Raman-Ir Spectroscopic And Xrd Analysis Of Samples From Fogo Island, Cabo Verde: Implications For Martian Volcanology. E. A. Lalla[1,*], M. Aznar[2], A. Sanz-Arranz[3], M. Konstantinidis[1], G. Lopez-Reyes[3], M. Veneranda[3], E. A. Lymer[1], J. Freemantle[1], E. Sawyers[1], M. G. Daly[1], E.A. Cloutis[4], J. Martinez-Frias[5], and F. Rull-Perez[3]. [1]York University, 4700 Keele St. M3J 1PC, Toronto ON, Canada; [2]FCT, Universidade de Cabo Verde, Zona K do Palmarejo Grande, Praia, Cabo Verde; [3]Unidad Asociada UVA-CSIC-CAB. C/ Francisco Valles 8, 47151, Boecillo, Spain; [4]Department of Geography, University of Winnipeg, 515 Portage Av, Winnipeg, MB, R3B 2E9, Canada; and [5]Dinamica Terrestre y Observacion de la Tierra, Instituto de Geociencias, Ciudad Universitaria, C/ del Dr. Severo Ochoa, 7, 28040 Madrid, Spain.

Introduction: Decades of scientific exploration have revealed that some places on Earth present similar features to some geological environments on Mars. These terrestrial analogues of Mars are places on Earth that are characterized by some combination of climatic, mineralogical, geomorphological and/or geochemical conditions similar to those observed on Mars. These terrestrial analogues environments give us the opportunity to study the characteristics of Mars without leaving our planet [1]. The study of Martian analogues allows us to better understand the processes that have shaped the surface of Mars, including its geological and geochemical evolution. Moreover, analogue site investigations allow us to evaluate the potential for the emergence of life and the preservation of different types of fossil biomarkers throughout the history of the planet [2].

Young volcanoes are environments with great importance as analogues of Mars because of the following characteristics: 1) they can have great mineralogical diversity; 2) high ultraviolet light irradiation, lower atmospheric pressure and lack of nutrients; and 3) the existence of fumaroles, volcanic tubes and associated hydrothermal processes [3]. These main characteristics are presented by young volcanic islands like Hawaii, Galapagos, Canary Islands, and Cape Verde archipelagos. In this abstract, we propose for the first time, Pico de Fogo outcrop, Cabo Verde as a Mars analogue, analogous to other young volcanic islands (i.e., Hawaii and Canary Islands), for its great geodiversity, volcanic structures, and geomorphological similarity to some ancient volcanoes on Mars. The Pico de Fogo outcrops can be used as a comparison to ancient Martian volcanism and their relevance in the possible existence of Martian life in the past.

Geological setting: The Cape Verde archipelago is comprised of 10 islands and several islets located about 550 km west of the west coast of Africa (west of Senegal), between 21-25º W, and 15-17º N. This archipelago, together with the Azores, Madeira and the Canary Islands form the so-called Macaronesia group. The geological evolution of Cape Verde is not yet known in as much detail as the Canary Islands. The formation of the Cape Verde islands was likely initiated by a central underwater volcanic eruption, and later on was complemented by a fissure network manifested as the Pico de Fogo outcrops. It is mostly dominated by eruptions of magmatic and pyroclastic materials (scoria, or "lapilli" and ash), of predominantly basaltic composition [4]. Thus, the archipelago is essentially constituted by basic volcanic rocks with a predominance of basaltic rocks and two different types of magmatism can be found: a) Tholeiitic magmatism (magnesium-rich, primitive initially erupted or emplaced rocks) and b) Alkaline magmatism (more iron-rich) [5]. In the special case of Fogo Island, the main edifice of Fogo Island is mainly constituted by four different geological structures: 1) the Monte Amarelo stratovolcano that controls the current morphology of the island, 2) the subsequent landslide of its eastern flank that left a geological amphitheatre with a 20 km perimeter, and sub-vertical walls of up to 1,100 m of uneven structures (so-called “Bordeira”), 3) the aforementioned Pico de Fogo, a stratovolcano nested inside this caldera, and 4) an almost flat plateau between both structures called Chã das Caldeiras, formed by the filling of volcanic materials from Pico do Fogo and secondary cones and eruptions that contact and accumulate against Bordeira [4]. The selected area is the Cha das Caldeiras, where the last volcanic eruption of Fogo began on November 23, 2014 in Chã das Caldeiras until 2015 (72 days). The eruption formed 6 eruptive mouths in the western foothills of Pico de Fogo, practically in the same place where the previous eruption of 1995 occurred. The lavas initially presented a’a morphologies, and the secondary flows exhibited pahoehoe morphologies. The eruptive cone is >100 m height and formed by the accumulation of pyroclastic materials of different sizes.

Experimental Setup: The XRD instrument is a portable inXitu (now Olympus) Terra-185 system. The diffractometer includes a CoKα excitation source (300 kv, 300 μA), a vibrating sample holder cell and a 2D Peltier-cooled CCD detector. X-ray diffraction is recorded in a range from 5 to 55º 2θ with an average resolution of 0.25 - 0.30º 2θ (FWHM).

The FTIR-ATR instrument is a Perkin Elmer Spectrum 100 FT-IR Spectrometer system, equipped with a universal ATR sampling accessory.

Figure 1. GoogleMaps image of the Pico do Fogo Volcano, Cape Verde (Credits: Google)

The measurement conditions chosen were a spectral resolution of 4 cm^{-1}, 16 scans, and a 500-4000 cm^{-1} spectral range.

The FT-Raman is a Raman Bruker RFS100/S system, with a 1064 nm Klastech laser and a Bruker D418 CCD detector. The measurement conditions chosen were: a laser power of 500 mW, a laser spot on sample of 1000 μm, to obtain a low irradiance and avoid thermal damage on samples. Spectral resolution was 4 cm^{-1}, 512 or 1024 scans, scanning speed of 1.6 kHz, and a spectral range from 0 to 3500 cm^{-1}.

A representative portion of the samples was ground to be used in three different analyses: XRD, FTIR-ATR spectroscopy, and FT-Raman spectroscopy. Bulk samples were analyzed by Raman spectroscopy, with no previous preparation of the sample. The points analyzed were visually chosen by the Raman system operator. The 785 nm Raman instrument used was composed by: a BWTEK BRM-OEM-785 laser; a BWTEK BAC100-785E Raman probe, a BWTEK Prime T spectrometer-Hamamatsu S10141-1107S CCD. Laser power on sample was chosen on each point to avoid thermal damage. The head probe focused the laser through a 20× lens, and the spot size was 85 μm with 0- 3000 cm^{-1} spectral range and a resolution of 4 cm^{-1}.

Results: We detected a great variety of minerals relevant to current Martian exploration. The XRD measurements shows the existence of the following minerals: 1) pyroxene (augite and diopside); 2) feldspars (orthoclase, bytownite, and sanidine); 3) olivine (forsterite); 4) zeolites (analcime, chabazite, and muscovite); 5) amorphous carbon; and 6) oxide (magnetite). Compared to XRD, Raman and FTIR combined were able to detect more minerals than XRD. The spectroscopic techniques also enabled detection of carbonates (dolomite and calcite), phosphate (apatite), other oxides (hematite, chromite, and anatase) and different forms of carbon (i.e., amorphous carbon and graphite). Moreover, Raman spectroscopy was able to detect both crystalline and amorphous forms of carbon and it allowed analysis of even single mineral grains such as phosphates and carbonates.

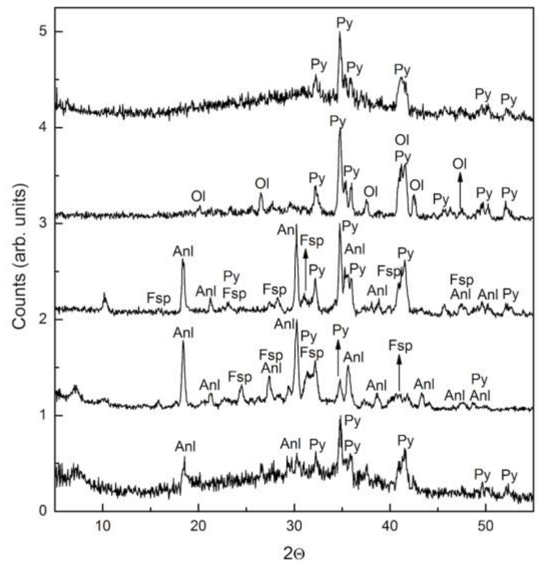

Figure 2. XRD of some selected samples from Chas Canada, Fogo. Pyroxene (Py), olivine (Ol), feldspar (Fsp), and analcime (Anl)

The continuous enlargement and analyses of different terrestrial analogues by Raman spectroscopy and other supporting techniques will assist planetary research with astrogeological implications, especially on the development of future Mars missions such as the Exo-Mars rover mission [1]. Moreover, volcanic sites such as Fogo could be extended as possible terrestrial analog to the Moon and to test future Raman systems like the LunaR System [6].

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