SPECTRAL ANALYSES IN THE VNIR OF IGNEOUS ROCKS: SURFACE COMPOSITION CHARACTERIZATION OF TERRESTRIAL PLANETS

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INTRODUCTION

Understanding the geological evolution of the Earth and extraterrestrial planets passes through the knowledge of the lithosphere composition. To this aim, remote spectroscopy has become an important tool for the spectral characterization of the surface composition, particularly during the last decades as a consequence of the improved spatial and spectral resolutions of the sensors. The criteria for the interpretation of the surface composition of extraterrestrial planets can be established through the study of rock samples from terrestrial analogues, using pure minerals, mineral mixtures and rocks (*e.g.*, King & Ridley, 1987; Cloutis & Gaffey, 1991; Burns, 1993; Harloff & Arnold, 2001; Pompilio *et al.*, 2007).

The spectra of the most important silicate minerals, like pyroxene, olivine and plagioclase, show several diagnostic absorption feature in the Vis and near-IR range (Burns, 1993). The qualitative evaluation of remote spectra is generally made by comparison with spectra of minerals and rocks measured in the laboratory under controlled conditions. The spectroscopy of rock slabs is still in a developmental stage. The problems include: the discrepancy between rock-slab spectra and mineral mixture spectra with identical compositions; the texture effects on shape and position of the diagnostic absorptions of minerals; and the possibility to resolve the spectral components in a rock spectrum applying mathematical models.

The ongoing MESSENGER (NASA) and the planned Bepicolombo (ESA and JAXA) missions will improve our knowledge about the geologic history of Mercury. Mercury is the extreme rocky planet in our solar system, and so far the less studied. Data from orbit were acquired in the 70's by Mariner10 mission, whereas until the first flyby of MESSENGER in January 2008 the majority of data was collected from ground based observations. According to these data, the known part of Mercury is cratered and ancient, with some similarities with the Moon's surface (see a review in Boynton *et al.*, 2007). The less cratered, younger plains have been interpreted as having a volcanic origin; however the spatial resolution of Mariner10's images was not suitable for a reliable identification of volcanic morphologic features. The knowledge of chemistry and mineralogy of the mercurian surface is based on several ground based observations in the VIS, NIR and MIR intervals. Spectral data revealed no or weak absorption features indicative of low FeO and TiO_2 content, and a systematic red slope, supporting a close similarity to lunar highlands anorthosites.

In this research, sets of rocks belonging to suites from various terrestrial geodynamics contexts were analyzed in the VNIR spectral range, and the relationships between spectral and petrographic parameters were established. These rock suites have been selected as possible analogues for the mercurian surface composition. The influence of texture was also analyzed, using rock powders at different sizes as well as rock-slabs. The spectra collected during this research will also be implemented in a spectral library of possible Mercury's analogues.

TERRESTRIAL ROCK SUITES

Co-genetic rocks from a cumulitic layered intrusion (Stillwater Complex) and two distinct suites of basaltic rocks (Pampas Onduladas Flow and Iceland) from different geological contexts, have been studied. The composition of the principal mineral phases was determined by microprobe analyses made with a CAMEBA SX50 at the microprobe laboratory of C.N.R., Earth Science Department of Padua University.

The Stillwater Complex (SWC) is a portion of a cumulitic layered intrusion, emplaced 2.7 Ga at a depth of 10-15 km. Tectonic deformation and subsequent erosion exposed part of the intrusive complex. The igneous stratigraphy of the SWC consists of genetically related rocks subdivided into three major zones: the Basal Series, the Ultramafic Series (US) and the Banded Series (BS; McCallum, 1996). Two compositionally different magmas built up the SWC: a MgO and SiO_2 rich magma which formed the US and a tholeiitic magma from which the BS was originated.

The samples studied in this thesis were collected in the US and in the BS and show a cumulitic texture. In detail, the US samples have orthopyroxene (Opx), clinopyroxene (Cpx), olivine (Ol) and opaque minerals as cumulus phases, and plagioclase (Pl) as intercumulus phase. The BS samples have Pl as cumulus phase, while Opx, Cpx and Ol could be cumulus or intercumulus phases.

Five ultramafic rocks and five mela-norites have been studied from the US, while the BS samples consist of three anorthosites, two leucogabbros, three gabbronorites, one norite and three Ol-bearing rocks. Ol is more forsteritic (Fo_{85}) in US than in BS (Fo_{78}) samples. Opx and Cpx show narrow ranges of variation in individual samples, but these phases show significant variations when the samples are considered all together, ranging from $En_{59-88}Wo_{1-9}$ and $En_{39-51}Wo_{36-47}$, respectively. Pl is scarcely zoned but it shows a wide variation (An_{65}-An_{90}) considering the samples all together.

Chromite is present in some US samples.

The Pampas Onduladas Flow (POF) is a very long (181 km) pahoehoe lava flow erupted in the Andean back-ark volcanic province of Payenia, Argentina. The lava flow outpoured during the Late Quaternary from the summit rift of a shield volcano and it is the longest known individual Quaternary lava flow on Earth. It has a hawaiite composition with Ol and minor Pl phenocryst (Pasquarè *et al.*, 2008).

The studied samples were collected from different portions of the lava flow: most of them derive from the proximal portion of the flow; a few samples from the middle and one sample represents the distal portion. They show P.I. index less than 8%, and an intergranular texture of the groundmass. The mineral association consists of Pl, Ol, Cpx and small amounts of opaque minerals. Only one sample shows a hyalopilitic groundmass for the presence of a dark glass.

Ol phenocrysts range from Fo_{72} to Fo_{84}, whereas microcrysts range from Fo_{30} to Fo_{70}. Cpx varies from Ca-rich augite ($En_{42}Wo_{44}$) to diopsidic-augite ($En_{32}Wo_{48}$). Pl varies in composition from An_{61} to An_{68}. Opaques are Chr-spinel.

Iceland is an island developed on the Atlantic middle ridge up to a mantle plume. Active volcanic systems are associated with three different rift-areas which comprise en echelon arrays of volcanic fissure swarms: the Reykjanes Eastern Rift Zones (ERZ), the Reykjanes Western Rift Zones (WRZ), the Reykjanes Northern Rift Zones (NRZ). Volcanic activity is also present in non-rift areas but this volcanic centres lack well-developed fissure swarms.

Different types of volcanic products have been observed in Iceland, but almost 85% consists of basalts with composition varying amount tholeiiti, Ol-rich, and transitional-alkaline, Ol-alkaline or Fe-Ti rich (Basaltic Volcanism Study Project, 1981).

The samples studied in this thesis are from different lava flows of the ERZ and the NRZ. They show a wide range of phenocryst content, with P.I. index from 0 to 85%. Also the groundmass texture is strongly variable: in some samples it is intergranular, in others intersertal or hyalopilitic due to the presence of a dark glass. The mineral association includes Pl, Cpx, opaque minerals and rare Ol.

Ol phenocrysts vary from Fo_{76} to Fo_{87}, whereas microcrysts range from Fo_{61} to Fo_{85}. Cpx is represented by augite, varying in composition from $En_{51}Wo_{44}$ to $En_{35}Wo_{27}$. Pl is scarcely zoned, but it shows a wide variation, ranging from An_{76} to An_{90} among the phenocrysts and from An_{44} to An_{80} among the microlites, considering the samples all together. Ilmenite and magnetite are ubiquitous as opaque minerals.

REFLECTANCE SPECTROSCOPIC DATA

Reflectance spectra were measured in the 0.35 to 2.50 µm interval using two spectrophotometers: a) Perkin-Elmer λ-19 at IFAC Institute of C.N.R., Florence and b) Fieldspec Pro at INAF-IASF Institute, Rome.

In this range of wavelength, several absorption features of silicate minerals are described in the literature (*e.g.*, Burns, 1993), as well as the spectral behaviour of mineral mixtures. In this work the spectra were measured on slabs and powders of rock.

Powdered specimens were however limited to selected representative samples.

The visual inspection of the spectra was useful to recognize the most evident absorption structures, and to assign the absorption bands to electronic and molecular interaction processes by comparison with the literature. Electronic and vibrational absorptions were described and labelled using roman numbers (Band I to V in Fig. 1) and lowercase letters (Band a to d), respectively. Band I (~ 1.00 µm) is due to the presence of Fe^{2+} in M2 of Opx, in M1 or M2 of Cpx and in both M2 and M1 of Ol, Band II (~ 2.00 µm) is due to the presence of Fe^{2+} in M2 of Opx and Cpx, Band V (~ 1.25 µm) is due to the presence of small Fe^{2+} amounts in Pl. Different associations of these bands identify spectral groups that represent "spectral classes" in the sense of Longhi *et al.* (2001); these spectral classes can

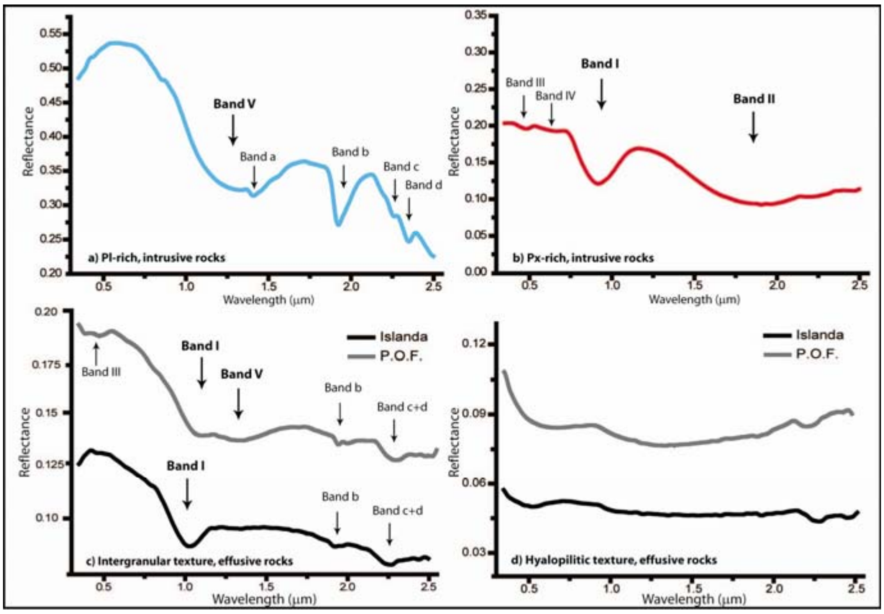

Fig. 1 - a, b) Exempla of slab spectra of first two classes of intrusive rocks (SWC). c, d) Exempla of slab spectra of basalts, samples with intergranular texture show absorption structures of minerals, samples with hyalopilitic texture do not show them.

be compared with petrographic features (rocks composition and texture). The parameters describing individual absorption bands (position on the wavelength axis, intensity and width at half maximum) are related to the mineral composition. For this analysis, statistical methods of spectral analysis (Sunshine *et al.*, 1990; Pompilio *et al.*, 2009) have been used to decompose the spectral curves both measured on slabs and powdered samples.

In general, slab spectra show a blue slope (reflectance decreasing towards IR). Powdered spectra show higher reflectance than the corresponding slab spectra and a horizontal or red slope (reflectance increasing towards IR).

In particular:

1) The slab spectra of SWC rocks are grouped into four classes: One class is characterized by a wide absorption band at about 1.25 µm, that can be due to Fe^{2+} in Pl; these rocks are anorthosites and leucogabbros, with Pl > 80% (Fig. 1a). The second class (Fig. 1b) shows two absorption bands at about 0.93 µm and 2.00 µm, due to Fe^{2+} in M2 site of Opx and in both M1 and M2 sites of Cpx (Burns, 1993). The other two classes, not shown in Fig. 1, comprise spectra characterized by a low reflectance and weak absorption band due to the influence of opaque minerals; and a group of spectra with no clear absorption features, dominated by variously altered Ol.

2) In the slab spectra of basalts the absorption features due to different mineral associations can be recognized in samples with an intergranular or intersertal texture (Fig. 1c). The absorption bands are smoothed in samples with a hyalopilitic texture (Fig. 1d).

Spectral curves measured on powdered samples of the first two groups of SWC rocks allowed us to quantify the spectral parameters and therefore to characterize the absorption features due to the spectrally active "facies". In this case, "facies" indicates an ion in a specific site in a mineral; *e.g.*, the Fe^{2+} content in Pl or in M2 site of Opx and Cpx, or in M1 and M2 sites of Ol.

The spectra of powdered basalts show absorption structures due to two different mineral associations; the absorption bands are well defined for samples with intergranular texture, and are almost absent in those containing dark-glass.

In the following section, the spectral parameters measured on spectra of powdered rocks are compared with the rock compositions.

SPECTROSCOPIC PARAMETERS *VS.* ROCK/MINERAL COMPOSITIONS

As reported above, different associations of absorption bands permit the spectral classification of rocks with different mineral associations and/or textures. The parameterization of these absorption features allows the evaluation of the content of the "facies", so that the relationship between absorption data and mineral chemistry can be established. Several models were proposed in the literature to quantify the absorption bands: empirical methods which measure position, depth and width of the absorption band; models of scattering which involve solving the equation of Radiative Transfer; models of decomposition which use a distribution of Gaussians or modified Gaussians superimposed to a continuum. In this research, a new decomposition model called EGO (Exponential Optimized Gaussian; Pompilio *et al.*, 2009) has been used.

The Band I, clearly expressed in both slab and powder spectra, is particularly diagnostic for Opx, Cpx and Ol. In our samples, it results in a composite band, due to the silicate absorptions of those silicate occurring in a restricted range of wavelength. EGO returns a Gaussian for each absorption process. The band centre position (b.c.) and the band depth (b.d.) of the Gaussians are compared with the parameters of mineral composition (ferrosilite or forsterite content) and the relative modal abundance of minerals.

The b.c. of Opx and Cpx for intrusive rocks (Fig. 2) and of Cpx and Ol for effusive rocks (Fig. 3) were compared with data from the literature relative to pure minerals (Cloutis & Gaffey, 1991; Burns, 1993).

In both cases, the b.c. positions measured in rocks approximate the correlation curves reported in the literature for pure minerals.

The b.d. or intensity of the absorption band is related to the probability of an electronic transition to occur. For a given allowed transition, the b.d. is related to the abundance of the absorbing phase in a mineral mixture (*e.g.* Opx in Fig. 4). A linear relationship was observed between b.d. and Fe^{2+} content in both Opx and Cpx (*e.g.* Opx in Fig. 5). However, because the band intensity depends on the amount of spectrally active "facies", saturation effects were observed as this amount increases (empty circles in Figs. 4, 5).

On the other hand, the intrusive rocks are classified on the basis of the relative modal abundance of the principal minerals; therefore, it is useful to establish the relationship between the b.d. of the absorption and the modal abundance of the absorbing phase. In fact, a linear relationship was observed between b.d. measured in powder spectra and both Opx mode (Fig. 4) and volumetric Fe^{2+} content, expressed as Fe^{2+} * mod Opx% (Fig. 5).

Similar linear trends are displayed in Figs. 4 and 5 for spectra measured on rock-slab spectra. In this case, however, a so called "bulk effect" is responsible for a strong reduction of b.d. with respect to b.d. measured in spectra of powder samples of the same rocks.

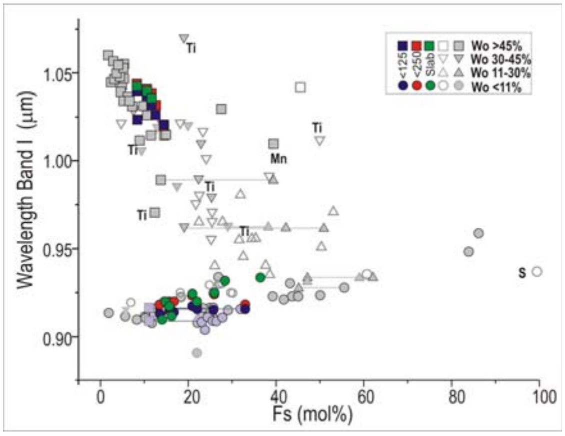

Fig. 2 - Position of Band I *vs.* Fs (mol.%) of pyroxene of SWC. Data of this thesis are colored; literature data are grey (modified after Pompilio *et al.*, 2007).

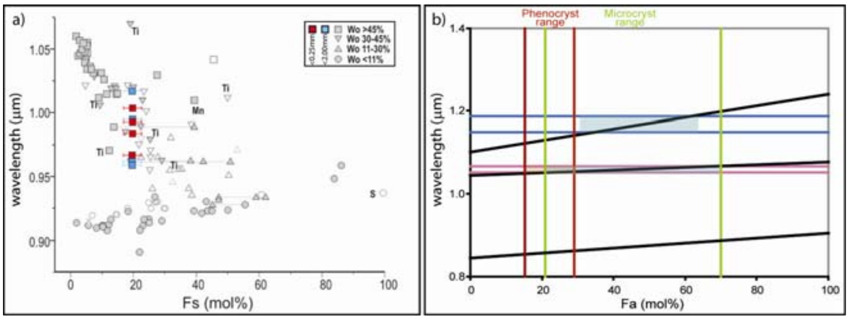

Fig. 3 - a) Position of b.c. *vs.* Fs (mol.%) of Ti-augite of POF. Data of this thesis are colored; literature data are grey (modified after Cloutis *et al.*, 1991); b) position of b.c. (powders < 0.25 µm) *vs.* Fa (mol.%) of Ol, black lines are data from literature (modified after Burns, 1993).

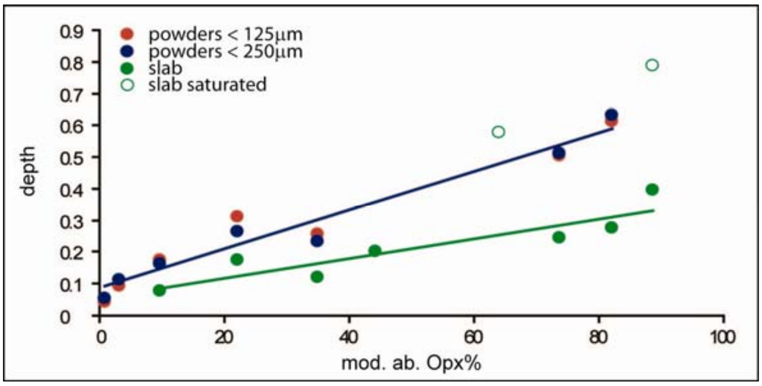

Fig. 4 - Band depth *vs.* mod. ab. of Opx for samples of SWC. Confidence level of 99%.

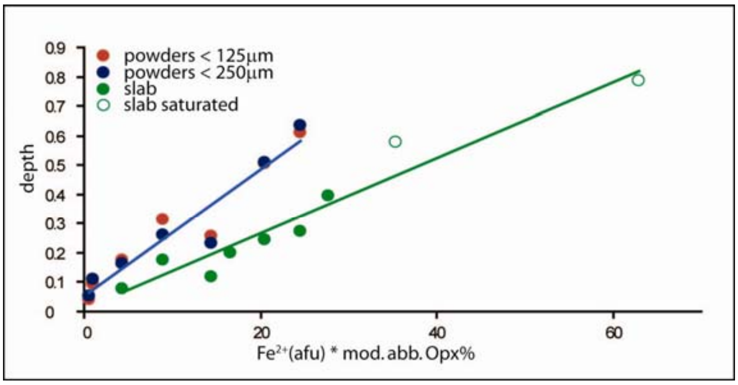

Fig. 5 - Band depth *vs.* modal distribution of Fe^{2+} of Opx for samples of SWC. Confidence level of 99%.

APPLICATION TO SPECTRA OF MERCURY

New data from the first MESSENGER's flyby show that Mercury's surface is morphologically and compositionally more heterogeneous then previously observed (Boynton *et al.*, 2007, and references therein). Areas characterized by different ratios in the VIS and NIR have been associated with distinct surface morphologies (Robinson *et al.*, 2008). Furthermore the spectra show evidence for the presence of pyroxene or olivine richer in Mg than predicted before. Finally, the effect of a darkening agent, possibly Ti-Fe oxides, was proposed.

Spectra of powders measured in this thesis have been recalculated to the slope of the average full-disk spectra of Mercury acquired by MASCS (McClintock *et al.*, 2008). Recalculated spectra show that the absorption band I in norites and gabbronorites is still clearly recognizable. In contrast, the shape of the anorthosite spectra is close to the average full-disk spectra and the basalt spectra do not show clear absorption structures.

Band ratios calculated according to Robinson *et al.* (2008) algorithms show that the basalts follow the trend described for the low reflectance material and the SWC samples partially fall in the range of immature areas, with a wider range of values for the NIR slope due to the presence of the band I (Fig. 6).

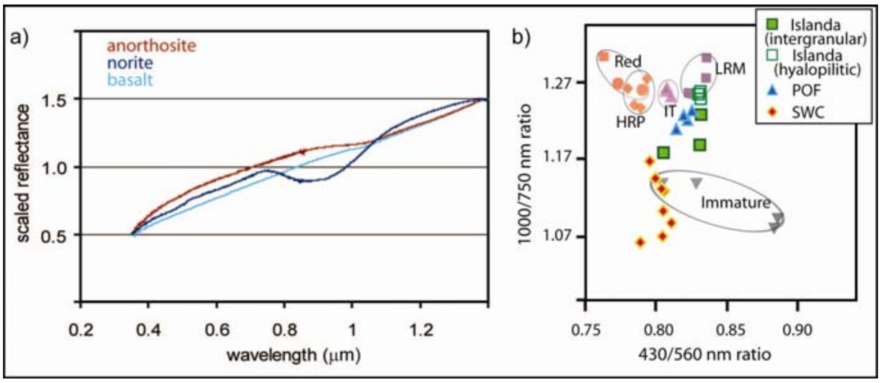

Fig. 6 - a) Recalculated spectra show a clear band I only for pyroxene-rich SWC samples. b) Band ratios calculated according to Robinson *et al.* (2008).

CONCLUSIONS

- Different associations of absorption bands permit the spectral description and the discrimination of the rock compositions of the three studied sites.

- The spectral parameters determined in rock spectra are comparable with those of pure minerals. In particular the b.c. of the modified Gaussians, resulting for the spectra of both slabs and powders match the correlation curves determined for pure minerals (Opx, Cpx and Ol). The b.d. for intrusive rocks always show a linear relationship with modal abundance. However, weaker b.d. were observed for the slabs with respect to the powdered samples of the same rocks.

- Spectra re-calculated according to the algorithms used for MASCS spectra of Mercury show a clear absorption structure of pyroxene for norites and gabbronorites, indeed up to now not detected in Mercury's spectra. However, both the anorthosite and basalts recalculated spectra, although these rocks contain pyroxene, do not show clearly absorption structure clearly indicative of mafic minerals.

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