Spectroscopic Integrated Method in the Way Towards the Search of the Origin of Libyan Desert Glass

/ LETICIA GOMEZ-NUBLA (1*), JULENE ARAMENDIA (1), SILVIA FERNÁNDEZ-ORTIZ-DE-VALLEJUELO (1), KEPA CASTRO (1), AINHOA ALONSO-OLAZABAL (2), Mª CRUZ ZULUAGA (2), LUIS-ÁNGEL ORTEGA (2) XABIER MURELAGA (3) JUAN-MANUEL MADARIAGA (1).

(1) Department of Analytical Chemistry, University of the Basque Country. Bº Sarriena s/n. 48940, Leioa (Spain)
(2) Department of Mineralogy and Petrology, University of the Basque Country. Bº Sarriena s/n. 48940, Leioa (Spain)
(3) Departament of Stratigraphy and Palaeontology , University of the Basque Country. Bº Sarriena s/n. 48940, Leioa (Spain)

INTRODUCTION

The Libyan Desert Glass (LDG) is a melt product whose origin is a controversy. Some authors mention that this material could be produced due to a high-temperature impact of a space material into the sand (impactite). Some others consider that the LDGs are the result of an airburst of a meteoroid, since there is a lack of crater (Swaenen, et al., 2010). However, the location of an impact crater is difficult to resolve because it would be covered by the Great Sand Sea desert or it would be destroyed by erosion (Barrat, et al., 1997). LDGs have been dated at 28, 5 millions of years in the Oligocene. These materials are spread along wide corridors between the dunes of the Great Sand Sea (South West of Egypt, near the Libyan border) (Ramirez-Cardona, et al., 2008). Aforetime, LDGs were used by prehistoric men to make various artifacts, as seen in several findings. It was also used in dynastic times on the scarab-shaped central motif of Tutankhamon's pectoral. (Pratesi, et al., 2002). LDGs are mainly composed by silica ($SiO_2 \approx 98\%$). Some compounds such as carbonates and sulphates were detected in previous studies (Aramendia, et al., 2011). These mineral phases could sustain the impact hypothesis, but it is not enough to elucidate the disagreement about the origin. The aim of this study is to carry out a deeper characterization of the inner part of Basque Country University collection specimens and to compare these results with data obtained from the surface of those materials. In this way, it has been avoided hypothetical crossed pollution present on the surface of the LDGs.

MATERIAL AND METHODS

In this work several specimens of Libyan Desert Glass was analyzed by Raman spectroscopy. For this purpose the samples were sliced making easier the measurements. Besides, in this way, inclusions trapped in the interior side of the LDG could be studied.

Raman spectroscopy is suitable for these prized materials. This is a non-destructive technique, therefore it is possible the identification of the molecular composition without the destruction of the sample. It was used several Raman equipments provided with two different laser wavelengths: 514 and 785 nm. Moreover, in order to improve the analysis of the inclusions, long range objectives of 5x, 20x, 50x and 100x were used. All the Raman measurements were done with laser power lower than 50 mW in order to avoid the thermodecomposition of the sample. Spectra were acquired between 5 and 15 seconds, and 10 to 15 accumulations.

In order to complement these results, an EVO 40 scanning electron microscope coupled to a X-Max energy-dispersive X-Ray spectroscopy equipment was used for electron image acquisitions and elemental composition determinations. SEM images were acquired at high vacuum employing an acceleration voltage of 20 KV. It was used a secondary electron detector. The elemental mapping analysis (EDS) was performed using an 8.5 mm working distance, a 35º take-off angle and an acceleration voltage of 20 KV.

RESULTS AND DISCUSSION

Macroscopically analyzed LDG are translucent glassy matrix with brownish spherical inclusions located all over the external surface before slicing. However, after the lamination of the samples, it could be observed that in the inner part the brownish inclusions were not discerned, whereas whitish inclusions could be easily perceived. Microscopically, it could be noticed little dark inclusions.

Raman spectroscopy allows determining the mineral phases of the inclusions. Comparing the results obtained from the inclusions of the surface and those obtained from the inner inclusions, it could be noticed important differences. Apart from the silica mineral phases such as cristobalite and quartz, other minerals were found in the inclusions distributed through the matrix of the LDG. In the inclusions located on the surface of the samples iron compounds were not detected, whereas they are the main component of the inner ones. In contrast, compound such as corundum is only present at the surface.

Besides, they were identified mineral characteristic phases of the LDG impact (high pressure) and of LDG settled state (low pressure). The presence of calcite suggests a possible transformation of high pressure aragonite to the low pressure calcite both detected in the present study.

Other couples of minerals similar in composition are also detected. In this way, sulphates as anhydrite and gypsum were detected. Anhydrite corresponds to the anhydrous phase of gypsum. During weathering, hematite can be transformed into a mixture of hydrated iron oxide-hydroxide known as *limonite*. The characteristic peaks and identified phases are summarized in Table 1. In the case of silicates, the identified cristobalite could be formed during high temperature, since it is a high-temperature mineral; in contrast quartz is the cristobalite low-temperature polymorph. High temperature mineral phases such as microcline and anatase 7

palabras clave: Vidrio, Desierto de Libia, Espectroscopia Raman, Inclusiones	***key words:*** Desert Glass, Libya, Raman spectroscopy, Inclusions

* corresponding author: **leticia.gomez@ehu.es**

Compound	*This work (Wavenumber/cm-1)*	*Other LDG works (Wavenumber/cm-1)*
LDG matrix	Silicate: ≈1370(br), ≈1600(br) Glassy matrix: 447 (br), 810 (br), 956 (br) and 1050 (br)	Glassy matrix: 480(br) and 820(br)
Quartz	204(m), 263(w), 354(w), 401(vw), 463(vs), 806(w), 1158(vw)	208(w), 465(m)
Anatase	141 (vs), 394 (m), 512 (w), 636 (s)	142(vs), 227(vw), 395(vw), 515(vw), 637(w)
Calcite	153(w), 279(m), 710(w), 1085(vs)	Not Found
Anhydrite	1018(w)	418(vw), 1018(vs), 1130(w)
Gypsum	411 (m), 618 (vw), 668 (vw), 1006 (m)	Not Found
Amorphous carbon	≈1300(br), ≈1600(br)	≈1300(br), ≈1600(br)
Microcline feldspar	513(m), 529(m)	Not Found
Natrite	695(vw), 1081(w)	Not Found
Cristobalite	230 (vs), 418 (vs)	230 (s), 418 (s), 780 (w), 1076 (w)
Corundum	416 (m)	Not found by Raman
Aragonite	1083 (m)	283 (w), 714 (vw), 1087 (s)
Unidentified Silicate	239 (w), 263 (vw), 300 (br), 373 (br), 504 (w), 764 (s), 785 (vs), 968 (s)	Nout Found
Hematite	226 (w), 292 (m), 410 (w)	Not found
Limonite	171 (w), 208 (m), 243 (m), 300 (s), 399 (vs), 471 (br), 551 (s), 1282 (br)	Not found

***Table 1**. Resume of Raman data summarizing characteristic Raman positions in cm -1 of different compounds present in LDG, where the intensity of the bands are represented by v: very, s: strong, m: medium, w: weak and br: broad.*

were distinguished. By Raman spectroscopy respective low temperature polymorphs were not found. However, by optical microscopy of fine rutile microlites can be observed. This phase can correspond to the transition of the anatase with high temperature.

In order to complement the previous results it was carried out an element mapping using SEM-EDS. In this way it could be seen how the elements are distributed in the inclusions. In Fig. 1 the first image is corresponded with the SEM image of an inclusion of LDG. The other images are elemental maps done with EDS over the same inclusion. In those maps, the white colour represents the presence of an element and the black the absence.

It can be seen that the inclusions are not formed by only one compound. The inclusion analyzed in the image, around the big cavity, is composed mainly by silicon but some elements are concentrated in certain areas, such as: C, O, Mg, Al, K, Ca, Ti and Fe.

On the one hand, calcium and carbon maps are very similar. The place where the carbon and the calcium are more concentrated is the same. This fact supports the presence of calcite and/or aragonite, both determined by Raman. On the other hand, silicon, iron and aluminium compounds appear similarly place and are in concordance the mineralogy detected by Raman spectroscopy. This chemical and mineralogical heterogeneity was observed in all the analyzed samples.
This work is an approach to the knowledge of the origin of the Libyan Desert Glass. It can be concluded that the silica is the main component in LDG glassy matrix. Inclusions are composed by different compounds and therefore are chemically more heterogeneous. Besides, Raman spectroscopy result a useful tool for the analysis of LDGs although some other supporting techniques are required.

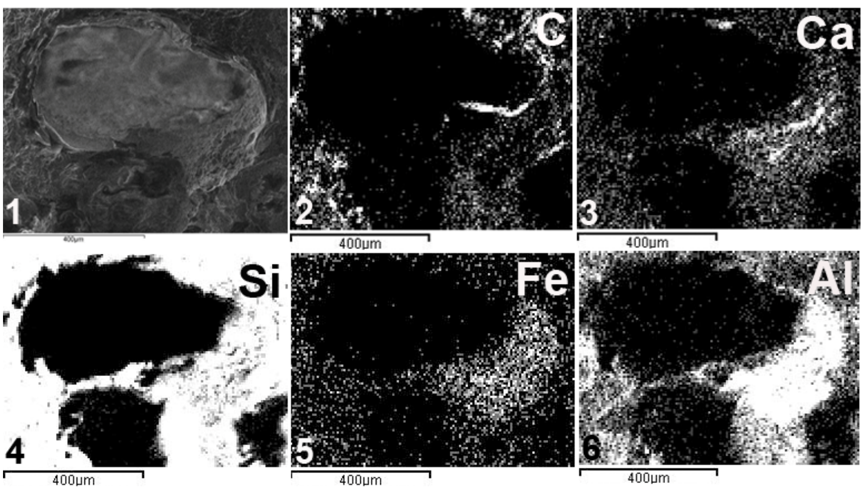

***fig 1**. 1) SEM image of a LDG inclusion with a big cavity, 2) Carbon map, 3) Calcium map, 4) Silicon map, 5) Iron map and 6) aluminum map of that inclusion.*

ACKNOWLEDGMENTS

L. Gomez-Nubla and J. Aramendia are grateful to the University of the Basque Country (UPV/EHU) and to the Basque Government respectively, for their predoctoral fellowships. The authors are grateful for technical and human support provided by the Raman-LASPEA Laboratory of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF. Moreover, this work has been financially supported by the project "*Estudio de material asociado a impactos meteoriticos*" from the University of the Basque Country (UPV/EUH) (ref: AE11/26).

REFERENCES

Aramendia, J., Gomez-Nubla, L., Fdez Ortiz de Vallejuelo, S., Castro, K., Murelaga, X., Madariaga, J.M. (2011): New findings by Raman micro spectroscopy in the bulk and inclusions trapped in Libyan Desert Glass. Spectrosc. Lett., **44***, 7-8, 521-525.*

Barrat, J.A., Jahn, B.M., Amossé, J., Rocchia, R., Keller, F., Poupeau, G. R., Diemer, E. (1997): Geochemistry and origin of Libyan Desert glasses. Geochimic. Cosmochimic. Acta, **61***, 1953-1959.*

Pratesi, G., Viti, C., Cipriani, C., Mellini, M. (2002): Silicate-silicate liquid inmmiscibility and graphite ribbons in Libyan Desert Glass. Geochimic. Cosmochimic. Acta, **66***, 903-911.*

Ramirez-Cardona, M., El-Barkooky, A., Hamdan, M., Flores-Castro, K., Jimenez-Martinez, NI., Mendoza-Espinosa M. (2008): On the Lybian Desert Silica Glass (LDSG) transport model from a hypothetical impact structure. International Gelogical Congress Oslo 2008. PIS-01.

Swaenen, M., Stefaniak, E.A., Frost, R., Worobiec, A., Van Grieken, R. (2010): Investigation of inclusions trapped inside Libyan Desert Glass by Raman microscopy. Anal Bioanal. Chem.. **397***. 2659-2665.*