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CHARACTERIZATION OF SELECTED MINERALS FROM CALATRAVA´S LAVAS BY MICRO-RAMAN AND MÓSSBAUER SPECTROSCOPY AND X-RAY DIFFRACTION. F. Rull[1], G. Venegas[1], G. Klingelhöfer[2], J. Medina[1], J. Martínez Frías[1], A. Sansano[1],[1] Unidad Asociada UVA-CSIC al Centro de Astrobiología, Valladolid, Spain (rull@fmc.uva.es). [2] Institut für Anorganische und Analytische Chemie, Johannes-Gutenberg-Universität, Mainz, Germany (klingel@mail.uni-mainz.de)

Introduction: Space missions to Mars and the Moon, have provided a wealth of geomorphological and geophysical data from these sites, but there is still a lot of ambiguity in the interpretation of the geological features of their surfaces and its evolutionary history. The Earth's geology has many of the keys to the exploration of other worlds, and the study of so-called "terrestrial analogs" is essential to formulate hypotheses about the genesis and extrapolate data from Earth to other planetary bodies.

Figure 1: Detail of one of the spectacular lava flows which crops out at the area (Calatrava Volcanic Field, Ciudad Real province).

Calatrava Volcanic Field (CVF) in Ciudad Real (Spain) shows a great potential as a terrestrial analogue for Martian studies [1], because of its geodynamic and petrological and geochemical features.

General description of the sites and samples: The Calatrava volcanic field (CVF) is mostly of Pliocene or late-Pleistocene age, although late-stage phreatomagmatic activity at Columba volcano was dated at the mid-Holocene. Fumarolic activity was recorded in the Sierra de Valenzuela area during the 16th-18th centuries. The CVF of central Spain is characterised by a intracontinental plate magmatic association of leucitites, melilitites, nephelinites and olivine basalts extruded during the late Miocene to Quaternary. Most of the rocks represent relatively primitive magmas and less than 45% have experienced small degrees (< 25%) of crystal fractionation. This volvanic region is linked with the rift system wich developed from late Miocene to Quaternary times in western/central Europe and shows strong geochemical similarities with this volcanism, in which both lithospheric and asthenospheric components have been detected [2]. In this work we have carried out a detail mineralogy study of volcanic rocks from CVF using Raman and Mössbauer spectroscopy and X-Ray Diffraction (XRD). These techniques are used or are being used for Mars missions and it is important to test in similar conditions and on the same samples their combined capabilities. Samples were collected trying to cover the most representative spectrum of the volcanic and weathering processes that includes mainly lava, basalts and olivines.

Experimental: Raman spectroscopy was performed in the laboratory on the samples without any preparation using a Kaiser Raman spectrometer HoloSpec illuminated with a laser at 633 nm. Detection was performed with an Andor CCD of 1024x256 pixels and a Raman probehead. The spectrometer is coupled by fiber optics to a Nikon Eclipse E600 microscope. Several objectives were used allowing a range of laser spots on sample between 30 and 10 µm diameter.

For XRD analysis a X-Ray diffractometer (Philips, PW1710) with automatic divergent slit graphite monochromator was used. Experimental conditions were: radiation CuKα, $\lambda = 0.154$ nm, 40 kV generator voltage, generator current 30 mA, and angle range (2θ) from 5 to 70 º.

For Fe-Mössbauer.spectroscopy a copy of the Mars-Exploration Rover (MER) instrument was used with a field of view of 15 mm diameter. The measurements were performed in the lab in backscattering geometry not needing any sample preparation.

Results and discussion:. For XRD crystalline powder was prepared from the same areas analyzed without preparation with Raman and Mössbauer.

The main species detected with XRD technique were oxi-hydroxides (goethite), carbonates (calcite), and silicates as quartz, olivine (forsterite), piroxene (augite) and orthoclase and plagioclase.

Micro-Raman technique detected also oxides (hematite, magnetite), carbonates (calcite), quartz, alkali feldspar (anorthoclase), olivine (forsterite) and piroxene (augite).

The Mössbauer data (Fig. 4) show the presence of magnetite (and small amounts of hematite). The dominating Fe-bearing phase in the spectrum (the doublet) is attributed to a Fe^{3+} phase (possibly nanophase Fe-oxides).

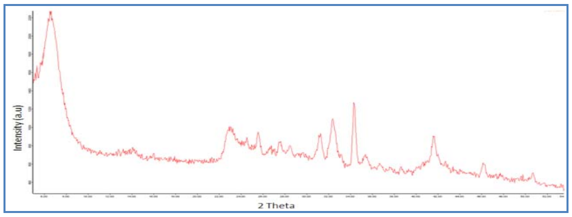

Figure 2. XRD obtained from lava samples at CVF.

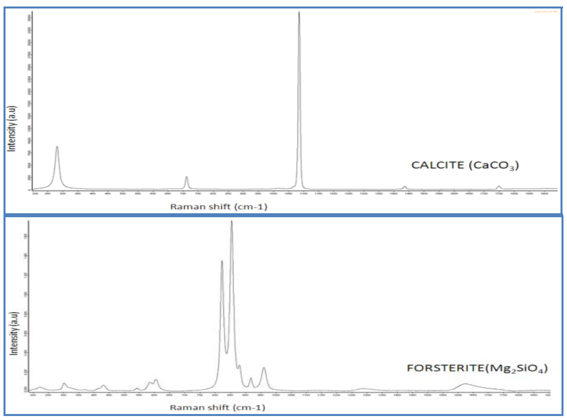

Figure 3: Raman spectra of Calcite (top) and Forsterite (bottom) from lava samples at CVF.

COMPOUNDS	CALATRAVA´S SAMPLES					
	LAVA		BASALT		OLIVINE	
	RAMAN	DRX	RAMAN	DRX	RAMAN	DRX
CALCITE	X	X			X	
HEMATITE	X					
ENSTATITE						X
ANORTHOCLA	X					
PLAGIOCLASE		X				X
MAGNETITE	X	X				
FORSTERITE			X	X	X	X
AUGITE			X	X		
QUARTZ				X	X	
ORTHOCLAS				X		
CLINO ENSTATITE					X	
CLAY MATERIAL		X				

Table I. Main mineral phases identified on different samples of CVF with Raman spectroscopy and XRD.

Summary and Conclusions: Results obtained with the combined techniques Raman, Mössbauer and XRD are in general agreement. These results confirm that when various instruments operate on the same samples, the results are generally consistent.

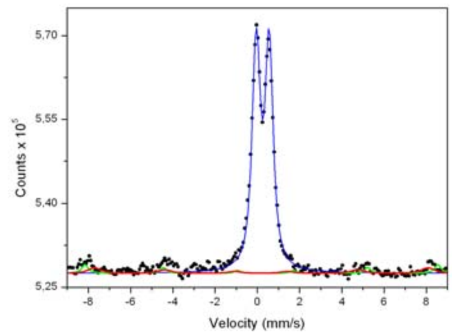

Figure 4. Mössbauer data obtained from a lava sample at CVF. The Fe-oxide magnetite (and small amounts of hematite) has been detected. The dominating doublet is attributed to nanophase Fe-oxides (Fe^{3+}).

This is very important for mineral species precise identification in robotic planetary missions. However, the different sensitivity of each technique and the different irradiated area and depth on the sample allow to introduce different insights on the data interpretation. Thus, Mössbauer and XRD are sensitive to each phase within the overall sample area irradiated (average mineral composition) but XRD need powder preparation which means the spatial distribution of species is lost. Raman acts superficially but at the mineral grain scale which means the possibility to detect phases in very low concentration. Finally the presence of calcite in Calatrava´s lava, detected by Raman and XRD is one of the most important aspects, as 1) aragonite in olivine from Calatrava, was previously suggested as an evidence for mantle carbonatite melts from >100 km depth [3-5], and 2) the recent finds of carbonates on Mars [6,7].

References:

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