

1 **Multispectroscopic methodology to study Libyan Desert Glass and its**
2 **formation conditions**

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16
17 **Abstract**

18 The Libyan Desert Glass (LDG) is a melt product whose origin is still a matter
19 of controversy. With the purpose of adding new information about this enigma, the
20 present paper analyzes the inner part of the LDG specimens and compares it with the
21 results of the LDG surfaces. An integrated analytical methodology was used combining
22 different techniques such as Raman spectroscopy, in point-by-point and imaging modes,
23 Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS), Energy-
24 Dispersive Micro X-ray Fluorescence spectrometry (μ -EDXRF), Electron Probe Micro
25 Analyzer (EPMA) and optical cathodeluminescence (Optical-CL). According to our

26 results, flow structures of the melt and the amorphous nature of the matrix could be
27 discerned. Moreover, the observed displacement of the Raman bands, such as the cases
28 of quartz and zircon, and the identification of certain compounds such as coesite (the
29 most clarifying phase of high pressures), α -cristobalite, gypsum, anhydrite, corundum,
30 rutile, amorphous calcite, aragonite and calcite allowed us to know that LDGs could be
31 subjected to shock pressures between 6 and more than 30 GPa, and temperatures
32 between 300 and 1470°C. The differences of temperature and pressure would be
33 provoked by different cooling process during the impact. Besides, in most cases the
34 minerals corresponding to high pressure and temperatures were located in the inner part
35 of the LDGs, with some exceptions that could be explained because they were trapped
36 subsequently to the impact; there was more than one impact or heterogeneous cooling.

37 Furthermore, nitrogen and oxygen gases were identified inside bubbles, which
38 could have been introduced from the terrestrial atmosphere during the meteorite impact.

39 These data helped us to clarify some clues about the origin of these enigmatic
40 samples.

41

42 **KEYWORDS:** Libyan Desert Glass; impact melt; mineralogy; analytical methodology.

43

44 **1. INTRODUCTION**

45

46 Libyan Desert Glass (LDG) is an enigmatic type of impact glass that was firstly
47 documented by Patrick A. Clayton in 1933. Clayton and Spencer first published a
48 scientific report on LDG that led to its official discovery [1]. Since then, many field
49 expeditions have been carried out and more than 200 tonnes of LDG have been
50 collected [2]. They are scattered over an area of 6500 km² located in north –south-

51 trending inter-dune channels between the Great Sand Sea and the Gilf Kebir Plateau
52 around the Western Desert of Egypt, near the Libyan border [2-4]. They are mainly
53 concentrated in two zones: a larger ring-shaped area in the south and a smaller oval area
54 in the north [2]. These lithologies are of the Cretaceous Nubian Formation outcrop.
55 Similarities between these sandstones and the LDG composition should clarify the
56 fusion of the ground material. However, the lithologic variation of these sandstones
57 makes difficult to identify them as the origin of LDGs [5, 6]. LDGs were found to a
58 depth of ~ 2 m, and the deeper they are located, the bigger they are [7]. Their weight
59 goes from less than 1g up to over 25 Kg [2]. Its formation age was determined by
60 fission track analysis, which indicated ranges from 28.5 ± 2.3 to 29.4 ± 0.5 My [8]. The
61 distribution of LDG fragments could be the result of fluvial transport that occurred
62 throughout the Oligocene boundary, where there was a humid climate with high
63 quantity of precipitation in lacustrine environment or coastal seawater [9-11]. In
64 general, LDG is a compact hard glassy rock, transparent, yellowish or greenish,
65 sometimes dark or milky. Chemically, bulk LDG has concentrations of approximately
66 98 wt% SiO₂ [12]. In addition, it can have other compounds. It usually contains air
67 bubbles, cristobalite inclusions and dark or brown inclusions appearing as streaks,
68 ribbons, misty waves or simply solid spots, possibly derived by melting or
69 decomposition of iron oxides. The concentrations of components are highly variable.
70 Inclusion grain sizes can vary between 0.1 to 0.3 mm in diameter, occasionally up to 1
71 mm [2-4, 13].

72 The origin of LDG is controversial and there are two main theories among other
73 hypothesis. One of them states that its genesis is related to an impact of an
74 extraterrestrial body into the sedimentary materials causing its fusion [7, 14]. The
75 second one considers the formation of LDG as the result of a low-altitude explosion of

76 an extraterrestrial body in the atmosphere, generating a thermal pulse (airburst) and
77 causing the melting of surface [15, 16]. Both theories have been instilled with numerous
78 non-conclusive experimental results. The impact origin of the LDG is supported by the
79 presence of schlieren structures, planar deformation features, partly digested mineral
80 phases, high pressure-temperature mineral phases and non-crystalline phases formed
81 during shock metamorphism. In addition, abundance patterns of platinum-group
82 elements (Ru, Rh, Pd, Os, Ir, and Pb), a reduced state of iron-rich portions, graphite-rich
83 bands in the glasses, iridium content and, finally, osmium ($^{187}\text{Os}/^{188}\text{Os}$), strontium
84 ($^{87}\text{Sr}/^{86}\text{Sr}$), argon ($^{40}\text{Ar}/^{36}\text{Ar}$) and neodymium ($^{143}\text{Nd}/^{144}\text{Nd}$) isotopic ratio values have
85 been regarded as the fingerprints of the supposed primitive meteoritic matter in the
86 LDGs [2, 4, 6,17-20].

87 To confirm both theories, a crater should be localized in the area. However, the
88 location of such a crater is difficult to resolve because it would be covered by the Great
89 Sand Sea desert or it would be destroyed by erosion [4, 16]. Despite this fact, the
90 existence of the geform called Kebira has been considered as possible crater and
91 source of LDGs [7]. Nevertheless, the study of the crater concluded that the impact
92 probably happened 100 million years ago approximately [21] and the LDG was formed
93 28.5 million years ago, therefore they would not coincide in time as LDGs are younger.

94 In spite of the controversy, a greater number of scientists came to terms with the
95 origin of the LDGs caused by an impact of an extraterrestrial body over the sand or
96 sandstone, which would be deposited in lacustrine environment or coastal seawater, the
97 fusion of material with the meteoritic component and its subsequent solidification
98 [5,7,12,14].

99 This work aims to find new experimental evidences following a
100 multispectroscopic methodology, looking at the mineralogy of the matrix, inclusions,

101 cavities and bubbles in the internal and external parts of LDG specimens to ascertain the
102 formation conditions (mainly temperature and pressure) of the identified compounds.
103 With all the collected information, it is possible to obtain more evidence about the
104 origin of this enigmatic material.

105

106 **2. MATERIAL AND METHODS**

107 **2.1 Samples and sample preparation**

108 Several specimens of LDG from the Meteorites Collection of the Basque
109 Country University (UPV/EHU) were analyzed in order to achieve the mentioned
110 objectives. The dimensions of the samples varied between 1-5 cm in length and 2-4 cm
111 in width, whereas their weight varied between 5-23 g. The analyzed LDGs were
112 translucent glassy samples. Some types of inclusions could be macroscopically
113 discerned: dark, brownish and whitish spheres.

114 The samples were sliced, and then, thick and thin sections were prepared to
115 detect differences between the surface and the inner part of the LDGs. The inner part is
116 better preserved since it has not been in contact with the environment. A Buehler-
117 PetroThin sectioning system with a diamond saw was employed. As a perfectly flat
118 surface free of deformations is necessary, the fragments were polished using silicon
119 carbide powder of different grain size on frosted glasses. The thickness of the fragments
120 was approximately 800 μm . Once the flat surface was obtained, in the case of the thin
121 sections, samples were mounted on glass slides (dimensions of 27 x 46 x 1.5 mm) with
122 an epoxy resin (composed of polyurethane, acrylic and cyanoacrylate) and then, the
123 samples were smoothed using progressively finer abrasive grit until they were only 30
124 μm thick.

125 After the lamination of the samples, the majority of the mentioned brownish
126 inclusions could not be discerned. However, whitish crystals with round shape were
127 predominant. Single embedded minerals and bubbles were observed by optical
128 microscope. More than 300 inclusions, around 200 crystalline forms in the matrix and
129 more than 30 bubbles were analyzed in the different LDG specimens.

130 **2.2 Analytical methods**

131 Several analytical techniques were used throughout this work. Optical
132 microscopy was performed with a NIKON optical polarizing microscope equipped with
133 a digital camera in order to observe the texture and the mineralogy of the melt. In
134 addition, a Technosyn cold-cathode cathodoluminescence stage, model 8200MKII, with
135 a vacuum chamber coupled to a polarizing microscope was used on the thin sections to
136 observe the internal structure of the melt. It worked under standard operating conditions
137 at 12-15kV of accelerating potential, 0.5-0.6 mA beam current, and a beam diameter of
138 4.5 mm.

139 For the elemental characterization Energy-Dispersive Micro X-ray Fluorescence
140 spectrometry (μ -EDXRF), Scanning Electron Microscopy with X-ray microanalysis
141 (SEM-EDS) and Electron Probe Micro Analyzer (EPMA) were employed. Due to the
142 size of the studied specimens it was not possible to analyze the external part by SEM-
143 EDS. For this reason, the elemental data in these areas were acquired by μ -EDXRF. A
144 μ -EDXRF ArtTax model by Bruker was used. The equipment is composed of an X-ray
145 tube with a Mo anode working at 50 kV voltage and 0.6 mA current. The X-rays were
146 collimated by a 0.65 mm diameter tantalum collimator. Light elements were measured
147 under a helium flow. Zr, which is a typical element in the LDG composition, could not
148 be measured by μ -EDXRF because it is also present in the source of the equipment.
149 Moreover, thick and thin sections were analyzed with an EVO 40 Scanning Electron

150 Microscope coupled to an X-Max Energy-Dispersive X-Ray spectroscopy equipment.
151 That device was used to acquire electron images, to obtain elemental mappings and to
152 determine semi-quantitatively the elemental composition of the matrix and the
153 inclusions. The SEM images were acquired at high vacuum, employing an acceleration
154 voltage of 20 kV without the need to metalize the samples using a detector of secondary
155 electrons. Besides, a JEOL JSM-6400 SEM with an Oxford Pentafet photon energy
156 instruments Link Isis X-Ray (EDX) system was used. Furthermore, a Cameca SX-100
157 electron probe microanalyzer (EPMA) was used principally to obtain quantitative
158 elemental data about the matrix in thin sections of LDGs, since this technique allows
159 performing more precise quantitative analysis. The SX-100 is equipped with five
160 wavelength dispersive spectrometers (WDS) (each containing a diffracting crystal), a
161 dispersive energy spectrometer (EDS) and SE, BSE, ABS and cathodoluminescence
162 (CL) detectors. The operating conditions for the samples were 100 nA beam current and
163 15 kV accelerating voltage with a beam diameter of 0.6 μm , 2 μm scan distance and 100
164 ms acquisition time of X-ray peak per point (10 points per sample were analyzed).

165 The molecular composition of the different components of the LGD specimens
166 was determined using Raman spectroscopy. A Renishaw InVia Raman micro
167 spectrometer, coupled to a DMLM Leica microscope with 5x N PLAN (0.12 aperture),
168 20x N PLAN EPI (0.40 aperture), 50x N PLAN (0.75 aperture; lateral resolution of 2
169 μm) and 100x (lateral resolution of 1 μm) long range objectives, was used with the 514
170 nm argon ion excitation laser and the 785 nm diode excitation laser. The power applied
171 was set at the source at a maximum of 50 mW while on the sample was always less than
172 20 mW. The spectra were obtained in the range 3000–100 cm^{-1} , accumulating several
173 scans from each spectrum to improve the signal-to-noise ratio.

174 In order to obtain Raman chemical images, the StreamLine technology
175 (Renishaw) was employed. The inVia's motorized microscope stage moves the sample
176 beneath the lens so that the line is rasterized across the region of interest. Data are swept
177 synchronously across the detector as the line moves across the sample, and are read out
178 continuously. Details of the working conditions are given elsewhere [22].

179 Data acquisition was carried out by the Wire 3.0 software package of Renishaw
180 and the analysis of the results was undertaken by Omnic 7.2 software. The results were
181 interpreted by comparing of the collected Raman spectra with Raman spectra of pure
182 standard compounds of the e-VISARCH and e-VISART Raman spectra databases [23]
183 and with the RRUFF database [24].

184

185 **3. RESULTS**

186 **3.1 Matrix**

187 The LDG is known to be elementally composed mainly by Si, as all the works
188 based on LDG reported. Besides, it also has little amounts of K, Ti, Ca, Mn, Fe, Al and
189 Sr, together with other elements such as V, Cl, Cu, S and Zn at trace level [3, 7, 13, 25].
190 All these elements were detected in our elemental analyses. Comparing several μ -
191 EDXRF spectra of the inner matrix and the superficial one, the main difference was the
192 relative intensity for some of those elements. Fe, Sr, Ca and Ti presented higher peak
193 areas in the inner matrix than on the surface. In contrast, in their sporadic appearances,
194 Mn, Cl and S were more intense on the surface (see Electronic Supplementary Material
195 Table S1).

196 The molecular composition of the matrix, observed by Raman spectroscopy, did
197 not show differences between the surface and inner part. However, three groups of

198 spectra can be seen related to the matrix composition depending on the excitation laser
199 used to obtain the Raman spectra [26].

200 The first group, obtained with the 785 nm excitation laser, presented three
201 intense and broad (br) bands at 1374, 1554, and 1636 cm^{-1} . A second type of spectrum,
202 also obtained with the same excitation laser, presented five Raman bands at 1277vs
203 (very strong), 1382vs, 1517s (strong), 1662br and 1842br cm^{-1} ; similar to that reported
204 by Swaenen et al. [3]. The third group, obtained with the 514 nm excitation laser,
205 presented bands at 447br, 602w (weak), 810br, 1061br and 1322br cm^{-1} (see Electronic
206 Supplementary Material Fig. S1), which was similar to that published by Swaenen et al.
207 [3], except for the bands located around 480 and 820 cm^{-1} [3]. The bands in the 1200-
208 1900 cm^{-1} range of the first two spectra are due to the luminescence emission produced
209 by the effect of the red laser (785 nm) over transition metals or rare earth element,
210 possibly present in the glassy matrix [4, 27]. These spectral features were not observed
211 with the green laser (514 nm). Thus, those signals in the 1200-1900 cm^{-1} range were not
212 considered for characterisation purposes.

213 The last mentioned group of Raman spectra should be considered as the typical LDG
214 matrix spectrum (spectrum A) (see Electronic Supplementary Material Fig. S1). In some
215 occasions, that A spectrum of the matrix varied a little bit showing its Raman bands at
216 447br, 810br, 956br, 1049br, 1195br and 1630br cm^{-1} (spectrum B) (see Electronic
217 Supplementary Material Fig. S1). In our further discussion, we will consider both, A
218 and B types as the Raman background due to the matrix. The broad band at 447 cm^{-1} is
219 related to the bending modes of the Si–O–Si bonds within the tetrahedral units. Besides,
220 the weak band around 600 cm^{-1} (only for A spectrum) is ascribed to Si-O bending
221 vibration modes. The band(s) at 400–600 cm^{-1} varies with the degree of polymerization
222 of the melt and with the Si-O-Si (and Si-O-Al) bridging bond angles [25]. The band

223 near 800 cm^{-1} involves symmetric motions of Si-O-Si bending while the band in the
224 range $850\text{-}1200\text{ cm}^{-1}$ is associated with symmetric Si-O stretching vibrations. The
225 doublet at 955 and 1052 cm^{-1} observed in the spectrum B is specific of alkali rich
226 glasses. Finally the band at 1630 cm^{-1} seems to be related with the presence of H-O-H
227 bonds [3, 28]. Although these last spectra have not been described before, their
228 wavenumbers and the presence of broad bands are related to the amorphous nature of
229 the glass bulk.

230 EPMA analysis revealed and corroborated distinct and heterogeneous
231 quantitative elemental composition of the melt. The inner part contained 99.2 ± 0.20
232 wt% SiO_2 while the outer decreased to 96.8 ± 0.20 wt%; Al_2O_3 varied from 0.20 ± 0.02
233 wt% at the inner part to 2.04 ± 0.01 wt% in the outer part. Other minor elements also
234 showed similar variations, Fe_2O_3 from 0.01 ± 0.003 to 0.22 ± 0.01 wt%, TiO_2 from
235 0.018 ± 0.009 to 0.51 ± 0.02 wt% and CaO varied from nearly 0 to 0.12 ± 0.007 wt% in
236 the inner and the outer part. This heterogeneity in elemental composition of the melt
237 was also detected by cathodoluminescence (see Fig. 1) as previous researches showed
238 [25]. Variations on element contents are reflected on CL images, on the differences in
239 colours and brightness within few microns, according with the highly heterogeneous
240 flow structures of the melt (see images on the right in the Fig. 1). This flow texture as
241 well as compositional variation on silicon and aluminium elements was also discerned
242 in images obtained by SEM/EDS, but not so spectacular as the CL images (see Fig.1).

243 **3.2 Crystalline forms inside the matrix**

244 Petrographic studies on thin sections by optical microscope showed that LDG
245 exhibit a holohyaline texture with some minerals occurrence such as aluminium rich
246 tiny crystallites, cristobalites and zircons. SEM observations revealed that these
247 euhedral and skeletal crystallites are dispersed along the matrix. These crystallites were

248 generally randomly oriented forming aligned clouds and/or aggregations of crystallites
249 defining flow patterns (see Fig. 2). Moreover, crystallites around 3 μm showed skeletal
250 structure (i.e. hollow crystallites) and swallowtail ends similar to typical structures of
251 those formed during rapid crystallization from a melt [29]. They were identified as
252 aluminium rich crystallites with traces of Ti and Fe by SEM/EDS analysis (see Fig. 2.b
253 and c). Besides, these aluminium oxides rich crystallites are related to aluminium rich
254 zones of the glass, according to SEM/EDS analysis (see Fig. 2.b and c). Unfortunately,
255 when analyzing these crystallites by Raman spectroscopy no signal was obtained.

256 In addition, glass spherules (considered as whitish inclusions) with great
257 variability on size, between 40 μm and 300 μm , were observed by optical microscope
258 dispersed within the silica glass matrix. They are crystals with different shape, circular,
259 ellipsoidal and irregular globules. Some of them exhibit internal cracks and with
260 spheroid bodies similar to grapes. The key mineral phase α -cristobalite was identified
261 by Raman spectroscopy in these crystals (SiO_2 , with the two main bands at 230vs and
262 418vs cm^{-1}). There was a specific case where zircon (ZrSiO_4) was detected within a
263 cristobalite inclusion (see Fig. 3a). This fact will be discussed below.

264 Raman spectroscopy analysis in the surface of the LDG samples determined the
265 following phases: anatase (TiO_2 ; main Raman band at 143s cm^{-1}), gypsum
266 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Raman bands at 411w and 1006w cm^{-1}), coesite (SiO_2 ; Raman bands at
267 270w and 521m cm^{-1} , its most fundamental vibration [30]) and a microcline feldspar
268 (KAlSi_3O_8 ; Raman bands at 328vw, 406w, 513m and 1096vw cm^{-1}). Apart from
269 coesite, other minerals were identified as crystals trapped in the inner parts of the
270 matrix, such as shocked zircon (ZrSiO_4 ; Raman bands at 351m, 435m, 973vw, 1000vs,
271 1050w, 1085m and 1140vw cm^{-1} ; see Fig. 3c), calcite (CaCO_3 ; Raman bands at 153w,

272 279m, 710w and 1085vs cm^{-1}), amorphous calcite (CaCO_3 ; Raman bands at 149w,
273 260m, 709w and 1080vs cm^{-1}) and rutile (TiO_2 ; Raman bands at 445s and 610s cm^{-1}).

274 From the molecular point of view, comparing the minerals found in the trapped
275 crystals of both outer and inner parts of the matrix, only coesite appeared in both sides.
276 This is a key mineral, a high pressure polymorph of SiO_2 , to understand the process of
277 formation of the LDGs. The presence of rutile in the inner part of the matrix and anatase
278 in the outer part of the matrix must be considered also relevant. Moreover, the presence
279 of shocked zircon in the inner parts of the matrix could help to understand the formation
280 process of the LDGs.

281 **3.3 Inclusions**

282 **3.3.1 Mineral inclusions**

283 They are considered minerals trapped within the body of the LDG, like grains in
284 the matrix. Some of these inclusions can be completely contained within another
285 mineral.

286 The μ -EDXRF measurements showed that these inclusions are defined by the
287 high presence of Al, Ca and Si. Furthermore, it was possible to distinguish Na, Ti, V,
288 Mn, Sr and Fe as minor elements, since they did not appear as often as the previous
289 ones, and S and Cl at trace level (they appeared in certain occasions), but with variable
290 peak areas for the different bands as a function of the inclusions. This suggests the
291 presence of several compounds and/or mineral phases in such inclusions.

292 There are dark brownish mineral inclusions characterized by a higher presence
293 of iron, as it has been reported in literature [26]. In order to study the elemental
294 distribution in these brownish inclusions, several elemental composition mappings as
295 well as semi-quantitative determinations were carried out by SEM-EDS. These analyses
296 corroborate the differences in the elemental composition of the internal and external

297 brownish inclusions. In general, Si is the main element in both but the Fe and Ti signals
298 were systematically increased in the inner ones (Fe: 0.5 ± 0.025 wt% (outer) to 5.9 ± 0.3
299 wt% (inner); Ti: 0.06 ± 0.003 wt% (outer) to 0.1 ± 0.005 wt% (inner)). Fig. 4 shows the
300 SEM image of an inner brownish inclusion formed mainly by Si and several elements
301 such as O, Ca, Al and Fe. Besides, Na, Mg, P, Cl, K and Ti were detected. The
302 distribution maps for the main elements (the presence of elements is represented in
303 white colour and the absence in black) show correlations among O, Si and Al, but also
304 correlations among Fe, O and Al. Some small areas showed correlations even among
305 Ca, Al and O.

306 The Raman spectroscopy analyses on several spots of the different brownish inclusion
307 detected several mineral phases: silica, sulphates, carbonates and oxides. Among them,
308 three compounds having the general silicon oxide form but with different structural
309 configurations were found: α -quartz (SiO_2 ; Raman bands at 205m, 263w, 354w, 398vw,
310 464vs, 696vw, 806w, 1081w and 1160vw cm^{-1}), a modified α -quartz with displaced
311 bands (distorted SiO_2 ; 202m, 261w, 353w, 390vw, 461vs, 693vw, 802w, 1064vw,
312 1080w and 1159w cm^{-1}) and α -cristobalite (SiO_2 ; main Raman bands at 230vs and
313 418vs cm^{-1}).

314 Besides, three different calcium sulphate modifications were also discerned
315 depending on the location of the inclusions within the LDG sample: gypsum
316 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Raman bands at 411m, 618vw, 668vw and 1006m cm^{-1}) and two forms
317 of anhydrite (CaSO_4), according to their Raman bands [31]. Anhydrite type II (β -
318 CaSO_4 , Raman bands at 417w, 610vw, 626vw, 1018m, 1128vw and 1161w cm^{-1}), with
319 an orthorhombic structure, stable in the 300-1180°C range, was detected in the outer
320 brownish inclusions, together with α -quartz. Anhydrite type I (α - CaSO_4 ; Raman bands
321 at 170w, 417w, 610vw, 628vw, 1017m, 1110w, 1128w and 1158vw cm^{-1}), with cubic

322 structure, stable at temperatures higher than 1180°C, was identified in the inner
323 brownish inclusion together with gypsum (overlapping of Raman bands causing a
324 displacement from 628 to 624 cm^{-1} and from 1017 to 1010 cm^{-1}).

325 Among carbonates, calcite (CaCO_3 ; Raman bands at 153w, 279m, 710w and
326 1085vs cm^{-1}), aragonite (CaCO_3 ; Raman band at 207w, 704w and 1083m cm^{-1}) and
327 magnesite (MgCO_3 ; Raman bands at 330w, 739w and 1095m cm^{-1}) were identified.
328 Hematite ($\alpha\text{-Fe}_2\text{O}_3$; Raman bands at 226w, 292m, 410w, 612w and 1300br cm^{-1}),
329 limonite ($\text{FeO(OH)} \cdot n \text{H}_2\text{O}$; Raman bands at 171w, 208m, 243m, 300s, 399vs, 471br,
330 551s and 1282br cm^{-1}), corundum ($\alpha\text{-Al}_2\text{O}_3$; Raman band at 416m cm^{-1}), rutile, anatase
331 (TiO_2 ; main Raman band at 143s cm^{-1}), cinnabar (HgS ; main Raman band at 252m cm^{-1})
332 and carbon were also identified in the inclusions.

333 Carbon was also detected in some small dark areas of brownish inclusions, areas
334 where the carbon lines in SEM-EDS were not correlated with any other element. Carbon
335 was identified through their main Raman bands at $\approx 1300\text{br}$ and $\approx 1600\text{br}$ cm^{-1} . The band
336 at $\approx 1580\text{-}1600$ cm^{-1} is assigned as the G band of the C (originates from the stretching
337 vibration of sp^2 carbon atoms C-C). The band at ≈ 1300 cm^{-1} is attributed to D band
338 (from the stretching vibration of sp^3 carbon atoms, which induces defects and disorders)
339 [32].

340 It is worth pointing out that commonly, the composition of these inclusions was
341 not homogeneous and they consisted of more than one compound. As an example of the
342 heterogeneous nature of the inclusions, Fig. 5 shows the Raman image obtained in an
343 inner brownish inclusion, having quartz and calcite as the main mineral phases, together
344 with hematite.

345 A difference in mineral composition was observed depending on the outer or
346 inner location of brownish inclusions. On the one hand, some mineral phases appeared

347 only in outer locations of inclusions such as anhydrite A-II, amorphous carbon,
348 corundum, magnesite and cinnabar. On the other hand, some other compounds were
349 only detected in the inner inclusions such as anhydrite A-I, aragonite (but only in the
350 inclusions near the border), gypsum, hematite, limonite (near the surface), displaced α -
351 quartz and rutile. Finally, the normal α -quartz, α -cristobalite, anatase, calcite and carbon
352 were found in both locations of brownish inclusions.

353 **3.3.2 Cavities and embedded bubbles**

354 Cavities are irregular areas observed in the matrix, and bubbles are spherical
355 cavities that could have been vesicles, gaseous or fluids.

356 Irregular cavities and bubbles were also observed in the LDG matrix by optical
357 microscope and SEM observations. According to optical microscopic and SEM
358 observations (see Fig. 6), some individual grains were observed inside the cavities that
359 could be pyroxenes due to their crystal shape revealed through the SEM microscope.
360 Correlations among Fe, Mg and Si, and among Al, K, Ca and Si were found in the
361 SEM-EDS elemental distribution maps. To verify their composition, Raman
362 spectroscopy and EPMA analyses were performed. Different kind of silicates were
363 identified by Raman spectroscopy, forsterite (Mg_2SiO_4 ; Raman bands at 303w, 430w,
364 604m, 820s, 854s and 961m cm^{-1}) and enstatite (MgSiO_3 ; Raman bands at 231w,
365 296vw, 336m, 389w, 657s, 678vs and 1005vs cm^{-1}) (see Fig. 6). These results
366 confirmed the existence of olivine and pyroxenes in the cavities (forsterite and
367 enstatite). Moreover, tephroite (Mn_2SiO_4 ; Raman bands at 811m and 843m cm^{-1}) was
368 identified in another cavity.

369 In addition, there were bubbles, spherical in shape, which suggested the presence
370 of vesicles, gaseous or fluids, but some were empty perhaps due to the slicing process.
371 Some others were still full and in order to ascertain the nature of the materials inside

372 these bubbles, point-by-point Raman analyses were performed identifying oxygen gas
373 (O_2 ; Raman band at 1554w cm^{-1}) [33] and nitrogen gas inside them (N_2 ; Raman band at
374 2328w cm^{-1} and 2342w cm^{-1}) [34] (see Fig. 7). Besides, a Raman band at 2337w cm^{-1}
375 attributable to stretching mode $\text{C}\equiv\text{N}$ was found [35].

376 All the compounds identified in this work are summarized in Table 1, indicating
377 where they were found in the LDGs samples.

378

379 **4. DISCUSSION**

380 The identified compounds in the inner and outer parts of the analyzed specimens
381 (see Table 1) give us the possibility to extend the knowledge of the LDG formation
382 because some detected minerals are characteristic phases for given temperatures and
383 others for certain pressures.

384 For example, by Raman spectroscopy it is possible to detect the variation due to
385 pressure and temperature in the structure of the compounds because their common
386 Raman bands are displaced. On the one hand, there are three compounds that give us an
387 idea of the pressures affecting the formation of the LDGs. In some inner inclusions of
388 the LDG samples, the main Raman band of α -quartz (464 cm^{-1} for ambient pressure and
389 temperature) appeared slightly displaced at 461 cm^{-1} (see Fig. 8). Besides, shifts from
390 205 to 202 , 263 to 261 and 806 to 802 cm^{-1} were observed as well. That displacement is
391 commonly attributed to molecules of crystalline quartz that have been subjected to
392 shock pressures of at least 26 GPa [36].

393 The Raman spectrum of zircon observed in the matrix (see Fig. 3b), corroborate
394 the pressure conditions in which these LDGs were formed. The main Raman band of the
395 zircon appeared at 1000 cm^{-1} , which corresponds to a shocked zircon (see Fig. 3c). The
396 change in the position of this main band from 1008 cm^{-1} for normal zircon (see Fig.3d)

397 to 1000 cm^{-1} means that the original zircon (probably trapped from the surface materials
398 during the impact) was shocked to a pressure of at least or around 20 GPa [25].

399 The most clarifying phase among the shocked minerals is coesite, which has
400 been found not only in the inner but also in the outer mineral embedded materials.
401 Coesite is a silica polymorph produced at high pressures (>30 GPa) from the α -quartz
402 [37, 38] and is commonly present in materials from large-scale impact craters [37].

403 The conditions mentioned above could be acquired by shock metamorphism.
404 Thus, the presence of shocked quartz and zircon, but mainly coesite, is a strong
405 indication of an impact, which can be estimated around 20 GPa.

406 In comparison with other studies, pressure during impact processes might exceed
407 10 GPa, even up to 50 GPa for dense quartz-rich lithologies [39]. Moreover, the nature
408 of LDG inclusions would speak in favor of high-pressure and high-temperature
409 formation initiated by a meteoritic impact, which would implicate the high quenching
410 temperature [3]. This information would corroborate our results.

411 On the other hand, mineral phases clearly related to high and low temperature
412 were identified. For example, the displacement of the main Raman band of zircon from
413 1008 to 1000 cm^{-1} can occur as a consequence of temperatures higher than 1400°C [40]
414 and not only due to high pressures.

415 The occurrence of α -cristobalite is an indirect evidence of a high temperature
416 event. The α -quartz phase, which is the low-temperature stable polymorph of SiO_2 , is
417 converted by heating into β -cristobalite at 1470°C . Then, α -cristobalite is normally
418 formed during the cooling process from the previously formed β -cristobalite. Therefore,
419 the presence of α -cristobalite indicated the former presence of β -cristobalite and hence,
420 a temperature greater than 1470°C and the following cooling process [7, 9].

421 The presence of α -anhydrite is remarkable. Anhydrite exhibits different Raman
422 spectra due to the different structures of its polymorphs [31]. Anhydrite III (A-III either
423 soluble anhydrite or γ -CaSO₄) is formed from hemihydrates above temperatures close to
424 110°C. Anhydrite II (A-II either insoluble anhydrite or β -CaSO₄) is formed at
425 approximately 300 °C and it corresponds to the mineralogical form of normal anhydrite.
426 Finally, anhydrite I (A-I or α -CaSO₄), is a high temperature form that is stable above
427 1180 °C [41], but below 1200°C reverts to insoluble anhydrite [41]. In the case of
428 gypsum, it loses its crystallization waters at around 100°C [42] and can be transformed
429 to the hemihydrate form and/or to anhydrite III.

430 Corundum (α -Al₂O₃) is formed from metastable phases of alumina at
431 temperatures higher than 1000-1200°C [43, 44]. Some Al and O areas were detected by
432 SEM-EDS in skeletal crystallites (see Fig. 2) but without showing Raman features. It
433 must be pointed out that when alumina is heated at temperatures below 1100°C, the
434 formed materials [45] do not exhibit Raman bands [44]. Therefore, those areas could be
435 crystallized under 1100°C during fast cooling processes. To confirm the absence of
436 Raman signals of those crystallites, an area of 200 x 200 μ m of the crystallites was
437 measured by Raman image, without finding the characteristic bands around 413-416
438 cm⁻¹ of corundum.

439 Regarding titanium oxides, it is worth pointing out that rutile (the high
440 temperature mineral phase) was only detected in the inner part. This fact could indicate
441 the differences of temperatures suffered by the different parts of the LDG.

442 Some authors state that high velocity impacts on Earth are able to generate high
443 temperature melted material that can be subsequently ejected away from the crater and
444 quenched as natural glasses [46]. Others mention that these LDGs quenched from high

445 temperatures ranging from 1700 to 2100°C [2, 12]. Therefore, they agree with our
446 results.

447 Finally, the formation of some other compounds depends on both temperature
448 and pressure. This is the case of calcium carbonate. This compound occurs in five
449 different crystalline polymorphs at ambient pressure and temperature: anhydrous phases
450 (calcite, aragonite, and vaterite), and hydrated phases (monohydrocalcite and ikaite).
451 However, there are also several amorphous forms. Metastable disordered calcium
452 carbonate is transient and transforms into one of the crystalline forms in presence of
453 water or when heated [47]. Below 1200°C and approximately at 10 GPa, the metastable
454 disordered (amorphous) calcite in the melt could be the precursor of the aragonite
455 enclosed in the glass. Then, a rapid cooling and decrease of temperature could transform
456 this aragonite to calcite, stable at ambient conditions [48, 49]. Besides, aragonite could
457 transform to calcite with time, and it becomes more stable than calcite only at high
458 pressure (approximately 350 MPa at 25°C and 700 MPa at 300°C) [50]. Also, it must be
459 taken into account that calcite and aragonite may come from the original substrate
460 materials.

461 In addition, the signals obtained in the analysis of the matrix were also indicative
462 of the temperature and pressure suffered by the LDGs. Colomban et al. [51-53] used the
463 Raman intensity of these broad bands to determine the degree of crystallisation of
464 amorphous/crystalline silicate glasses as well as their temperatures of formation [51-
465 53]. They defined the Polymerization index (I_p) as the ratio of the areas under the broad
466 bending band (around 500 cm^{-1}) and the stretching band (around 1000 cm^{-1}) of the
467 silicate group, because that ratio is strongly correlated to the processing temperature
468 [51]. In our case, two different kinds of Raman spectra were found in the matrix: A and
469 B, as described in the previous section. Following the approach of Colomban et al. [51-

470 53], two ranges of index were determined in the LDG matrix spectra. In the matrix
471 spectrum A, I_p was in the range of 6.1-6.8 (<7), typical of glasses formed at 600-
472 1400°C, whereas in the matrix spectrum B, I_p was in the range of 10.2-16.9, which
473 corresponds to glass formation temperature higher than 1400°C.

474 These two different Raman responses in the matrix structure of the studied
475 LDGs suggest that the melt was subjected to two different ranges of temperatures: 600-
476 1400°C and higher than 1400°C reflecting different polymerization of the melt.
477 Moreover, the compounds found allowed us to know that higher temperatures affected
478 the specimens. The most meaningful data was that rutile, the compound that needs a
479 high temperature to form, was only identified in the inner parts. Besides, shocked
480 zircon, which needs temperatures higher than 1400 °C, was in the inner part as well. In
481 contrast, temperatures around 1470°C were also found in the surface due to the presence
482 of α -cristobalite.

483 A specific case mentioned before was the case of an idiomorphic zircon within
484 α -cristobalite. This finding could indicate that zircon could be earlier in the
485 crystallization than cristobalite (see Fig. 3a). The zircon was formed by pressure, since
486 if the zircon Raman peak had been displaced by temperatures around 1470°C as the
487 same time as cristobalite, they would have had the same crystallization grade. Besides,
488 if the cristobalite had been present in the inclusion when the zircon was formed at 20
489 GPa, its Raman bands would have been changed [54]. Therefore, this discovery proves
490 that this inclusion experimented a high pressure episode and, later, an increase of
491 temperature.

492 The high pressure conditions in the formation of the LDGs were also
493 corroborated by the presence of coesite (high-pressure polymorphs of quartz), aragonite,
494 amorphous calcite and displaced quartz, all of them only found in the inner part.

495 Therefore, it could be thought that only the core of the studied specimens was subjected
496 to high pressures, which is not logic. Moreover, low pressure or settled state compounds
497 appeared all over the samples. For instance, the shape of the tiny size and morphology
498 of the crystallites detected in the inner matrix (Fig. 2) can be explained by a high degree
499 of undercooling process (become supercooled) during the crystal formation.

500 An impact process is a wide but rapid process that implies different physical
501 processes which promote very high pressure and temperature conditions during the
502 formation of the melts. After the impact, the pressure conditions drop but the
503 temperature conditions would maintain in part to support the molten material. As the
504 impact process progress, melt fragments can trap minerals and rock debris at a given
505 temperature and pressure, and consequently the Raman signatures of such materials will
506 reflect the different shock and thermal conditions. Hence, the accumulation of high
507 pressure and temperature minerals in the inner parts of the recovered LDGs could be
508 explained if we consider that the LDGs started at high pressure (more than 30 GPa) and
509 temperature (more than 1470°C) conditions after the first impact, flying short distances
510 (unlike tektites). Then each melt fragment could undergone a second collision event
511 while cooling, trapping more materials (at low pressure but intermediate temperature,
512 i.e. 600-1400°C) from the terrestrial surface.

513 Moreover, regarding gypsum, on one side, we may assign its bands to normal
514 gypsum according to bibliography [55]. It would have adhered from the soil to the LDG
515 surface after the impact during the cooling or whenever in the LDG existence. On the
516 other hand, Knittle et al. [56] assigned its 1006 cm⁻¹ Raman peak to low pressure
517 (around 6 GPa) gypsum. In both cases the gypsum could be trapped during the
518 successive impacts after the first one. It is also conceivable that the pressures of these
519 subsequent impacts would have been much lower and therefore, the Raman bands

520 would appear more displaced according to the bibliography. In addition, gypsum
521 appeared with cristobalite, which involves high temperatures (1470°C) but gypsum
522 starts to lose the crystallization waters at around 100°C [42], then it could be trapped
523 after the first impact (formation of cristobalite at high temperature). Other option could
524 be the formation of gypsum as a secondary product from a soluble anhydrite hydration
525 with time, given the long period from LDG formation and the cracks and fissures
526 connected to the surface of the glass, which would explain the presence of water of
527 crystallization in the interior of the LDG. This anhydrite could be terrestrial or pre-
528 terrestrial, and could be formed either by the reaction of the LDG superficial carbonates
529 and the atmospheric SO_x, or by extreme heating from a previous gypsum trapped during
530 the first impact as well.

531 It is difficult to say which compound was the precursor, gypsum, anhydrite or
532 maybe both. According to previous works [6], anhydrite was seen in white deposits
533 inside the sand of the Libyan Desert. For that reason, the anhydrite found in the LDG
534 samples could belong to these latest deposits. The same situation could have happened
535 with gypsum, which could be also present in the substrate [57].

536 In relation to the temperature, the distribution to the anhydrites found in the
537 LDGs is rather reasonable. A-I, stable above 1180 °C, was identified inside where it
538 could have been formed by the high temperatures of the impact. A-II, stable from 300 to
539 1180 °C, was detected in the surface of the LDG, possibly formed in a cooling process
540 but still remaining partially melted and with capacity to trap materials [6].

541 Concerning carbon, Kramers et al. [20] found carbon phases with G broad band
542 at a high wavenumber (1597 cm⁻¹) in a stone called “Hypatia”, sampled from the same
543 area of LDG. Those authors considered that stone being a remnant of a cometary
544 nucleus fragment that it could have been part of a bolide that formed the LDG. In our

545 case, the Raman bands suggested amorphous carbon, which is typical from sedimentary
546 rocks [2]. However, it is noteworthy that Abate et al. [58] did not find traces of carbon
547 in the target rocks of the LDG area.

548 Finally, important data can be extracted from the found cavities and embedded
549 bubbles. The identification of olivine and pyroxene has not been mentioned in this type
550 of samples so far.

551 Vesicles could have been trapped during boiling of geothermal/hydrothermal
552 fluids. The vesicles indicate that there were gas bubbles in the melt when it solidified.
553 Gaseous vesicles could have been formed in the melt with a decrease of the solubility of
554 dissolved gases, due to changes of the physical conditions (temperature, pressure and
555 oxygen fugacity). Therefore, the formation of gases and fluid bubbles should have
556 occurred during the impact process. The contact with the terrestrial atmosphere could
557 have also introduced terrestrial heavy noble gases to the samples [59]. During this
558 event, volatiles from the target rocks, water from the pores or fractures water, nitrogen
559 and organics could be released. If pressure was elevated, water and nitrogen could
560 dissolve in the liquids and upon pressure decrease, water and nitrogen soon degassed
561 again, leaving trapped bubbles after solidification [34, 60]. After the impact, when the
562 bubbles were already formed, the temperature should have been lower than 1600°C,
563 because above it, the bubbles would disappear [16].

564 Apart from all this about the mineral distribution hypothesis in the LDGs, it
565 should be taken into account that the surface of the LDGs could not be the original and
566 belongs to the inner part of a bigger fragment that has been eroded with time.

567

568 **5. CONCLUSIONS**

569 It must be pointed out that by means of Raman spectroscopy it was possible to
570 determine the effect of the pressure and temperature. The identification of compounds
571 related to high and low temperatures and pressures allowed us to know the temperatures
572 and pressures at which samples could be subjected (from 300 to >1470°C, and from 10
573 to >30 Gpa). The compounds belonging to high pressure and temperature could be
574 formed during the meteorite/asteroid impact or airburst, and subsequently, with the
575 cooling, mineral phases corresponding to low pressure and temperature crystallized.
576 Moreover, if the impact process had progressed (flying short distances), melt fragments
577 could have trapped other minerals from the terrestrial surface until just before the end of
578 the cooling process. In general, the cooling of the different areas of the LDG could have
579 been heterogeneous and, as a consequence its mineral distribution too. It should be also
580 highlighted that the LDG surface may not be the original and belong to the inner part of
581 a bigger fragment.

582 Furthermore, compounds which were not found in previous LDG studies were
583 recognized, such as microcline feldspar, coesite, corundum, calcite, amorphous calcite,
584 magnesite, gypsum, cinnabar, hematite, limonite, fosterite, enstatite, tephroite and
585 nitrogen and oxygen gases.

586

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597

598 **Conflict of interest**

599 The authors declare that they have no conflict of interest.

600

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