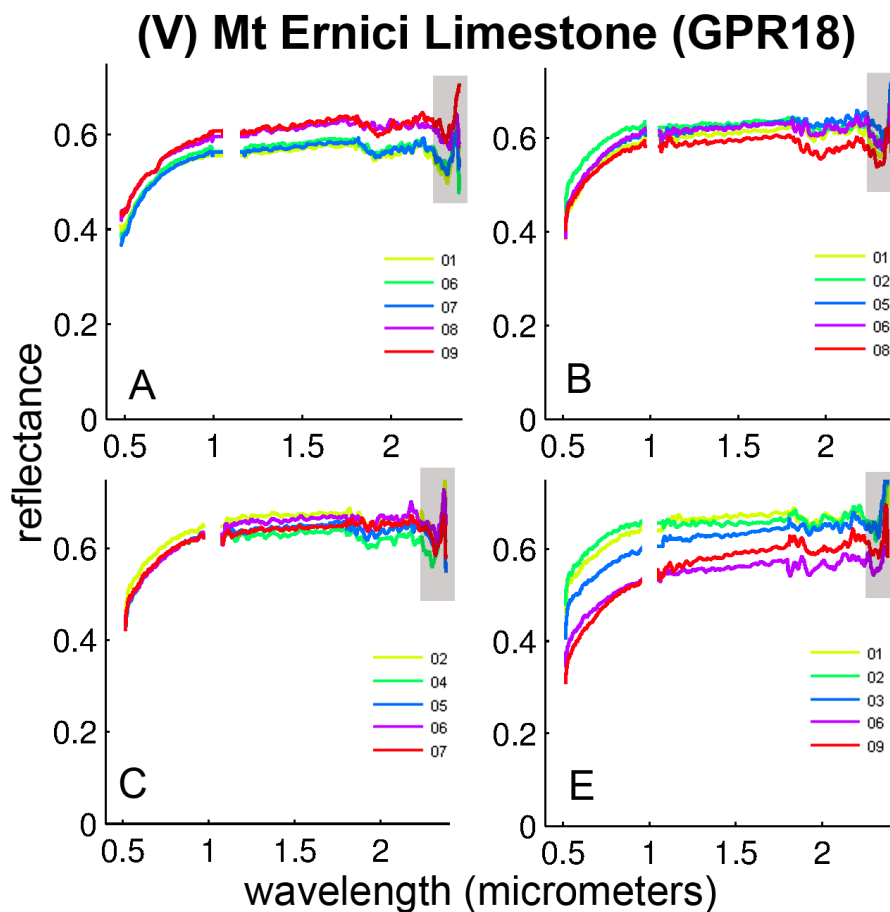
521

#### 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  $\text{CO}_3^{2-}$  absorptions near 2.2  
524 and 2.35  $\mu\text{m}$ . The carbonate feature at 2.16-2.2  $\mu\text{m}$  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  $\mu\text{m}$ . XRD analyses show that this sample is constituted by  
527 anhydrous dolomite and ankerite, so the 1.9- $\mu\text{m}$  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  $\mu\text{m}$ , that could be  
529 attributed to an  $\text{Fe}^{3+}$  spin-forbidden band or to the presence of chlorophyll.

530

531



532

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

538

539

## 540 **5. Comparison between different spatial scales**

### 541 **5.1 Method 1. Average**

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

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

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

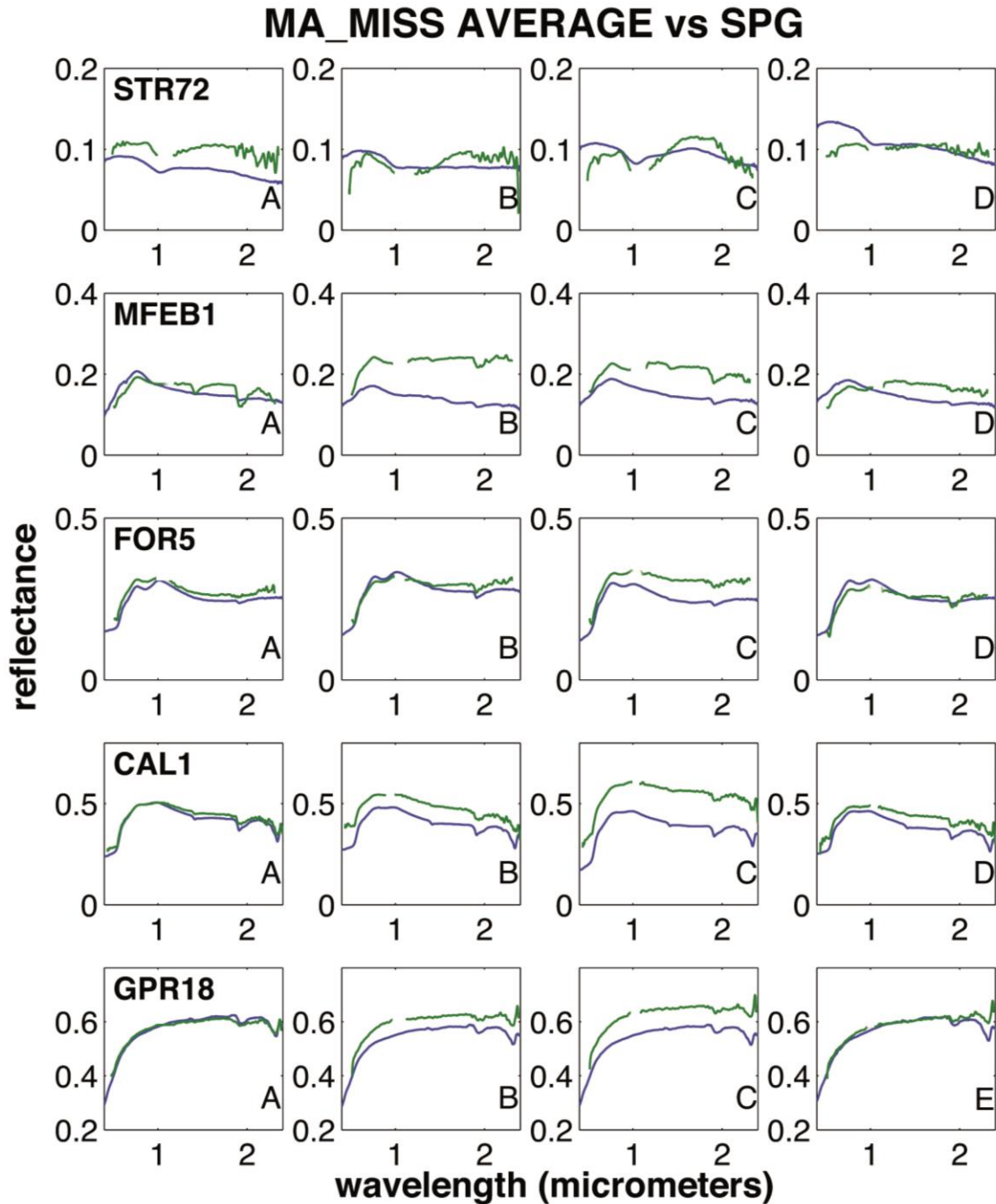
$$R_{avg} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (S_{avg} - S_{spg})^2}$$

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

556 Concerning the sample STR72 there are some differences in spectral slope and in reflectance,  
 557 and generally SPG spectra appear more flattened. Ma\_Miss spectra in positions B,C show a  
 558 more prominent and broad absorption at 1 μm than do SPG spectra: in the average spectra,  
 559 olivine and pyroxene content constitute a major contribute, thus with the arithmetic average  
 560 method they are overestimated by Ma\_Miss. On the contrary SPG spectra of these areas are  
 561 dominated by dark absorbing phases (magnetite, oxides). Spectral regions better  
 562 approximated by Ma\_Miss average spectra are the VIS (0.4-1 μm) in area B, and NIR-IR (1-2.2  
 563 μm) in area D (fig.13). SPG spectra of sample MFEB1 also appear more flattened with respect  
 564 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.*

576

## 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  $0.9 \mu m$  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  $0.65 \mu m$  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  $1.9 \mu m$  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  $1.0 \mu m$ ) and for CAL1 (pos.C,D,  
606 below  $1.0 \mu m$ ). Carbonate  $CO_3^{2-}$  features visible in SPG spectra of CAL1 and GPR18 in the  $1.9$ -  
607  $2.3\text{-}\mu m$  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

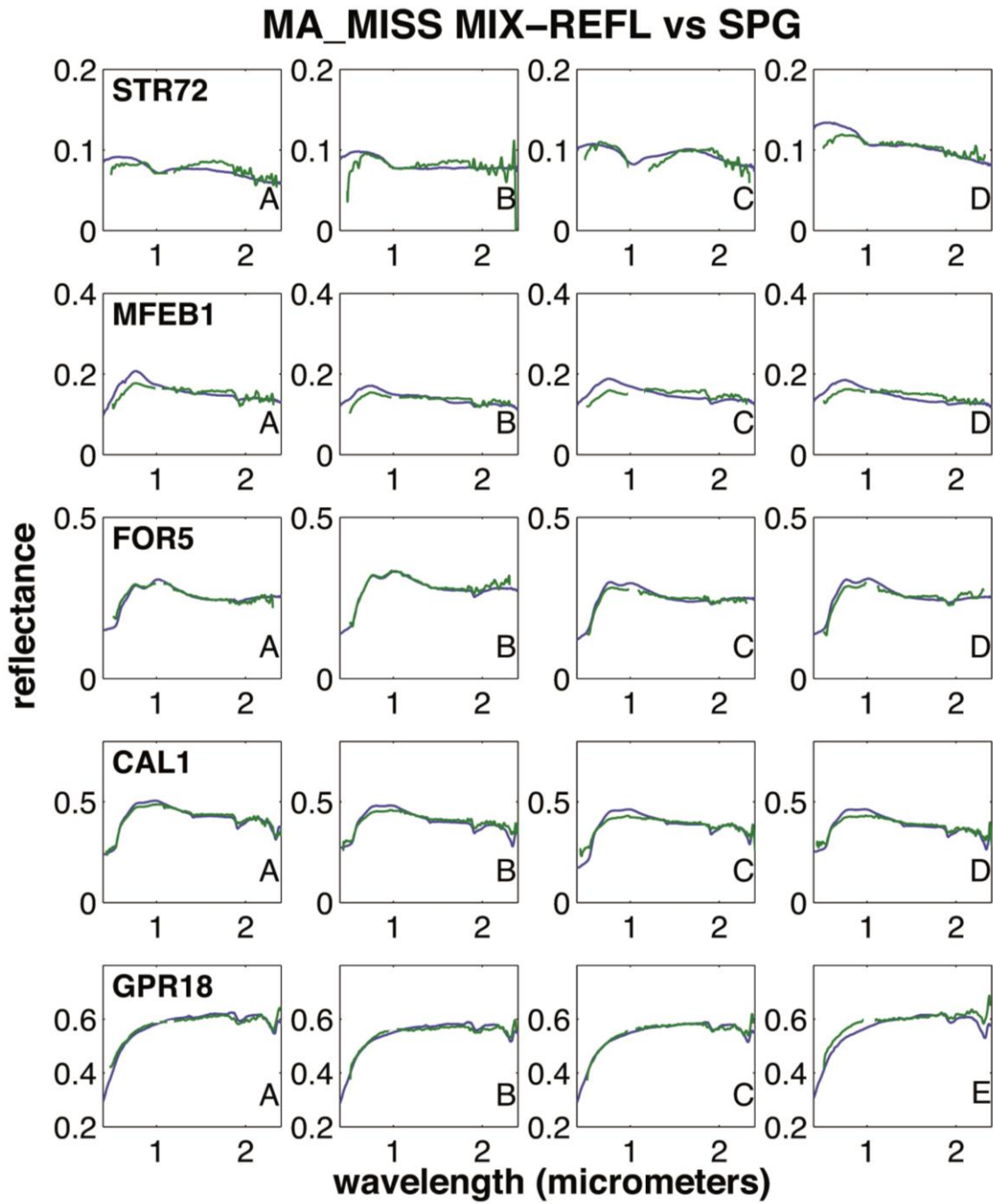
<i>Ma_Miss spectra endmembers</i>					$S_{\text{MIX-REFL}} = a*S_1 + b*S_2 + c*S_3$		
sample:	STR72	<i>Endmember spectrum number</i>			a	b	c
	area A	2	5	10	0.3	0.1	0.3
	area B	3	6	9	0.1	0.8	0.2
	area C	1	2	10	0.2	0.2	0.5
	area D	1	6	7	0.1	0.3	0.4
sample:	MFEB1						
	area A	2	7	10	0.1	1.0	0.1
	area B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



622

623 *Fig.18. Comparison between SPG and Ma\_Miss measurements: spectral linear mixing of reflectance spectra. Green*  
 624 *lines: Ma\_Miss BB. Blue lines: SPG.*

625

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629

630 **5.3 Method 3. Spectral linear mixing of Single-Scattering Albedo spectra**

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

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

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

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

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

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

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

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

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

650 The derived parameters are listed in tab.2, and the Ma\_Miss SSA spectra  $w_{mix}$  are compared  
 651 with SPG SSA spectra  $w_{spg}$  in fig.19. They show very good agreement for the two carbonate  
 652 samples (CAL1 and GPR18) and the volcanic sample FOR5. Concerning the CAL1 and GPR18  
 653 carbonate samples, the  $\text{CO}_3^{2-}$  absorptions in the 1.9-2.3- $\mu\text{m}$  region are well represented in the  
 654 Ma\_Miss linear mixing SSA spectra. Absorptions at 0.9  $\mu\text{m}$  related to  $\text{Fe}^{3+}$  in FOR5 sample are  
 655 visible in SPG spectra and well approximated by Ma\_Miss linear mixing spectra for almost all  
 656 areas. The albedo values are mutually consistent along the overall spectral range for these  
 657 three samples. The matching is less good for the other two volcanic samples, MFEB1 and  
 658 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- $\mu\text{m}$  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  $R_{\text{avg}}$ , 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

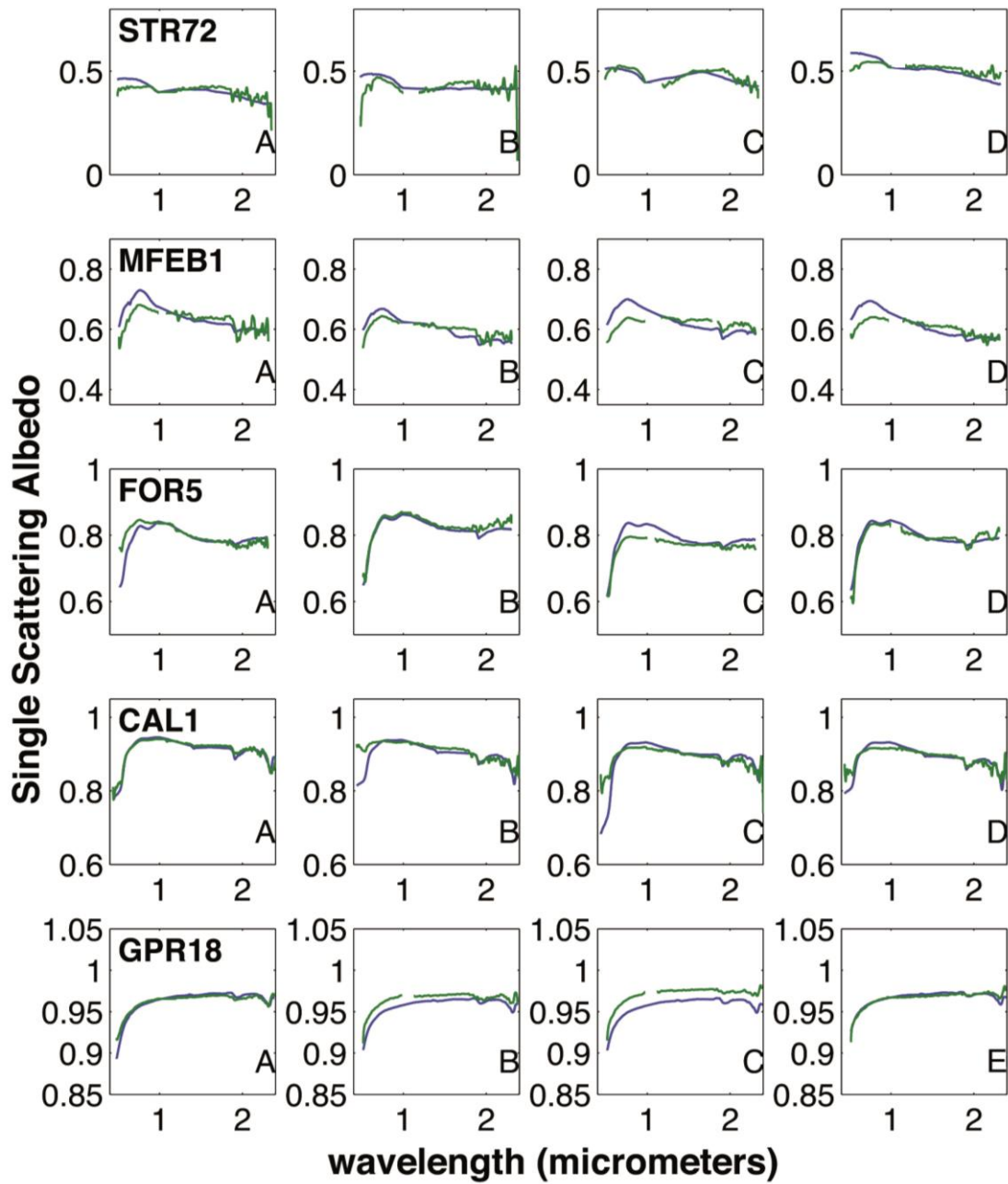
$W_{\text{MIX-SSA}} = a \cdot w_1 + b \cdot w_2 + c \cdot w_3$				
		a	b	c
sample:	STR72			
	area A	0.2	0.1	0.5
	area B	0.2	0.6	0.2
	area C	0.1	0.3	0.5
	area D	0.1	0.4	0.4
sample:	MFEB1			
	area A	0.1	0.9	0.1
	area B	0.1	0.6	0.2
	area C	0.3	0.1	0.4
	area D	0.1	0.2	0.6
sample:	FOR5			
	area A	0.1	0.5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



674

675 *Fig.19. Comparison between SPG (blue lines) and Ma\_Miss (green lines) measurements: spectral linear mixing of*  
676 *Single Scattering Albedo (SSA) spectra.*

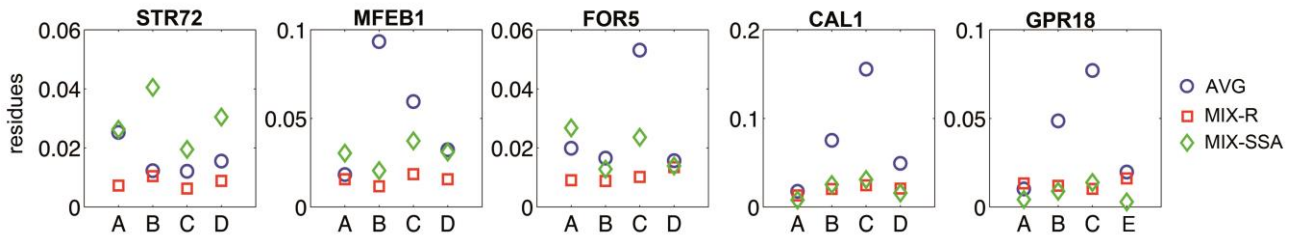
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682

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

686

## 687 6. Discussion

### 688 *Differences between the two instruments and spatial scales*

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

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

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

717 *Applicability of Hapke model to bulk rock slabs*

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

724 Widely dispersed particles can be treated as a continuum medium, in which no  
725 interferences arise between light rays propagating among particles, and grains don't cast  
726 shadows on each other. When particles get more closely packed each other or they are in  
727 contact, the medium can no longer be considered as continuum. Interferences arise  
728 between portions of waves scattered by adjacent grains; nevertheless for irregular shaped  
729 and random oriented particles all coherent effects will be averaged and erased (Hapke,  
730 1981).

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

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

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

751

752 *Comparison of the three methods and endmember retrieval*

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

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

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

777

## 778 **7. Conclusions**

779 In this work we analyzed a set of five rock slabs by mean of VNIR spectroscopy in order to  
780 characterize the Ma\_Miss instrument capability to accomplish mineral investigations. For  
781 this purpose, we used two different instruments: (i) the Spectro-goniometer setup, that is  
782 a Fieldspec Pro coupled with a goniometer, with spectral range 0.35-2.5  $\mu\text{m}$  and spatial  
783 resolution spot of 6 mm; (ii) the ExoMars/Ma\_Miss BreadBoard setup, with analogous  
784 spectral range and higher spatial resolution (spot of 0.12 mm).

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

792 For each analyzed zone, spectra acquired with Ma\_Miss at 120  $\mu\text{m}$  spatial resolution were  
793 combined in different ways in order to be compared with the SPG spectrum of the same  
794 zone: (i) by arithmetic average of all ten spectra; (ii) by linear mixing of three endmember

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

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

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

807

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812 (STR72) with relative chemical analyses. We are grateful to Ed Cloutis for his helpful  
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814

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