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Authors	PISELLO, ALESSANDRO, DE ANGELIS, Simone, FERRARI, MARCO, Porreca, Massimiliano, Vetere, Francesco Pasqualino, Behrens, Harald, DE SANCTIS, MARIA CRISTINA, Perugini, Diego
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Visible and Near-InfraRed (VNIR) reflectance of silicate glasses: characterization of a featureless spectrum and its implications for planetary geology.

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Corresponding Author:	alessandro pisello ITALY
First Author:	Alessandro Pisello, Dr.
Order of Authors:	Alessandro Pisello, Dr. Simone De Angelis Marco Ferrari Massimiliano Porreca Francesco Pasqualino Vetere Maria Cristina De Sanctis Diego Perugini
Abstract:	<p>Silicate glasses represent a major component in volcanic products, both in pyroclastic deposits and lavas. To date, their spectral characteristics are not thoroughly investigated in the context of their characterization as possible analogues of planetary surfaces, mainly due to their lack of spectral features. Nevertheless, featureless VIS-NIR spectra for which it is only possible to retrieve relative parameters (slope, albedo) are commonly observed on the surface of planetary bodies, and volcanic structures are supposed to be widely present in all terrestrial planets within the Solar System. Therefore, the correct interpretation of their geochemical signature is important in the attempt to shed new light on the evolution of these planets, and detailed knowledge about of spectral response of silicate glasses is fundamental for such a purpose.</p>
Suggested Reviewers:	Rachel Klima Rachel.Klima@jhuapl.edu Katrin Stephan katrin.stephan@dlr.de Faith Vilas fvilas@psi.edu Alessandro Vona alessandro.vona@uniroma3.it Sebastienne Besse sbesse@sciops.esa.int
Opposed Reviewers:	

Highlights for the submitted manuscript: “Visible and Near-InfraRed (VNIR) reflectance of silicate glasses: characterization of a featureless spectrum and its implications for planetary geology”

- Silicate glasses are an important constituent of igneous products, especially volcanic, yet they are not deeply investigated in terms of relationship between spectral response and chemical composition.
- Investigation of reflectance in the VNIR range is commonly performed on geologically relevant material to build up databases for the characterization of planetary surface.
- A series of 14 silicate glasses with complex chemical composition were produced starting from natural material with the aim to obtain large chemical variability by means of silica and alkaline content.
- Silicate glasses were characterized with reflectance in the VNIR, and parameterization allowed to individuate relationships between chemical composition and spectral characteristics (slope, albedo).
- Results from such investigation will be useful to interpret occurrence of volcanoclastic products on planetary surfaces.

Visible and Near-InfraRed (VNIR) reflectance of silicate glasses: characterization of a featureless spectrum and its implications for planetary geology

Pisello Alessandro¹, De Angelis Simone², Ferrari Marco², Porreca Massimiliano¹, Vetere Francesco Pasqualino¹⁻³, De Sanctis Maria Cristina², Perugini Diego¹.

- 1) Department of Physics and Geology, University of Perugia, I-06123 Perugia, Italy.
- 2) Institute for Space Astrophysics and Planetology (IAPS-INAF, Rome, Italy)
- 3) Institute of Mineralogy, Leibniz Universität Hannover, D-30167 Hannover, Germany.

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Abstract

Silicate glasses represent a major component in volcanic products, both in pyroclastic deposits and lavas. To date, their spectral characteristics are not thoroughly investigated in the context of their characterization as possible analogues of planetary surfaces, mainly due to their lack of spectral features. Nevertheless, featureless VIS-NIR spectra for which it is only possible to retrieve relative parameters (slope, albedo) are commonly observed on the surface of planetary bodies, and volcanic structures are supposed to be widely present in all terrestrial planets within the Solar System. Therefore, the correct interpretation of their geochemical signature is important in the attempt to shed new light on the evolution of these planets, and detailed knowledge about of spectral response of silicate glasses is fundamental for such a purpose.

In this study, experimental petrology techniques have been used to produce 15 silicate glasses having complex chemical composition corresponding to three of the most common magmatic series on planet Earth. These glasses have been investigated in the Visible and Near/Infrared range to observe and interpret the variation of slope, albedo, and spectral ratio $R_{1.55}/R_{0.8}$ as a function of chemical composition. We found that, despite the complexity of factors influencing the spectral response, a good correlation can be derived linking spectral parameters with both iron content and composite Silicium-Calcium-Iron-Magnesium content (SCFM parameter). Results presented in this work might represent the baseline for new research lines focused on deciphering the significance of silicate glasses in the context of planetary exploration, opening new windows to access information on planetary differentiation that cannot be obtained using only existing materials and methods.

34 Spectroscopic investigations of geological materials for the characterization of possible analogues
35 useful for planetary investigations within the Visible and Near-Infrared region (hereon, VNIR), have
36 been extensively carried out mainly because electronic transitions of Fe or FeO occur within this
37 range, allowing the identification of iron-bearing rocks (Adams 1967, Adams 1975). Indeed, the
38 majority of planetary igneous rocks are supposed to have mafic or ultramafic bulk compositions,
39 which means relatively low silica content (45-50 wt.%) and relatively high iron content (7-15 wt.%),
40 making VNIR a particularly suitable spectral range for planetary geology research. Previous spectral
41 investigations by VNIR spectroscopy regarded the main rock-forming minerals of mafic igneous
42 rocks: olivine (Mustard et al. 2005, Mølholt et al. 2008, Isaacson et al. 2014, Penttilä et al. 2020),
43 pyroxene (Pompilio et al. 2007, Klima et al. 2008, Klima et al. 2009, Markus et al. 2018) and An-rich
44 plagioclase (Hiroi et al. 2012, Serventi et al. 2013, Carli et al. 2014.). Further, in order to provide
45 insights on the possible traces of life on other planetary bodies, a great deal of work on other (also
46 water-bearing) crystalline phases, formed through alteration of igneous minerals, has been performed.
47 This is the case of various types of phyllosilicates like montmorillonite, chamosite, and nontronite
48 (Poulet et al. 2005, Ferrari et al. 2019), serpentine-related hydrated silicates (Cloutis et al. 2018), and
49 hydrated sulphate minerals like gypsum or kieserite (Gendrin et al. 2005, Murchie et al. 2009, De
50 Angelis et al. 2017). Moreover, because of some putative carbonaceous-dominated areas on the
51 planetary surfaces (Kargel et al. 1994, Wray et al. 2011, Boynton et al. 2009, Morris et al. 2010), even
52 carbonaceous rocks were characterized in the VNIR region, taking into consideration carbonates
53 hosting Fe, Mg, and Ca (Harner and Gilmore 2015, Bishop et al. 2011). Additional studies include
54 VNIR investigations of rocks (i.e. mineral assemblages) such as meteorites (Gaffey 1976, Cloutis et
55 al. 2011 and 2018), and igneous rocks, both intrusive and effusive, with composition ranging from
56 mafic to felsic (Singer 1982, Evans et al. 1982, Crown and Pieters 1987, Walter and Salisbury 1989,
57 Harloff and Arnold 2001, Anbazhagan and Arivazhagan 2010, Sgavetti et al. 2006).

58 Although existing literature offers a plethora of studies regarding crystalline phases (which can be
59 associated with magmatism, volcanism, or alteration of such products), amorphous materials, such as
60 glasses, are not widely taken into account. However, glasses represent an important volcanic product.
61 Volcanic glasses can occur in a wide spectrum of effusive and rapidly cooled rocks, from pure glassy
62 rocks (such as obsidian) to the large majority of volcanic rocks (often termed porphyric or
63 hypocrySTALLINE) that, therefore, can show variable volumes of interstitial glass or amorphous material.
64 Moreover, igneous products commonly show important variations of the spectral response not only
65 with varying chemical composition but also as a function of the grain size of the investigated sample
66 (De Angelis et al. 2014). This behaviour was also observed for glassy samples, where optical
67 constants and particle size of glasses were retrieved from VNIR spectra (Carli et al. 2016). In
68 addition, further studies on the VNIR reflectance of glasses were performed with various purposes:

69 Bell et al. (1976) and Wells and Hapke (1977) investigated lunar-like glasses to characterize changes
70 in the spectral response with varying Fe or Ti contents and oxygen fugacity; Minitti et al. (2002)
71 investigated the effects of crystallization on the spectral response; Moroz et al. (2009) focused on the
72 influence of melting and cooling rates on the spectral response; Tompkins and Pieters (2010), studied
73 possible lunar impact glasses; Cloutis et al. (1990) and Carli et al. (2014) observed substantial
74 difference between the spectral response of crystalline and glass-bearing rocks; finally, Cannon et al.
75 (2017) compared the spectral response of possible glasses with Lunar, Martian and Hermean
76 compositions.

77 In this study, we aim at providing new and original data on VNIR spectroscopy of silicate glasses, by
78 investigating the systematic variation of spectral response in reflectance on experimentally produced
79 glasses. We focus not only on mafic or impact-like compositions, but we enlarge the variability of
80 chemical compositions by including silica-rich compositions for different magmatic series. Our aims
81 are: i) widening the existing databases for the interpretation of planetary rocks and ii) identify which
82 features of glassy products are comparable with those of bulk rocks. We show that despite the
83 difficulty to parameterize glassy materials since there are almost featureless and with a strong
84 influence of grain size on the spectral parameters (albedo, slope, etc.), new and interesting
85 information can be indeed derived. We anticipate that our results can aid in shedding light on possible
86 silica-rich rocks cropping out on terrestrial bodies and, perhaps more importantly, the presented
87 dataset can be used for deconvolution of spectra acquired in areas suspected to be volcanic in origin,
88 where amorphous materials might reasonably play a central role in defining their spectral response.

89 2. Methodologies

90 2.1. Sample collection and preparation

91 Silicate glasses were synthesized starting from natural rocks collected on three different volcanic
92 areas on Earth. In each area two rocks were collected, one representing the most mafic end-member
93 (low-silica) and the other the most felsic end-member (high-silica). In detail, the two end-members
94 from the Island of Vulcano Island (Aeolian Islands, Italy) are a shoshonite and a rhyolite. This
95 sampling site was chosen because the Island of Vulcano is emplaced above an active subduction zone
96 in the SE Tyrrhenian Sea, and the products of the area have a particularly alkaline character (De Astis
97 et al. 1997, Rossi et al. 2017, Vetere et al. 2015a). Two other rocks, a basalt and a rhyolite, were
98 collected in the Snake River Plain area (USA, hereon SRP). This area is emplaced in an intraplate
99 tectonic setting, and the products of this area have a sub-alkaline character (Morgavi et al. 2013).
100 Finally, two other rocks (a Hawaiite and a Benmoreite) were collected in the area of Mount Etna
101 (Sicily). Products from this area show sub/alkaline to moderate alkaline character (Corsaro and
102 Métrich 2016).

103 Each end-member was crushed, pulverized down to a grain size lower than 200 μm , and molten at
104 supra-liquidus temperature (1400 $^{\circ}\text{C}$) for 4 hours in air. The obtained melts were quenched in air to
105 glass and subsequently re-crushed and pulverized. This procedure was repeated twice in order to
106 obtain homogeneous glassy materials (see Vetere et al. 2015b for further details). Glasses were finally
107 crushed to powders with size ranging from 500 to 200 μm and then mixed to obtain a series of
108 products with intermediate compositions. For the Vulcano series, three further intermediate samples
109 were synthesized by mixing the shoshonite and the rhyolite end-members in different weight
110 proportions. Hence, five glass compositions with variable shoshonite:rhyolite ratios of 100:0, 70:30,
111 50:50, 30:70, and 0:100 (hereafter referred to as S, S7, S5, S3, RS, respectively) were prepared.
112 Similarly, six samples were synthesized by mixing basalt and rhyolite from the Snake River Plain in
113 the following ratios: 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 (hereafter referred to as B, B8, B6,
114 B4, B2, RB). Finally, three samples were synthesized by mixing the hawaiite and the benmoreite from
115 Mount Etna in the following ratios: 100:0, 50:50, and 0:100 (hereafter referred to as M, M5, and V).
116 Glasses were crushed and sieved down to $<36 \mu\text{m}$ for the spectral analysis.

117 2.2. Chemical composition determination

118 Chemical compositions for all samples were determined at the Department of Earth- and
119 Environmental Sciences, University of Munich LMU (Germany), with a Cameca SX100 electron
120 microprobe analyzer (EMPA). Glass fragments were embedded in epoxy resin, polished, and then
121 covered with a 13 nm carbon coating. Analyses were performed using an acceleration voltage of 15
122 kV and an electron beam current of 20 nA, with a defocused beam of 10 μm on the sample. Standards
123 used for calibration were: orthoclase (Al, K), albite (Si, Na), wollastonite (Ca), periclase (Mg),
124 ilmenite (Ti), iron(II) oxide (Fe), and chromium oxide (Cr). The chemical homogeneity of glasses was
125 tested by performing five chemical analyses for each sample.

126 2.3. Iron speciation and SCFM determination

127 Ferrous–ferric ratio is dependent on the glass composition and may also depend on the conditions at
128 which the melting process occurred. In this study, glasses were always prepared at air oxygen
129 fugacity. The iron oxidation state determination was performed using a wet chemical micro-
130 colorimetric method (Schuessler et al. 2008). 7–10 mg of glass chips were dissolved in concentrated
131 HF with the addition of a solution of ammonium vanadate in 5M sulfuric acid. The released ferrous
132 iron reacts with V^{5+} and forms V^{4+} and ferric iron (for details, see ref. Schuessler et al. 2008 and
133 Vetere, Holtz, et al. 2014). After complete dissolution, boric acid was added to bind fluorine, and the
134 pH value was increased by adding ammonium acetate so that Fe^{2+} was formed again. The
135 concentration of bivalent iron was measured by means of spectroscopy after complexation with
136 bipyridyl, using a 1 cm transmission cell in a UV/VIS spectrometer Shimadzu UV 1800. To measure

137 the total iron concentration (Fe_{tot}), hydroxylamine hydrochloride was added to the solution for the
138 reduction of Fe^{3+} . By combining this information with EPMA analyses, also the SCFM parameter was
139 calculated, as defined by Walter and Salisbury (1989), taking its name from the cations of the oxides
140 involved in its definition [i.e. $SiO_2/(SiO_2+CaO+FeO+MgO)$].

141 2.4. Spectral characterization within VNIR

142 All the samples (in the form of $<36 \mu m$ powders) were characterized at the C-Lab of the Institute for
143 Space Astrophysics and Planetology (IAPS-INAF) in Rome, Italy. The instrument we used is
144 described in detail in De Angelis et al. (2014), consisting of Field Spec-4 spectrometer, having a
145 detection spectral range of $0.35-2.5 \mu m$. This range is covered by three separate detectors: the VIS
146 ($0.35-1.0 \mu m$), the SWIR1 ($1.0-1.8 \mu m$), and the SWIR2 ($1.8-2.5 \mu m$). Thus, the entire VNIR
147 spectrum is obtained by joining the spectra detected in each spectral sub-region. The spectral
148 sampling is 1 nm , whereas the spectral resolution is in the range of $3-8 \text{ nm}$. A Quartz-Tungsten-
149 Halogen (QTH) lamp was used to illuminate the sample, with a spatial spot of about 5 mm . Optical
150 fibers were used both for illuminating and collecting the reflected light. The specimen (in our case
151 powdered glass) was placed on a three-stage sample holder, which allows for the movement of the
152 target along with the XYZ directions using three micrometric screws.

153 As for the quantitative determination of albedo and slope parameters, we have followed the
154 methodology shown in De Angelis et al. 2014: three slopes were determined, one in the visible region
155 (VIS slope, in the range between $0.5-0.8 \mu m$), a second one in the near-infrared region (NIR slope in
156 the range between 1.2 and $1.8 \mu m$), and a third one including the whole region (VNIR slope, in the
157 range 0.6 and $2.0 \mu m$). As for albedo, two values were taken into account at $0.8 \mu m$ and $1.62 \mu m$.
158 Moreover, we have taken into account a newly defined parameter: the spectral ratio of reflectance
159 values at 1.55 and $0.8 \mu m$: $R_{1.55}/R_{0.8}$. These two wavelengths were chosen because no absorption
160 occurs in these zones.

161 3. Results

162 3.1. Chemical characterization

163 The chemical composition of all glasses is reported in Table 1, integrated with information about iron
164 speciation determination. It is observed how the procedure described above for the production of
165 compositional series successfully resulted in regular variations of the chemical content of all main
166 oxides. Results from chemical determinations are plotted in the Total Alkali vs Silica (TAS) diagram
167 in Figure 1 (LeBas et al. 1986). Here, the chemical variability of the products can be appreciated for
168 both the silica and the alkaline content. Noteworthy is the fact that the analyzed dataset within this
169 graph roughly covers more than the 90% of rock compositions cropping out on Earth (Best, 2013).

170 Here, datapoint colors are orange for SRP series, blue for Etna, and green for Vulcano series. Note
171 that this color-coding will be maintained for each additional plot presented in this work.

172 3.2. Spectral characterization

173 All spectra acquired with FieldSpec 4 are reported in Figure 2, except for sample V from Etna series,
174 which was found to experience incipient crystallization of magnetite (probably because of the
175 occasional slow quench that might have been caused by laboratory bias, and therefore was not
176 included for further analyses. Figure 2 is divided into three panels, each showing the set of spectra of
177 a single series. For all three panels, the darker the colour, the most mafic is the composition. In
178 general, spectra belonging to mafic products have lower reflectance and steeper slope, with the
179 reflectance increasing and the slope flattening with increasing silica content and decreasing iron
180 content. Vulcano products show generally higher reflectance and flatter slopes, even for the most
181 mafic products. All spectra show three weak absorption bands, the two well-known absorption bands
182 relative to Fe²⁺ absorption located at 1 and 2 μm (Hunt 1977, Cannon et al. 2017, Carli et al. 2016)
183 and another small shoulder at ca. 0.45 μm , particularly evident only for the Vulcano series.

184 4. Discussion

185 4.1. Slope and albedo

186 Absorption features in VNIR reflectance are superimposed to a continuum, a background level of the
187 reflectance spectra that is not constant with varying wavelengths. An exhaustive explanation of the
188 nature of this phenomenon is not yet available. However, it is thought to be the combination of
189 various processes, such as a larger absorption feature within the ultraviolet region, (Clark et al. 1999).
190 For this reason, two of the spectral parameters that are usually taken into account when dealing with
191 this kind of spectra are the albedo, which is the reflectance level at a certain wavelength, and the
192 spectral slope. These two parameters can be retrieved from reflectance of planetary surface, even from
193 low-resolution spectral characterization. These parameters are observed to be dependent not only on
194 chemical composition but also on physical features, such as the grain size, and the observational
195 conditions, such as the phase, incidence, and emission angles. The dependence of slope and albedo on
196 grain size has been studied for rocks (De Angelis et al. 2014) and glasses (Carli, et al. 2016). As
197 mentioned in section 2.4, we have characterized the spectra quantitatively with albedos and slopes as
198 defined by De Angelis et al. 2014, and, moreover, we have introduced a novel parameter: $R_{1.55}/R_{0.8}$.
199 These values are reported in Table 2 and plotted as a function of three different chemical parameters
200 in Figure 3 and 4: i) total iron (taken into account as FeO) as determined by EPMA analyses, ii) ferric
201 iron (Fe₂O₃), and iii) SCFM parameter. SCFM is a chemical parameter introduced by Walter and
202 Salisbury 1989. It is typically used for spectroscopic characterization and describes the degree of

203 evolution (in the petrological jargon) of a given composition. The more mafic and primitive the
204 composition, the closer SCFM will be to zero (although for bulk igneous natural compositions, it is
205 never lower than 0.5). The more felsic and evolved the compositions, the closer SCFM will be to 1.
206 The latter is the case of quartz or pure silica. Therefore, SCFM is a parameter that accounts for both
207 chemical evolution of igneous products (SiO₂ content) and for iron content and speciation (iron in
208 SCFM is accounted only in its ferrous form, FeO). By observing the trends of slopes changing with
209 chemical composition three observations can be made:

210 i) regarding VIS slopes (Figure 3 a, b, and c) of SRP series, SRP and Etna values are decreasing with
211 increasing iron (i.e. decreasing SCFM), whereas the trend is reversed for Vulcano alkaline series.
212 Data-points appear more scattered in those plots where the slope is shown as a function of iron
213 content. When observing the VIS slope-SCFM plot, data-points are better distributed along a line,
214 with S7 and S5 still within the trends of the others series, and S3 and RS outlying the trend; ii) as for
215 NIR slope (Figure 4 d, e and f), it appears to increase with increasing iron content and decreasing
216 SCFM, except for mafic alkaline products, for which the trend is reversed; iii) regarding the slope
217 within the entire VNIR range (Figure 3 g, h, i) datapoints of slopes are scattered around 0.021 ± 0.02 ,
218 again with the exception of Vulcano series, mainly driven by the above-mentioned trend in the visible
219 region, that makes the slope of the whole series to drop down to ca. 0.09. For VIS and NIR slopes, we
220 have observed how value variation is substantially different, depending on whether we are observing
221 sub-alkaline or alkaline series. For the sub-alkaline series, the VIS slope increases from mafic towards
222 felsic compositions, as the iron content decreases. This trend is inverted for alkaline series: in this
223 case, VIS slope drops from mafic to felsic compositions, and this trend is progressively more evident
224 as the compositions become more evolved. As for the NIR slope, generally, it is steeper for mafic
225 compositions and flatter for felsic compositions, although alkaline mafic compositions tend to show
226 flatter slopes. The influence of iron-poor and alkaline-rich composition on the spectral response of
227 silicate glasses within VNIR has already been observed by Cannon et al. 2017, who investigated
228 Mercury-like mafic compositions. However, in this study, we had a closer look at a wider range of
229 chemical compositions, and we have confirmed the complexity of this phenomenon.

230 For what concerns the variation of albedo as a function of SCFM, it appears more uniform, as it is
231 possible to observe in Figure 4. Generally, both for NIR and VIS, albedo is decreasing with increasing
232 iron content, and therefore the global reflectivity is higher moving from mafic compositions towards
233 felsic compositions. However, the general trend differs when different parameters are taken into
234 account. When the albedo is plotted as a function of total iron as FeO, trends are slightly different for
235 alkaline and sub-alkaline products, the latter decreasing more rapidly in albedo as iron content
236 increases. When plotting albedo and Fe³⁺, data collapse into a single trend, and this phenomenon is
237 even more pronounced if albedo values are plotted vs. SCFM. In general, we can say that the larger
238 SCFM, the higher is the albedo in all the VNIR range. The same observations can be made when

239 observing parametrization with spectral ratio $R_{1.55}/R_{0.8}$ (Figure 4 g, h, i), although this parameter
240 seems to make the data-points to collapse in a single trend for all the three chemical parameters taken
241 into account.

242 4.2. Band centres and absorption areas

243 Absorptions bands in VNIR spectra of materials occur for two reasons: electronic processes or
244 molecular vibrations. Among the former, there are crystal field effects, occurring in the transitional
245 elements with inner unfilled electron shells; the crystalline field modifies the degeneration of atomic
246 orbitals allowing the electronic transitions between shells. For what concern minerals and rocks, Fe is
247 by far the most abundant transitional element, and therefore the observation of crystal field
248 absorptions of Fe in the VNIR is diagnostic for mineralogy since this absorption varies among
249 different mineral phases. Another electronic absorption process is the so-called charge transfer
250 absorption, caused by interelement transitions of electrons between ions or between ions and ligands;
251 this is also often diagnostic for mineral phases (Hunt 1977, Burns 1993, Clark et al. 1999).

252 On the other hand, vibrational processes occur when the bonds in IR active molecules or functional
253 groups vibrate. Bonds behave like springs, and a molecule can vibrate or rotate, although rotational
254 modes occur in gas or liquid phases. This phenomenon occurs within the VNIR region for many
255 bonds involving C, O, and OH, and therefore it can be diagnostic for phyllosilicates, carbonates, or
256 water-bearing phases (Ferrari et al. 2019). Due to the lack of a regular crystalline structure, absorption
257 bands are very weak for glasses. However, in the VNIR region, literature reports four absorption
258 phenomena (Hunt 1977, Burns 1993, Clark et al. 1999, Cannon et al. 2017). The most evident are two
259 absorption bands at ca. 1.05 μm and 1.9 μm , relative to crystal field absorptions of octahedral Fe^{2+} ,
260 and tetrahedral Fe^{2+} , respectively. Two other absorption phenomena can be attributed to oxygen-metal
261 charge transfer (at the boundary with the ultraviolet region) and heterovalent charge transfer
262 absorptions $\text{Fe}^{2+}\text{-Fe}^{3+}$ around 0.8 μm (Bell et al. 1976). For our set of spectra, bands at ca. 1.1 μm and
263 1.9 μm are evident, whereas another little absorption feature is detectable at ca. 0.5-0.6 μm for alkaline
264 and very felsic products. To refine and quantitatively describe the absorption phenomena within this
265 range, data analysis was performed using the Origin © software. Smoothing of spectra was performed
266 by applying a Fast Fourier Transform filter (FFT filter) on a window consisting of 50 to 100 data-
267 points, depending on each spectrum's characteristics. FFT filter method is particularly suitable for
268 noises whose frequency is higher than the frequency of the true signal. For our set of spectra, this
269 occurs towards the upper limit of the spectral range, between 2.2 and 2.5 μm . Continuum removal was
270 performed by subtracting baseline to each spectrum considered as 1-Reflectance. The baseline was
271 designed individually for each spectrum by selecting anchoring points in the ranges where no
272 absorptions were observed (ca. < 0.8 μm , 1.5 and > 2.3 μm) and by connecting these points with a
273 spline function. The different steps of the described processes can be visualized in Figure 5.

274 Finally, peak fitting was performed on the two bands of absorption at ca. 1.15 and 1.9 μm . Indeed, by
275 taking into consideration the spectra as 1-Reflectance, the typical two local reflectance minimums
276 became two peaks that were possible to be deconvoluted to two Gaussian functions, through the
277 option PeakFit Pro of the Origin software. Peak centers were picked manually, and then let free to
278 oscillate during the fit process. Table 3 reports all the parameters resulting from the fitting process,
279 whereas Figure 6 reports band centers and area percentage of both absorptions bands, plotted with
280 total iron content.

281 Band centres (Figure 6a) generally slightly shift with iron content and there is no clear difference
282 between different series. There is a slight shift (up to 0.01 μm) towards higher wavelengths for
283 extremely felsic (low-iron) compositions, but this is indeed quite small and, if considered as one series
284 all together, the absorption relative to Fe^{2+} crystal field octahedral absorption is averagely positioned
285 at 1.15 μm (covering a span between 1.12 and 1.18 μm), while the one relative to tetrahedral
286 absorption is averagely positioned at 1.93 μm (covering a span between 1.89 and 1.99 μm). Carli, et
287 al. 2016 have observed how, for glasses having the same composition and different granulometry, the
288 shift of centers of absorption is apparent, and it is not visible after continuum removal. However, in
289 the mentioned study, only mafic compositions were investigated, as in the vast majority of planetary-
290 related studies. Our set of spectra is also presenting a variation of the slope with changing chemical
291 composition that creates an apparent shift of the centers. After being treated by smoothing, continuum
292 removal, and having performed quantitative analyses, we conclude that the observed weak shift is an
293 artifact, and we can state that no shift in the band centers is present for silicate glasses. In Figure 6b it
294 is also reported the relationship between the absorption areas of each centre (expressed as a
295 percentage over the total for both absorption bands) and, again, the total iron content. Even if some
296 scatter is visible, there is a general trend: with increasing iron, absorption linked to tetrahedral Fe^{2+}
297 increases, whereas octahedral Fe^{2+} decreases. This phenomenon looks stronger for Vulcano alkaline
298 series rather than for SRP sub-alkaline series, whereas the Etna series looks too restricted to make
299 detailed considerations. An interpretation of this phenomenon could be related to the fact that, with
300 increasing iron content, we are decreasing silica content (Table 1). This way, the tetrahedral network
301 (mainly composed of SiO^{2+} tetrahedral cells) becomes less polymerized, so that iron Fe^{2+} is freer to
302 occupy these slots, given also the fact that a lower viscosity results in larger mobility of the elements
303 within the melt. This trend is considerably stronger for alkaline series, because, as already known
304 (Mysen and Richet 2005), alkalis act as charge balancers and trigger other elements (such as iron) to
305 act as network former in the tetrahedral network.

306 Conclusions

307 Three different series of glasses, for a total of 15 samples, have been produced from natural rocks
308 under controlled conditions. Fine powders of such glasses were characterized spectroscopically in
309 reflectance in the Visible and Near-Infrared region (VNIR). Such investigation revealed that

310 i) Extremely fine powders of silicate glasses have always positive slopes. For the sub-alkaline
311 series, glasses presenting mafic composition have a steeper slope if compared to felsic composition,
312 this trend is inverted for alkaline series, which have generally a flatter aspect. There is therefore a
313 fundamental difference in the variation of slopes between alkaline and sub-alkaline products.

314 ii) For such silicate glasses powders, the variation of albedo is similar for all series, with mafic
315 glasses being always darker in comparison with felsic glasses. If compared to SCFM parameter, the
316 albedo of all investigated glasses clusters into a close-to-unique trend. However, according to our
317 analysis, the best parameter to describe iron content and SCFM is the one proposed for the first time
318 here: $R_{1.55}/R_{0.8}$

319 iii) Silicate glasses having widely different chemical composition are characterized by two weak
320 absorptions, at 1.15 μm and 1.93 μm . A small shoulder at ca. 0.5 μm is observable for felsic glasses,
321 in particular for alkaline series. The relative area of absorption at 1.1 μm increases moving from mafic
322 to felsic products (and therefore is inversely proportional to iron content), whereas band depth
323 absorption at 1.9 μm decreases moving from mafic towards felsic composition (and therefore directly
324 proportional to iron content).

325 In order to suggest possible applications of this study for the interpretation of planetary data, we
326 highlight that VIS slopes analyses can be useful for distinguishing sub-alkaline and alkaline products
327 for felsic composition, whereas NIR and VNIR slope analyses are more helpful for distinguishing
328 sub-alkaline and alkaline products for mafic composition. On the other hand, albedo is certainly a
329 good marker for the degree of evolution of chemical composition, in particular when expressed as
330 SCFM. The novel parameter $R_{1.55}/R_{0.8}$ appears to be the best one to determine both the abundance of
331 iron and the SCFM parameter.

332 It has to be noted that this study concerned samples having the same, very fine, grain size ($<36 \mu\text{m}$),
333 but grain size has been observed as having a large influence on slopes and albedos. Although
334 therefore, additional efforts must be done to include in the analysis also these variables, this study
335 represents a step forward in the knowledge of the possible factors influencing spectral response within
336 the VNIR range of glasses. This integrates the state of the knowledge on the spectral response of
337 geologically relevant material, especially for what concerns igneous products, of which glassy or
338 hypohyaline products represent the most plausible occurrences.

339 The new presented dataset can be helpful in the context of future missions aimed at understanding the
340 nature of rocks on other planets and, especially, for the important upcoming mission ExoMars, by
341 ESA/ROSCOSMOS (Vago et al., 2017). Such a mission comprises different launches and, in 2022, it

342 will deliver a European rover, Rosalind Franklin, and a Russian surface platform, Kazachok on the
343 surface of Mars. In particular, Rosalind Franklin will carry nine different instruments for the physical
344 and chemical *in situ* analysis of the Martian surface. This rover will be able to drill 1x3 cm rock cores
345 from up to 2 meters depth, with a drill integrated with the Mars Multispectral Imager for Subsurface
346 Studies (Ma_MISS) to constrain mineralogy and rock formation dynamics by characterizing the
347 spectra in the visible and near-infrared (De Sanctis et al., 2017). Data presented within this study will
348 be fundamental to interpret possible volcanic ash occurrences on future missions to Mars.

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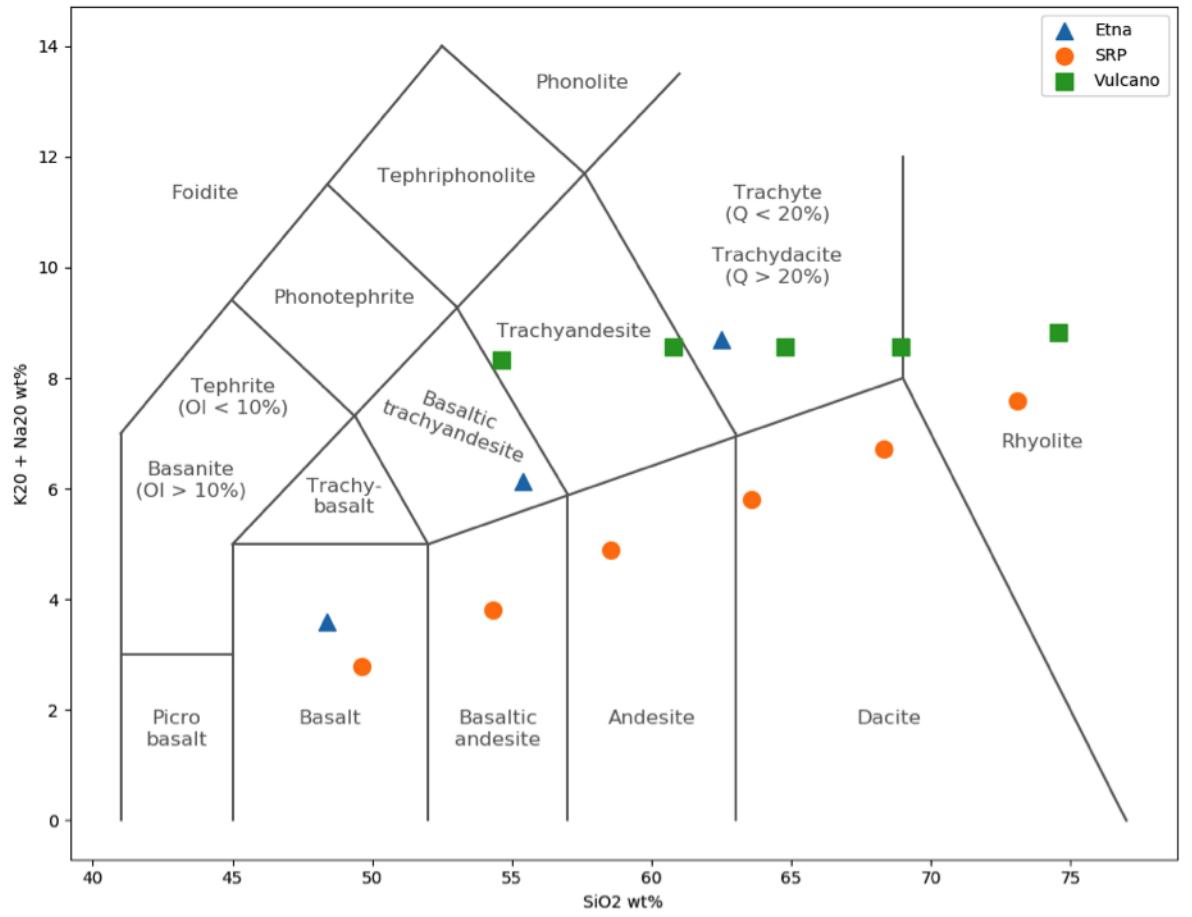


Figure 1: TAS diagram reporting chemical composition of all analysed samples

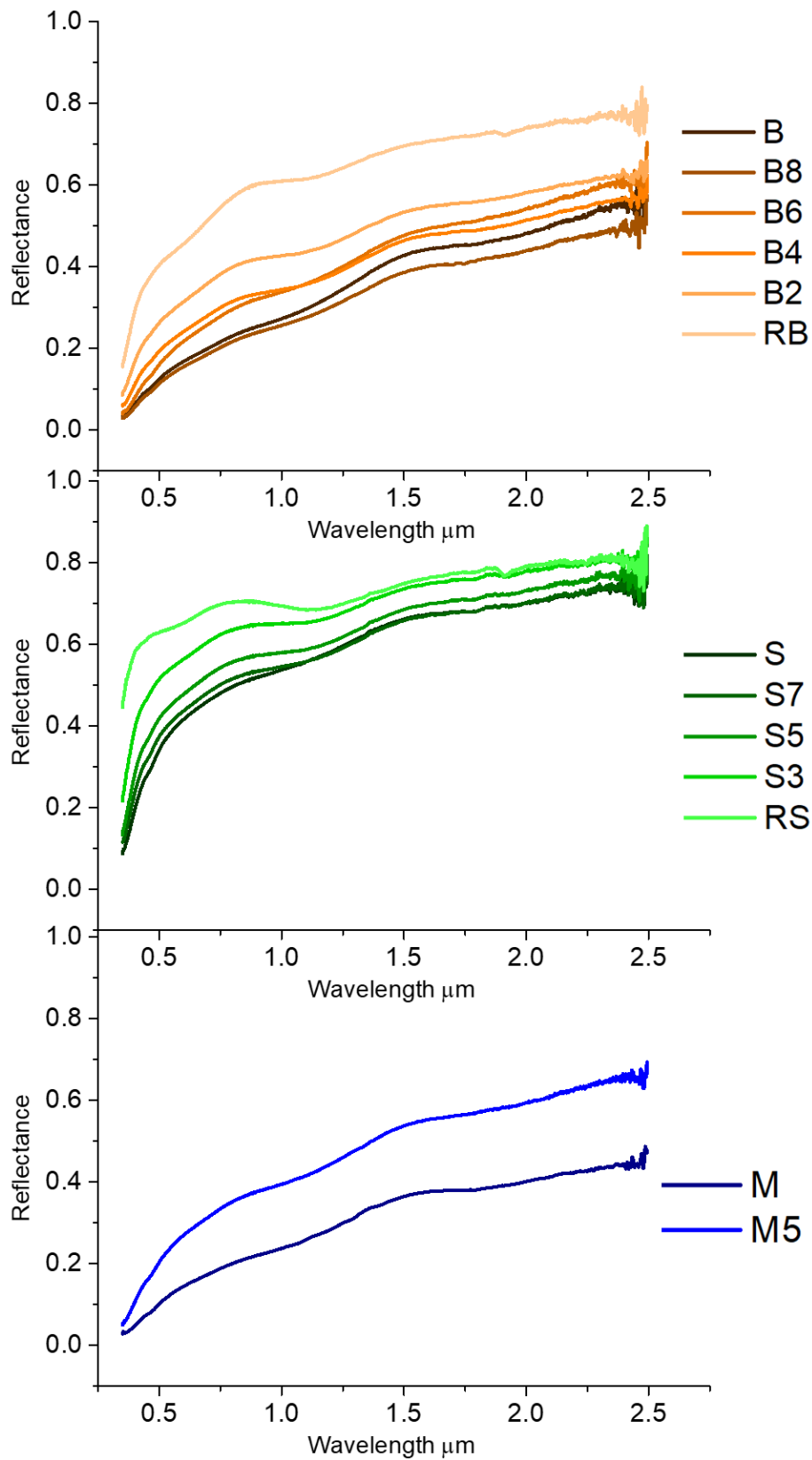


Figure 2: Spectral dataset for the three series: SRP (above, orange), Vulcano (middle, green), Etna (bottom, blue). Darker colour in the graph indicates more mafic, iron-rich composition.

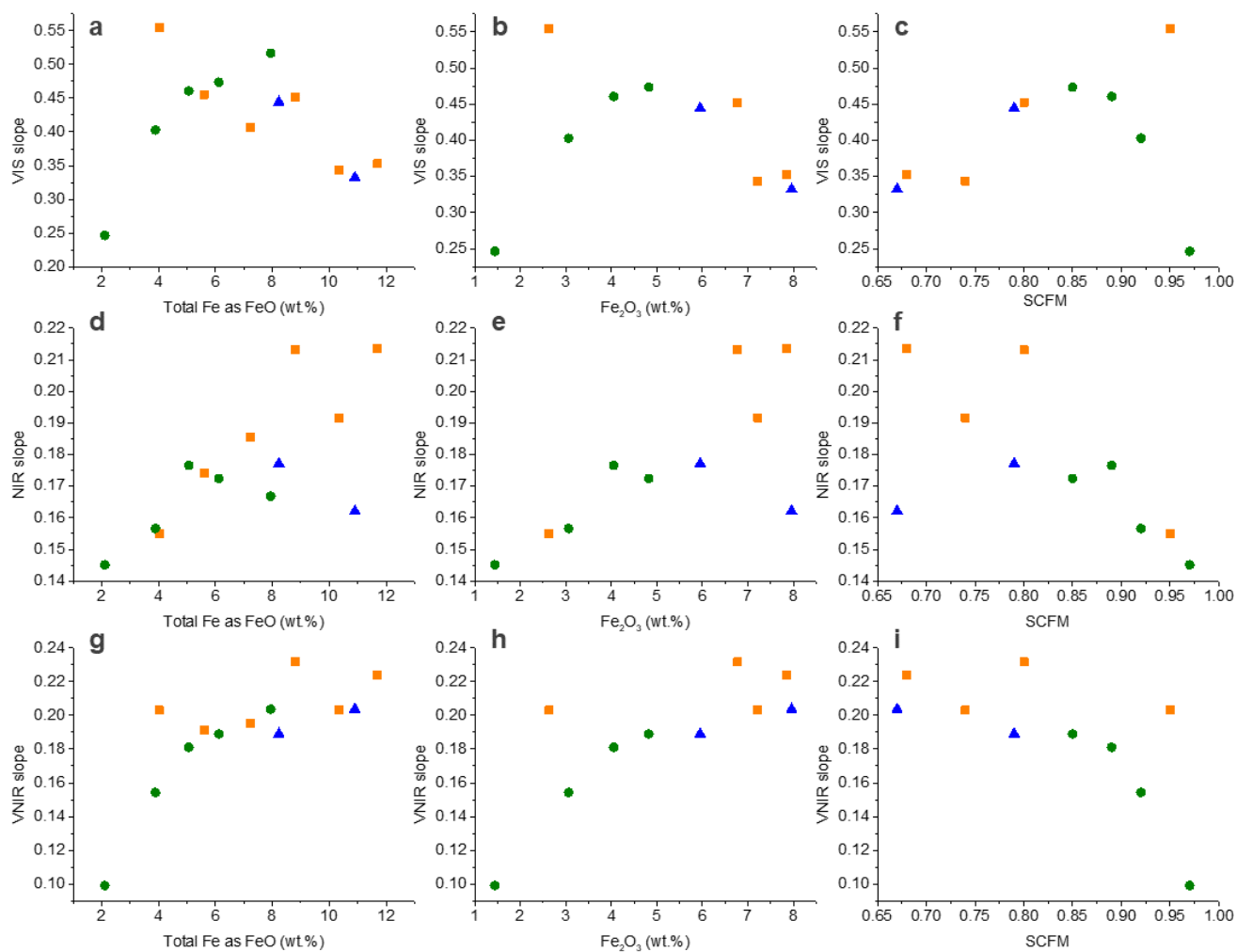


Figure 3: Slopes of spectra in Figure 2 plotted versus different chemical parameters: total iron content, ferric iron content and SCFM. Orange squares represent SRP, green circles represent Vulcano and blue triangles represent Etna samples. Slopes σ are reported in Table 2, showing how vertical error bars would be smaller than symbols in this picture.

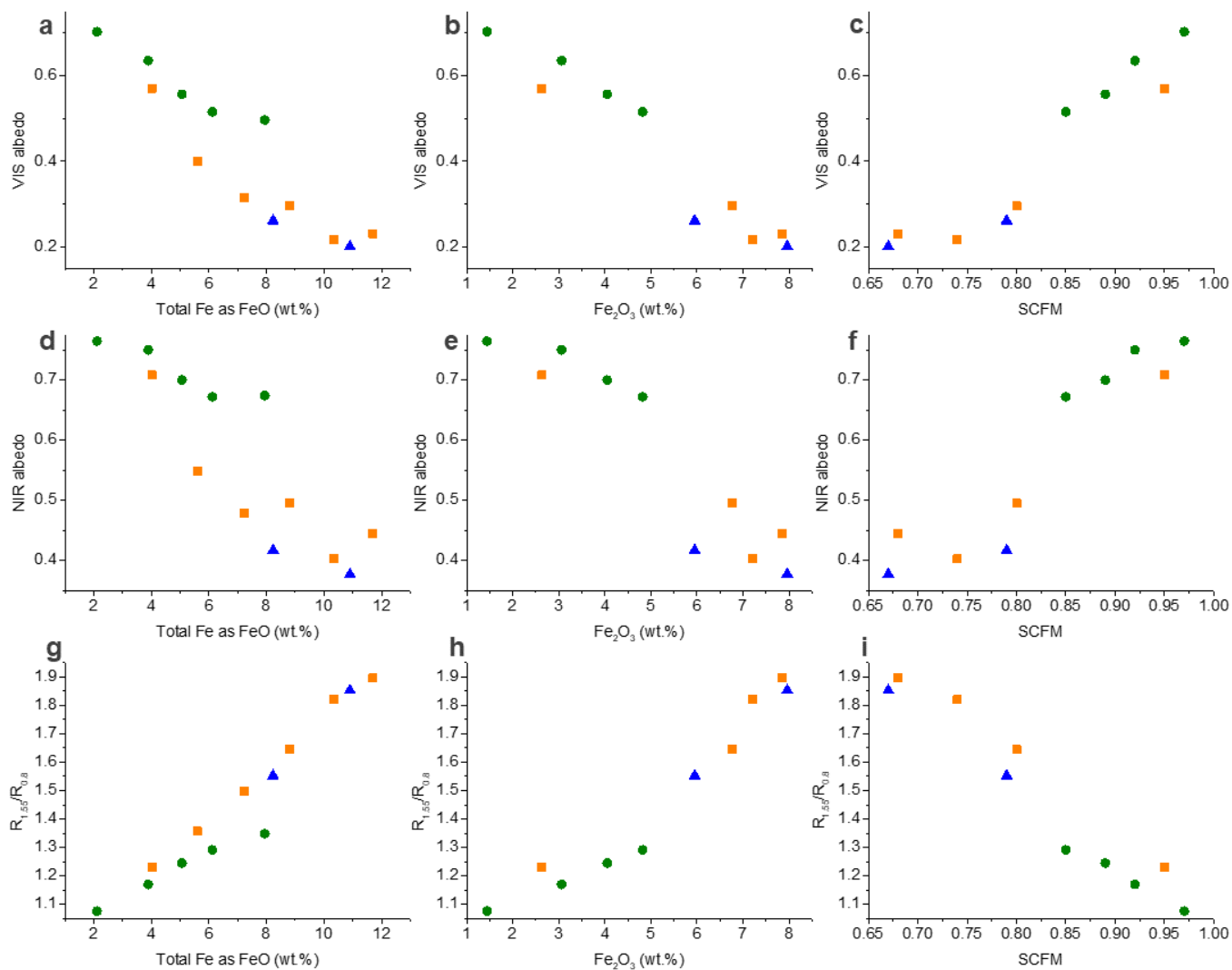


Figure 4: Albedos and spectra ratio $R_{1.55}/R_{0.8}$ of spectra in Figure 2 plotted versus different chemical parameters: total iron content, ferric iron content and SCFM. Orange squares represent SRP, green circles represent Vulcano and blue triangles represent Etna samples. Values σ are reported in Table 2, showing how vertical error bars would be smaller than symbols in this picture.

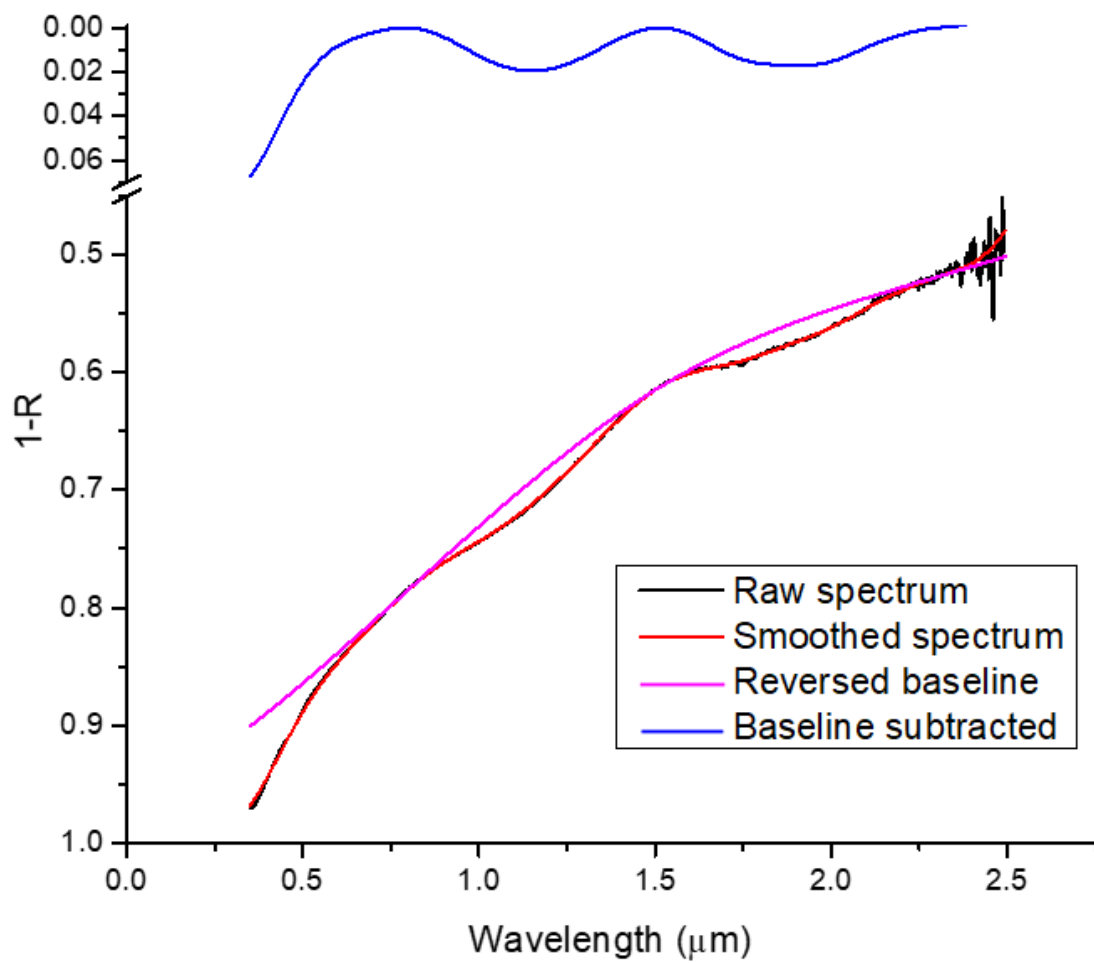


Figure 5: Example of the refinement passages performed from starting from the raw spectrum (black line) which is smoothed (red line). On the smoothed spectrum it is applied a reversed baseline (pink line) to obtain continuum-subtracted spectrum (blue line)

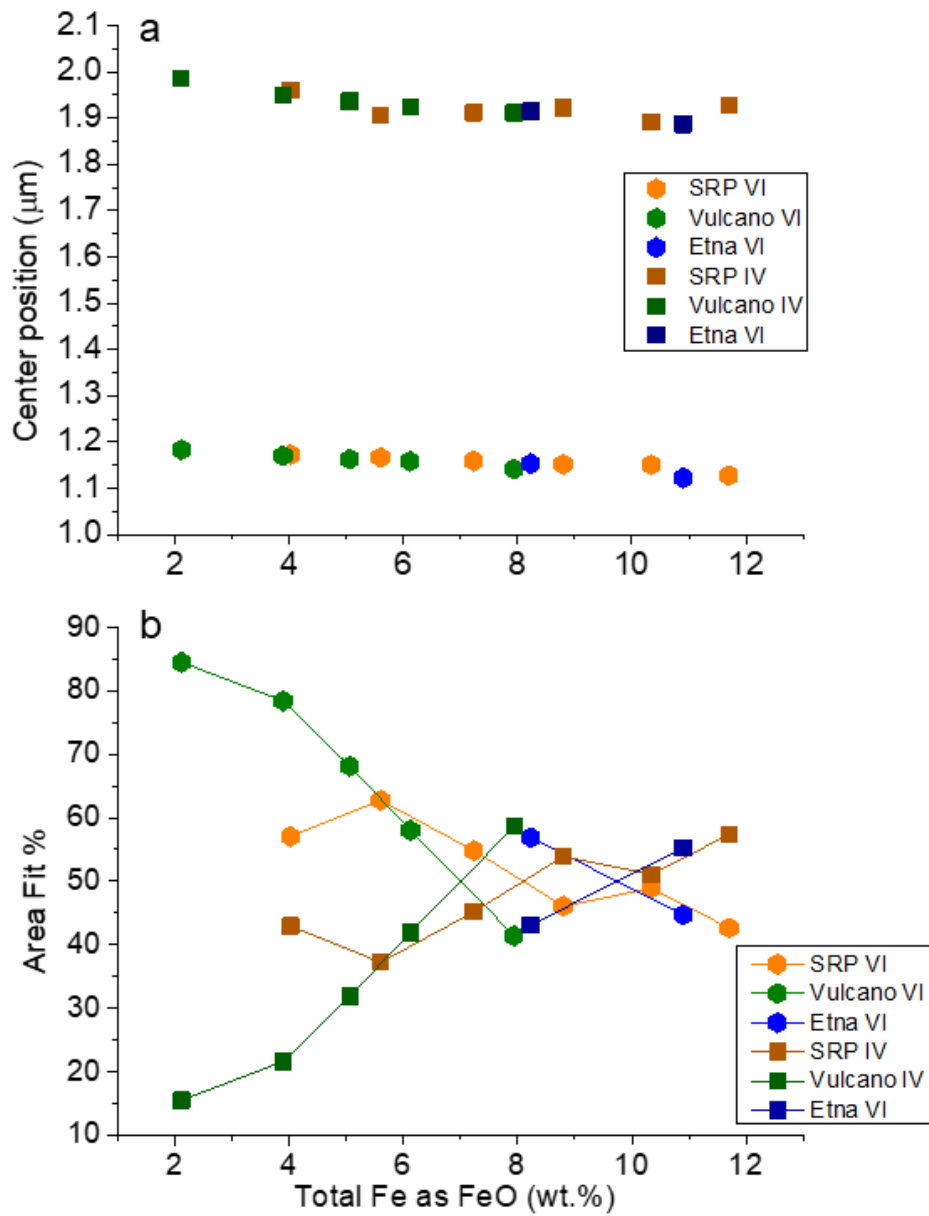


Figure 6: Variation of centres of absorption (above) and area percentage (below) in relationship with total iron content changing.

	SiO ₂	TO ₂	Al ₂ O ₃	FeO ^a	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	FeIII/Fe _{tot} ^b	SCFM
B	48.32	1.82	16.23	11.70	0.18	7.62	10.81	2.57	0.36	0.34	0.61	0.68
	0.15	0.05	0.08	0.10	0.03	0.05	0.07	0.05	0.02	0.03		
B8	53.06	1.60	15.52	10.34	0.15	6.14	8.88	2.69	1.22	0.29	0.63	0.74
	0.11	0.04	0.09	0.08	0.05	0.04	0.07	0.07	0.04	0.03		
B6	57.75	1.35	14.94	8.80	0.13	4.68	7.08	2.83	2.08	0.24	0.70	0.80
	0.16	0.04	0.08	0.11	0.03	0.05	0.08	0.06	0.04	0.03		
B4	62.68	1.11	14.26	7.23	0.10	3.19	5.26	2.91	2.97	0.22	-	-
	0.21	0.04	0.09	0.12	0.02	0.05	0.07	0.07	0.06	0.03		
B2	67.49	0.88	13.71	5.60	0.08	1.70	3.42	3.05	3.84	0.17	-	-
	0.17	0.03	0.06	0.11	0.02	0.03	0.05	0.06	0.07	0.02		
RB	72.13	0.65	13.20	4.02	0.04	0.25	1.62	3.17	4.75	0.14	0.59	0.95
	0.10	0.03	0.06	0.08	0.03	0.01	0.03	0.05	0.05	0.02		
S	54.23	0.69	16.02	7.94	0.17	4.13	7.68	5.34	3.11	0.49	-	-
	0.20	0.03	0.11	0.11	0.04	0.05	0.09	0.14	0.04	0.03		
S7	60.38	0.51	15.37	6.12	0.14	2.94	5.71	4.84	3.63	0.29	0.71	0.85
	0.20	0.02	0.08	0.14	0.02	0.04	0.10	0.09	0.05	0.03		
S5	63.83	0.39	14.78	5.06	0.12	2.17	4.44	4.68	4.08	0.27	0.72	0.89
	0.24	0.02	0.09	0.08	0.03	0.03	0.07	0.27	0.07	0.03		
S3	67.57	0.29	14.28	3.90	0.10	1.40	3.09	4.49	4.51	0.18	0.71	0.92
	0.11	0.02	0.09	0.09	0.03	0.03	0.05	0.06	0.05	0.02		
RS	73.25	0.12	13.53	2.12	0.07	0.25	1.12	4.17	5.13	0.047	0.61	0.97
	0.08	0.02	0.08	0.07	0.02	0.02	0.03	0.06	0.05	0.02		
M	48.50	1.53	14.53	10.90	0.18	7.82	12.13	2.61	1.23	0.45	0.66	0.67
	0.18	0.04	0.08	0.11	0.02	0.07	0.13	0.04	0.03	0.03		
M5	55.36	1.36	15.64	8.23	0.17	4.58	7.62	4.34	2.20	0.37	0.65	0.79
	0.14	0.05	0.12	0.16	0.02	0.05	0.11	0.07	0.02	0.03		
V	63.25	1.20	17.11	5.05	0.17	1.45	3.18	4.92	3.22	0.35	0.61	0.91
	0.25	0.04	0.05	0.08	0.03	0.03	0.05	0.16	0.05	0.04		

Table 1: Chemical composition of investigated products. For oxide, relative abundance in Wt.% is reported together with the standard deviation of the same value over five measurements. ^arefers to total iron taken into account as FeO, ^breports measured iron speciation. SCFM refers to the parameter defined by Walter and Salisbury (1989): SiO₂/(SiO₂+CaO+FeO+MgO) with oxides accounted as Wt.%. For *B2*, *B4* and *S* it was not possible to calculate Fe_{III}/Fe_{tot}, due to insufficient sample amount, and therefore SCFM is missing as well.

	WL/range	B	B8	B6	B4	B2	R	S	S7	S5	S3	R	M	M5
VIS slope	0.5-0.8 μm	0.35	0.34	0.45	0.41	0.46	0.56	0.52	0.47	0.46	0.40	0.25	0.33	0.44
σ VIS slope		0.0007	0.0005	0.0009	0.0007	0.0008	0.0007	0.0017	0.0013	0.0012	0.0010	0.0007	0.0007	0.0007
NIR slope	1.2-1.8 μm	0.21	0.19	0.21	0.19	0.17	0.15	0.17	0.17	0.18	0.16	0.15	0.16	0.18
σ NIR slope		0.0002	0.0001	0.0002	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	0.0002	0.0002
VNIR slope	0.6-2.0 μm	0.22	0.20	0.23	0.20	0.19	0.20	0.20	0.19	0.18	0.15	0.10	0.18	0.19
σ VNIR slope		0.0001	0.0001	0.0002	0.0001	0.0001	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	0.0001	0.0002
VIS albedo	0.8 μm ref.	0.23	0.22	0.30	0.31	0.40	0.57	0.50	0.52	0.56	0.64	0.70	0.20	0.26
σ Vis albedo		0.0016	0.0016	0.0018	0.0015	0.0018	0.0026	0.0017	0.0015	0.0014	0.0012	0.0006	0.0013	0.0013
NIR albedo	1.62 μm ref.	0.44	0.40	0.50	0.48	0.55	0.71	0.67	0.67	0.70	0.75	0.76	0.38	0.42
σ NIR albedo		0.0002	0.0003	0.0002	0.0002	0.0004	0.0002	0.0005	0.0003	0.0002	0.0003	0.0002	0.0002	0.0002
$R_{1.55}/R_{0.8}$	Ratio of ref. at 1.55 and 0.8 μm	1.90	1.82	1.65	1.50	1.36	1.23	1.35	1.29	1.25	1.17	1.08	1.85	1.55
		0.0006	0.0007	0.0008	0.0006	0.0007	0.0011	0.0008	0.0009	0.0009	0.0009	0.0007	0.0004	0.0002

Table 2: Values of slopes, albedoes, and spectral ratio for each sample, with relative errors σ as defined within De Angelis et al. 2014. For $R_{1.55}/R_{0.8}$, σ is calculated from the albedo errors at 1.55 and 0.8 μm following the rule of error propagation in a ratio.

	B	B8	B6	B4	B2	R	S	S7	S5	S3	RS	M	M5
Octahedral absorption Fe²⁺													
Area Fit	0.0109	0.0074	0.0073	0.0092	0.0082	0.0075	0.0061	0.0086	0.0106	0.0107	0.0166	0.0068	0.0055
Area Fit%	42.65	48.92	46.08	54.82	62.76	57.06	41.39	58.03	68.13	78.42	84.50	44.72	56.88
Center Max	1.13	1.15	1.15	1.16	1.17	1.17	1.14	1.16	1.16	1.17	1.18	1.12	1.15
Max Height	0.0277	0.0205	0.0212	0.0267	0.0252	0.0237	0.0181	0.0250	0.0298	0.0299	0.0409	0.0198	0.0159
FWHM	0.37	0.34	0.33	0.33	0.31	0.30	0.32	0.32	0.34	0.34	0.39	0.32	0.33
Tetrahedral absorption Fe²⁺													
Area Fit	0.0147	0.0077	0.0085	0.0076	0.0049	0.0057	0.0087	0.0062	0.0050	0.0030	0.0031	0.0084	0.0042
Area Fit%	57.35	51.08	53.92	45.18	37.24	42.94	58.61	41.97	31.87	21.58	15.50	55.28	43.12
Center Max	1.93	1.89	1.92	1.91	1.91	1.96	1.91	1.92	1.94	1.95	1.99	1.89	1.92
Max Height	0.0305	0.0185	0.0193	0.0184	0.0126	0.0127	0.0186	0.0141	0.0116	0.0073	0.0095	0.0205	0.0100
FWHM	0.45	0.39	0.42	0.39	0.36	0.43	0.45	0.43	0.41	0.38	0.31	0.39	0.39

Table 3: Parameters obtained from fitting processes on the two areas of absorption