MULTI-SPECTRAL INVESTIGATION OF PLANETARY ANALOG MATERIAL IN EXTREME ENVIRONMENTS - ALTERATION PRODUCTS OF VOLCANIC DEPOSITS OF VULCANO / ITALY.

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Introduction: During the fifth International Summer School held on Vulcano (Eolian Islands, Italy) in June 2019 we used the opportunity to investigate volcanic deposits with three different spectroscopic instruments, i.e. a portable visible and near infrared spectro-radiometer, a portable LIBS (laser-induced breakdown spectroscopy) instrument and a portable Raman system and thus combining mineralogical, elemental and molecular information. The summer school brings together space and deep sea research in the context of robotic exploration missions. The three applied spectroscopic methods are of particular interest for planetary exploration by mobile spacecrafts.

The island of Vulcano presents an extremely large variety of volcanic deposits (from lava flow to phreatomagmatic ash deposits) and geochemical features (from basalts to shoshonite to alkaline rhyolites) [1, 2]. The spectrally sampled areas reach from classical lava blocks with dark and bright phenocrysts and dark glass to extensive ash deposits from different phases of the volcanic activity on the island. In addition, recently active fumaroles offered the measurements of numerous partially crystallized sulfur samples deposited onto the surface. Of particular interest, however, were alteration products of the volcanic deposits under extreme environmental conditions with the lava directly deposited at the coastline and thus under influence of sea water and ongoing (submarine) volcanic activity.

Instrumentation: In the field we used a portable spectro-radiometer (PSR+3500) that works in the visible and near-infrared spectral range (350 – 2500 nm) with a spot size of 3 by 3 mm for studying the mineralogical content of the volcanic deposits.

LIBS - a form of atomic emission spectroscopy for the elemental analysis at a sub millimeter scale - (commercial hand-held LIBS instrument /SciAps Z 300) uses a laser to ablate a small amount of sample material and to produce a plasma spark, whose spectral analysis permits rapid in-situ multi-elemental analysis in the field [3].

Finally, the RaPort handheld Raman instrument by EnSpectr equipped with a 532 nm (same wavelength as used for the ExoMars2020 rover mission) excitation laser operating at <60 mW laser power has a spectral range of 120 - 4000 cm^{-1} (> 2.5µm) at 6-9 cm^{-1} spectral resolution and a spot size of around 0.5 mm.

Results: The preliminary analysis of the acquired VIS/NIR spectra in comparison with the spectral libraries provided by PDS (https://speclib.rsl.wustl.edu/) implies a remarkable enrichment in alteration minerals in this area. So far next to iron bearing oxides and clay minerals several sulfates could be identified (Fig. 1 a). The spectra analyzed so far show a nice transition from more iron-bearing lava blocks to material dominated by sulfates such as Alunite and Jarosite with the characteristic Al-OH and Fe-OH absorptions near 2.17 and 2.27µm, respectively [4]. Both minerals appear to be rich in K in the studied area, which was also seen in the LIBS data (accompanied by a strong signal of Sr) (Fig. 2 a).

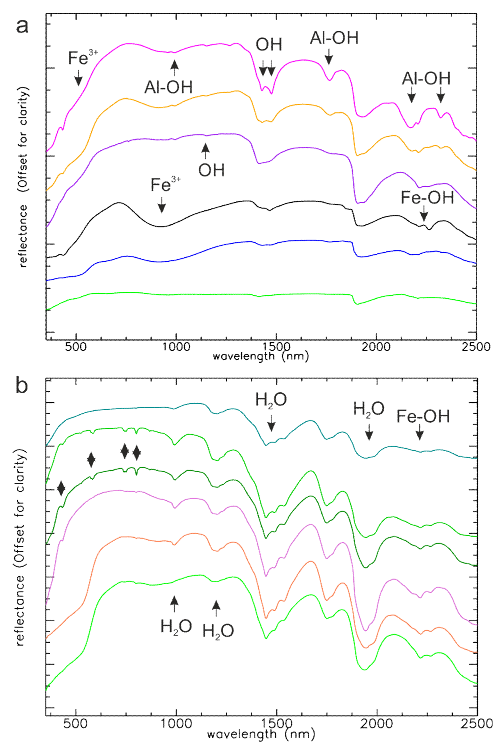

Fig. 1: Sequence of visible and near-infrared spectra showing (a) the transition from less weathered lava rocks to strongly weathered surface with (b) the alteration products partly appearing as individual gypsum crystals.

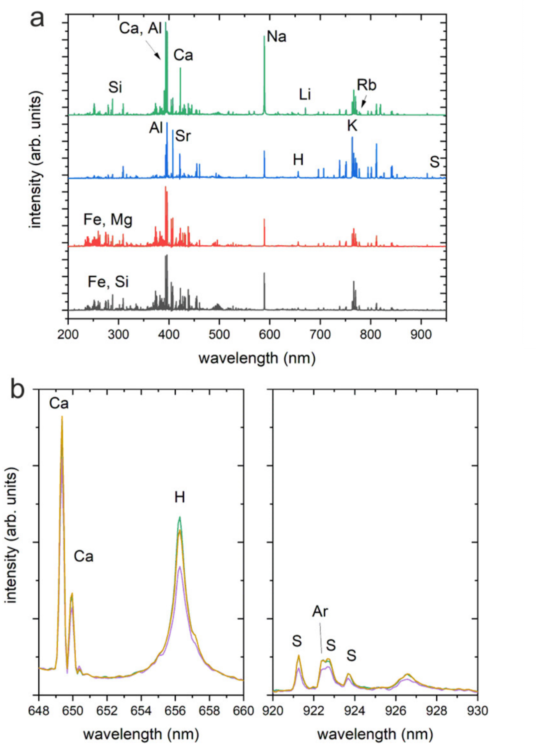

Fig. 2: Elemental variations seen in LIBS data supporting the composition implied by the VIS/NIR spectra (Fig. 1).

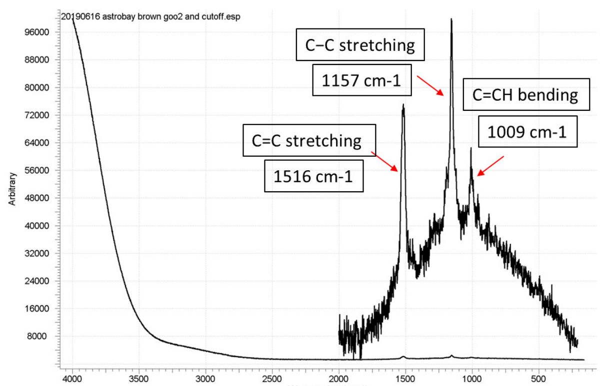

Fig. 3: Example Raman spectra showing high fluorescence after 3500cm^{-1} and a typical carotenoids´ signature (zoomed in part shown above) with peaks at 1009, 1157 and 1516 cm^{-1} corresponding to C=CH bending, C−C stretching and C=C stretching modes, respectively.

Jarosite is a common weathering product of oxidized iron sulfides under acid conditions and is known to be formed together with ferric oxyhydroxides. Alunite - an analog of jarosite - is a well-known weathering product in volcanic rocks and often found near hydrothermal activity and fumaroles [4].

Strongly altered rock portions often showed peculiar crystal growth, which could be mainly associated with gypsum ($CaSO_4 \cdot 2H_2O$) due to their characteristically shaped H_2O absorption near 1.5µm (Fig. 1 b) and a high Ca and S signal in the LIBS data (Fig. 2 b). Gypsum is typically deposited from seawater, hot springs or volcanic vapors [5]. Numerous tiny absorptions in the visible spectral range of several samples, which are rich in gypsum imply the possible existence of phosphor bearing minerals such as apatite ($Ca_5[(F,Cl,OH)|(PO_4)_3]$) (Fig. 1 b).

The hand-held Raman spectroscopy confirmed the VIS/NIR data for mineral recognition and was also able to identify traces of biomolecules such as carotenoids on the colonized rock surfaces, which are of highest interest for the characterization of the habitability and the search for life on Mars (Fig. 3).

Conclusions: This *in situ* survey will serve to inform on the capacities of such observation techniques to characterize extreme extraterrestrial environments as expected in the past evolution of planet Mars and partially on icy satellites in the Jovian systems such as Europa, where sulfur compounds originating from the volcanically active neighboring satellites Io possibly interacts with Europa's icy surface and/or ocean material. Therefore the investigated area provides an unique training ground for instruments and techniques foreseen for future robotic missions to Mars (e.g. Mars2020 and ExoMars2020 rovers [6, 7], but also to other bodies of high astrobiological interest such as the missions Europa Clipper [8] and JUICE [9].

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