1	Detection of organic compounds in impact glasses formed by the collision of an
2	extraterrestrial material with the Libyan Desert (Africa) and Tasmania (Australia)
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4	Leticia Gómez-Nubla*, Julene Aramendia, Silvia Fdez-Ortiz de Vallejuelo, Kepa
5	Castro, Juan Manuel Madariaga
6	
7	Department of Analytical Chemistry, Faculty of Science and Technology, University of
8	the Basque Country UPV/EHU, P.O. Box 644, E-48080 Bilbao, Basque Country, Spain.
9	*Corresponding author: leticia.gomez@ehu.es
10	
11	ABSTRACT
12	Impact glasses are rich silica melted formed at high temperature and pressure by the
13	impact of an extraterrestrial body on Earth. Here, Libyan Desert Glasses (LDGs) and
14	Darwin Glasses (DGs) were studied. Two non-destructive analytical techniques were
15	used to detect and characterize organic compounds present in their inclusions: Raman
16	spectroscopy and Scanning Electron Microscopy coupled to energy dispersive X-ray
17	spectroscopy (SEM-EDS). Phytoliths, humboldtine, palmitic acid, myristic acid, oleic
18	acid, 4-methyl phthalic acid and S-H stretching vibrations of amino acids were
19	identified. The presence of these particular organic compounds in such materials has not
20	been reported so far, providing information about (a) the ancient matter of the area
21	where the impact glasses were formed, (b) organic matter belonging to the

extraterrestrial body which impacted on the Earth, or (c) even to current plant or bacterial life, which could indicate an active interaction of the LDG and DG with the surrounding environment. Moreover, the identification of fullerene allowed us to know a pressure (15 GPa) and temperatures (670 K or 1800-1900 K) at which samples could
be subjected.

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Keywords: impact glass; Libyan Desert Glass; Darwin Glass; organic compounds;
Raman spectroscopy

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31 **1. Introduction**

The presence of organic matter has been already mentioned in meteorites, comet and 32 asteroidal dust [1, 2]. This is an important fact to the search of life in the Solar System, 33 34 because these molecules are used as biomarkers (i.e. chemicals that indicate life) on Earth. However, there is always a dilemma with the origin of organic compounds in 35 extraterrestrial or impact materials. Their survival is difficult to understand after certain 36 37 conditions, such as the impact on Earth with high temperature and/or pressure. Thus, they could be considered like a terrestrial contamination according to some literature [1, 38 39 3]. Normally, the identified terrestrial organic contaminants in meteorites are low molecular weight or solvent-soluble hydrocarbons [3]. 40

The same situation could happen with the organic matter in impact glasses. They are natural rich silica-melts produced by hypervelocity impact events of a meteorite, asteroid or comet on any geographic area on Earth, probably at pressures higher than 20 GPa [4]. They can be ejected away from the impact site to short or large distances and are usually named with the location of their origin. In this work, organic content in Libyan Desert Glasses (LDGs) and Darwin Glasses (DGs) was analyzed by nondestructive analytical techniques.

48 LDGs fragments are scattered in the Western Desert of Egypt (near the Libyan border)
49 in the soils' surfaces lying in interdune channels over an area of 6500 km [1, 5]. They

are commonly small irregular pieces with yellow to whitish translucent colour together with dark inclusions [5], and they are estimated to be 28.5 million years old [6]. Chemically, LDGs are nearly pure silica (95.5-99% wt SiO₂) [7]. Nonetheless, they are also composed by other compounds, which are sometimes forming bubbles, black or brownish inclusions (possibly derived by melting or decomposition of iron oxides), dark or brown streaks and white cristobalite spherulites. The concentration of impurities is highly variable [5, 8, 9].

In the case of DGs, they are located in the Western Tasmania (Australia) in a densely
forested valley [10, 11]. Glass fragments were recovered 20 km from the source crater
and within a 400 km² strewn field [10]. They are estimated to be 796-815 million years
old [11]. Chemically, DGs contain different percentages of SiO₂, Al₂O₃, TiO₂, FeO,
MgO and K₂O [10].

Both impact glasses were found in two terrestrial areas with diversity of climates: a desert, arid and dry, and a forest, wet and with numerous vegetation. The different terrestrial weathering processes of both climates could influence the composition of the samples.

66 Most of investigations about LDG and DG are focused on the identification of inorganic 67 mineral phases [4-10, 12-15]. In contrast, the study of organic compounds trapped in them is hardly mentioned. Despite this fact, it is a remarkable point that can provide 68 information about the ancient life in the area where they were formed, or even about 69 70 organic compounds belonging to the extraterrestrial body, since some elements found in LDGs and DGs have been assigned to meteoritic matter [8, 14, 15]. The impact, with its 71 corresponding high pressures and temperatures, could mean the removal or 72 transformation of the organic remains. However, some authors mention that there is 73

always a gradient of temperature and pressure during the impact. Hence, there could bea chance of survival at relatively low temperatures and pressures [16].

Among the techniques employed in the analysis of organic compounds in impact 76 77 glasses are those in charge of the elemental characterization: two-step Laser desorption/Laser ionization Mass Spectrometry (L2MS), Field Emission Scanning 78 Electron Microscopy (FE-SEM) and Scanning Electron microscopy (SEM) or 79 80 Transmission Electron Microscopy (TEM) [17,18] with Energy Dispersive X-ray spectroscopy (EDS), and Scanning Transmission X-ray Microscopy (STXM) near edge 81 X-ray Absorption Fine structure Spectroscopy (NEXAFS) [19]. Besides, those 82 83 techniques are employed for the molecular analysis: Fourier Transform infrared (FT-IR) 84 spectroscopy [19] and Pyrolysis–gas chromatography–mass spectrometry [16].

In our work, SEM-EDS was firstly employed to detect inclusions where carbon (an 85 86 indication of possible organic matter) was present. Then, micro-Raman spectroscopy was used to obtain the molecular information about the compounds in the inclusions. 87 Raman spectroscopy has been already employed in the identification of organic matter 88 in meteorites [20]. Besides, it will be used onboard ExoMars2020 and Mars2020 89 missions, in order to identify organic compounds as indication of life in the 90 91 extraterrestrial environment of Mars [21]. Therefore, despite no works about using Raman spectroscopy to detect organic compounds in LDGs and DGs were found in 92 literature, we thought that this technique would be appropriate because of its experience 93 94 in the study of terrestrial and extraterrestrial materials. Moreover, the capabilities shown 95 by micro-Raman spectroscopy to analyze the nature of inclusions give benefit to our approach. In addition, Raman analysis was carried out without sample destruction and 96 any kind of pre-treatment, maintaining the integrity of the samples to new analysis in 97 the future. 98

100 2. Material and methods

101 **2.1 Material**

102 Eighteen impact glasses from the Meteorites Collection of the Basque Country University (UPV/EHU) were analyzed, of which 8 are LDGs and 10 are DGs. They 103 were collected during an expedition to the Western Desert of Egypt and to the Western 104 105 Tasmania respectively. The LDGs have a translucent glassy matrix, with whitish spherical, brownish and dark inclusions in some cases (see Fig.S1). Their dimensions 106 range between 1-5 x 2-4 cm and 5-23 g weight. On the contrary, DG samples are mainly 107 108 spheroid, and with different shades: a green brownish dark colour, black or very light 109 and translucent and most of them have some bubbles inside the bulk (see Fig. S1). Most 110 of the specimens are mainly not higher than 1×1 cm, but some of them have dimensions 111 of 4.5×3.7 cm, 3×1 cm and 2.8×1 cm.

In general, the silica glass matrix of the LDGs exhibits a holohyaline texture with some 112 113 mineral occurrence such as aluminum-rich tiny crystallites, cristobalites (SiO₂) and 114 zircons (ZrSiO₄). Moreover, there are other minerals trapped within the LDG matrix, 115 such as silicon oxides (quartz (α -SiO₂), coesite (SiO₂)), silicates (microcline feldspar 116 (KAlSi₃O₈), forsterite (Mg₂SiO₄), enstatite (MgSiO₃), tephroite (Mn₂SiO₄)), sulphates (gypsum (CaSO₄ \cdot 2H₂O), anhydrite (CaSO₄), carbonates (calcite (CaCO₃), magnesite 117 $(MgCO_3)$), etc. [22]. In the case of the DGs, they are vesicular with a glassy 118 119 groundmass. The glassy groundmass is holohyaline defining Schlieren structures. These structures are characterised by the presence of abundant elliptical vesicles. Among the 120 121 mineral compounds found in our DGs are cristobalite (SiO₂), malachite (Cu₂CO₃(OH)₂) and ponsjankite (Cu₄SO₄ (OH)₆ H₂O) [13]. 122

123 **2.2 Methods**

124 **2.2.1** Thick and thin section preparations.

125 Some LDGs and DGs were sliced in order to facilitate the analysis of the inner inclusions. Thick and thin sections were prepared to get samples of small thickness. 126 127 Sections were obtained by slicing the samples using a cutting (Buehler-PetroThin) with a diamond saw. In order to acquire a perfectly flat surface without deformations, the 128 fragments were polished using silicon carbide powder of different grain size on frosted 129 130 glasses. The thick of the fragments was approximately 800 µm. Once obtained the flat surface, in the case of the thin sections, the samples were mounted on glass slides 131 (dimensions of 27 x 46 x 1.5 mm) with epoxy resin (a fixer compound composed of 132 133 polyurethane, acrylic and cyanoacrylate) and then, the samples were smoothed using progressively finer abrasive grit until they were only 30 µm thick. 134

135 2.2.2 Scanning Electron Microscopy coupled to Energy Dispersive X-ray 136 spectroscopy (SEM-EDS).

It was used an EVO 40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, 137 138 Germany) coupled to an X-Max Energy-Dispersive X-Ray spectroscopy (EDX) system (Oxford Instruments, UK) for the elemental mapping. The equipment is also installed 139 140 on an antivibratory table inside a temperature-controlled room. SEM images were 141 acquired at high vacuum employing an acceleration voltage of 20 KV. Magnifications up to 10 000× were reached using a Secondary Electron (SE) detector for image 142 acquisitions. Moreover, elemental mappings were performed using an 8.5 mm working 143 distance, a 35° take-off angle and an acceleration voltage of 20 kV. 144

145 **2.2.3 Raman spectroscopy.**

Two Raman spectrometers were employed in order to use three lasers (785 nm, 514 nm
and 532 nm). Firstly, it was used a Renishaw RA 100 Raman Spectrometer, coupled to
a fibre optic micro-probe (Oxford, UK), equipped with 785 nm excitation laser and a

Peltier cooled CCD detector. At 100% laser power, the nominal power of the excitation source is 150 mW and in the sample 30 mW. Neutral filters allow working at 1% (5 mW at the source and 1 mW at the sample) and 10% (50 mW at the source and 10 mW at the sample) as well. This parameter was varied if thermodescomposition was observed.

The micro-probe was joined to different long range lenses (4×, 20× and 50×) that allowed us to focus the laser beam around 5-100 μ m at the sample. The spectral resolution is around 2 cm⁻¹. The instrument is also coupled to a micro-camera whose positioning is controlled by a micrometric stage, which permits a perfect focusing on the areas of interest.

159 The second spectrometer was an InVia confocal micro Raman instrument (Renishaw, 160 UK) provided by 514 nm and 532 nm excitation lasers (at highest powers, the nominal 161 laser power at the source is 50 mW, and at the samples 20 mW) and Peltier cooled CCD detector (-70°C). The instrument is coupled to a Leica DMLM microscope (Bradford, 162 163 UK). For visualization and focusing 5x N PLAN (0.12 aperture) and 20x N PLAN EPI 164 (0.40 aperture) lenses were used. The spectra were acquired using 50x N PLAN (0.75 165 aperture, lateral resolution of 2 µm) long-range objectives. At high magnifications, the 166 laser spot was reduced to 1 µm diameter. The microscope implements a Prior Scientific motorized XYZ positioning stage with a joystick, and has a micro-camera for searching 167 points of interest. In order to obtain Raman chemical images, the StreamLine 168 technology (Renishaw) was employed. The inVia's motorized microscope stage moves 169 170 the sample beneath the lens so that the line is rasterized across the region of interest. Data are swept synchronously across the detector as the line moves across the sample, 171 and are read out continuously. Moreover, the equipment is installed on an antivibratory 172 table inside a temperature-controlled chamber. The spectral resolution is of 1 cm⁻¹. 173

In order to achieve the best signal-to-noise ratio the number of accumulations and integration time were varied in both spectrometers. WIRE 3.2 software (Renishaw, UK) was used for data collection and initial pre-treatment, while the data treatment was carried out with the Omnic software (Thermo Fisher-Nicolet, Madison, Wisconsin, USA). Furthermore, the results were compared with standard Raman spectra from the e-VISARCH and e-VISART Raman spectra databases [23] and spectra obtained from the on-line database RRUFF [24].

181

182 **3. Results and discussion**

183 **3.1 Darwin glasses (DGs)**

According to SEM images and elemental mappings performed over sections of DGs (Fig. 1), carbon was identified in some of inner inclusions. The spatial distribution of elements such as C, O, Al, Si, etc. (see elemental mappings of Fig. 1) allowed us to distinguish that the carbon elemental mapping did not coincide with any element detected in the sample, indicating the possible presence of organic carbon. Therefore, Raman spectroscopy was centered on such inclusions to detect organic compounds.

In our previous work about DGs, a group of Raman bands around 3000-2800 cm⁻¹ was 190 191 observed, and they were attributed to C-H stretching vibrations [13]. In the present work, other Raman bands appeared at 3009sh, 2930vs, 2892vs, 2851vs, 1653m, 1606m, 192 1460sh, 1439m, 1301m, 1265sh and 1060vw cm⁻¹ as well (see Fig. 2). According to 193 bibliography [25, 26], they correspond to a mixture of oleic acid ((Z)-9-octadecenoic 194 195 acid, CH₃(CH₂)₇CH=CH(CH₂)₇COOH) and 4-methyl phthalic acid (Benzene-1,2-dioic acid, $CH_3C_6H_3-1,2-(CO_2H)_2$). Oleic acid is a common fatty acid that plays a key role in 196 plants [27], and the methyl derivative of the phthalic acid is a constituent of combustion 197 products and could be released from plants into the air [28]. Therefore, the presence of 198

both compounds would be an indication of the interaction of the DGs with the
surrounding environment, characterized by being densely forested and wet. Moreover,
degradations products of those compounds have not been identified in the DGs.
According to literature [16], organic components inside DGs could be trapped into the
impact melt in a low-oxygen environment and preserved when the melt quenched to
glass, avoiding the organic breakdown by oxidation since the impact [16].

The oleic acid and the methyl derivative of the phthalic acid have been identified in the inner inclusions of our samples, so their initial trapping during the impact is highly probable. Moreover, those inclusions could have acted as closed low-oxygen environment avoiding the oxidation of the organic matter.

In addition, the presence of halite, sulphates, carbonates, phyllosilicates, silica, hematite and phosphates can isolate and biosignatures [29]. Sulphates, carbonates and silica are present in our DGs [13], so they could have conserved the organic compounds. Also, silica-rich water derived from hydrothermal systems is another well-established medium that promotes faithful preservation [29].

Notwithstanding, it cannot be ruled out the presence of partially soluble organiccompounds due to terrestrial weathering processes.

Fatty acids and polycyclic aromatic hydrocarbons (PAHs), such as 4-methyl phthalic acid, have been previously found in meteorites [30], but not so often in these impact glasses.

219 **3.2 Libyan Desert Glass (LDGs)**

In this case, we also found carbon in the inner bubbles of LDG specimens by means of Raman image analysis, again suggesting the presence of organic compounds in such inclusions. However, not only inclusions were detected inside our LDGs, but also in their outermost part.

Among superficial inclusions distributed through the translucent glassy matrix of the 224 225 LDG specimens, Raman spectra with bands at 3074m, 2963sh, 2938vs, 2905sh, 1716m, 1607s, 1450w, 1367vw, 1273w, 1189w, 1101w, 1020vw, 930vw, 860vw, 833vw, 724w, 226 635w and 462vw cm⁻¹ were found (see Fig. 3). Except for the feature at 462 cm⁻¹, which 227 corresponds to quartz from the glassy matrix of the LDGs [12], no similar spectrum has 228 been previously described in any of the LDG studies. According to bibliography, the 229 230 Raman spectrum could be assigned to phytoliths [31]. Phytoliths are silica particles 231 stemming from living plants that provide support and protection to the plant. During the silicification process, small amounts of organic matter are trapped [31]. In our spectrum 232 233 (see Fig. 3), such organic matter has been observed with peaks in the range about 3100-3000 cm⁻¹, characteristics of aromatic C-H stretching modes, and Raman bands between 234 3000-2800 cm⁻¹ attributed to C-H stretching vibrations. The range from 1650-1300 cm⁻¹ 235 236 includes various aromatic C-C stretching vibrations, and the range from approximately 1250 to 1000 cm⁻¹ contains bands commonly attributed to C-H bending modes [32, 33]. 237 238 Normally, when the plant dies, phytoliths are released into the soil, where they can be 239 accumulated for thousands of years [31]. In this way, those terrestrial materials could have been adhered to the LDGs after or during the impact of the extraterrestrial body on 240 the Libyan Desert. Moreover, phytoliths have been already found in cracks of 241 242 meteorites and in impact glasses as well, with high probability of containing terrestrial 243 organic materials [18, 34].

In other superficial dark inclusions, Raman spectra showing only a band centred at 1572m cm⁻¹ was found, suggesting the presence of a high ordered fullerene-type compound. According to literature, that band could correspond to the crystalline 3Dpolymeric C_{60} structure after high-pressure/high-temperature treatment at 15 GPa and 670 K [35]. Moreover, some Raman spectroscopic studies on the so-called onion-like

fullerene spherical nanostructures have also identified a Raman band at 1572 cm⁻¹ when 249 250 a high degree of structural perfection of the graphitic network is attained (subjecting nanodiamonds to temperatures in the range 1800-1900 K) [36, 37]. Therefore, the LDG 251 252 specimen could have been subjected to pressure of 15 GPa and temperatures of 670 K or 1800-1900 K. These conditions are in accordance with previous ones, obtained in the 253 identification of other mineral phases in a precedent work [22]. Apart from synthetic 254 origin, fullerenes can be of natural origin from energetic events such as volcanic 255 eruptions, flame generation or from biological algal remains [38-40]. In LDGs its 256 presence was previously described [9]. 257

The origin of the carbon in the LDG might be in the extraterrestrial body or in the terrestrial target rocks [41]. Kramers et al. (2013) [14] identified carbon phases in a stone found in the southwestern part of the LDG field. They considered the stone as a remnant of a cometary nucleus fragment of the bolide that formed the LDG. Moreover, it is noteworthy that traces of carbon have not been found in the target rocks of the LDG area [42].

In inner inclusions of the LDG, apart from carbon, Raman bands at 1586m, 1555vw, 264 1460sh, 1450vw, 1432m, 1391vw, 1331s and 913m cm⁻¹ were distinguished in a thick 265 section, as is shown in Fig. 4. The 1586 and 1331 cm⁻¹ bands are the G and D Raman 266 bands of amorphous carbon respectively [43] while the 914 cm⁻¹ Raman band 267 corresponds to v(C-C) stretching mode [44], and those bands at 1460 and 1432 cm⁻¹ 268 could be assigned to the v(C-O) stretching mode of oxalate anions [44]. Oxalates are 269 270 widespread in nature and are formed by reaction of metals and oxalic acid excreted from fungi, lichens and plants [44]. It is possibly an iron oxalate called humboldtine 271 (FeC₂O₄· $2H_2O$), since no other metal oxalate matches this spectrum [45]. Nonetheless, 272 the intensity of our spectrum Raman bands does not exactly coincide with those of the 273

humboldtine Raman spectra found in bibliography at ambient conditions [45]. In 274 275 accordance with some studies of oxalates, these changes of intensities are due to high pressures suffered by the samples [46], as those suffered in the LDG formation. 276 277 Therefore, the oxalate would be present in the Libyan Desert before the impact and could have been trapped and preserved within the matrix of the LDG during its 278 279 formation. Its degradation with time and high temperatures, typical of Libyan Desert, could have resulted in FeO and CO₂ [44], however, they have not been detected but 280 hematite (Fe₂O₃) or limonite (FeO(OH)) [22], which could be degradation products of 281 FeO or could have been incorporated subsequently from the environment. 282

The identification of carbon and the oxalate within the glass, and therefore their preservation, indicates that melting does not destroy all organic matter. As has been mentioned before, the conservation of organic compounds would be aided by the presence of sulfates, carbonates, silica and hematite [29], previously identified in these samples [22].

288 Furthermore, in some other inner inclusions of other LDG, Raman bands at 2963sh, 2925sh, 2880vs, 2846vs, 2723br, 2439m, 1462s, 1441s, 1426sh, 1295s, 1178vw, 289 1128m, 1095w, 1062m, 960w, 890w, 810br, 602vw and 482br cm⁻¹ were found (see 290 Fig. 5). In accordance with bibliography [47], they correspond to a mixture of palmitic 291 acid (hexadecanoic acid, CH₃(CH₂)₁₄COOH) and myristic acid (tetradecanoic acid, 292 293 CH₃(CH₂)₁₂COOH). The Raman signal of the LDG matrix was observed together with them as well (see Fig. 5). Palmitic acid is the most common fatty acid found in plants 294 295 (including palm oil, palm kernel oil and coconut oil), animals and many microorganisms [47]. Myristic acid is a widely spread saturated fatty acid too, present in 296 palm and coconut oil, cow's milk fat and some fish oils [47]. Moreover, Raman bands 297 in the 2600-2400 cm⁻¹ region were present. They correspond to S-H stretching 298

vibrations of amino acids residues containing sulfhydryl groups [48]. The presence of 299 300 those compounds could be an indication of an active interaction of the LDG with the surrounding environment (terrestrial weathering). Palmitic and myristic acid are by-301 302 products of oleic acid when is subjected to certain anaerobic conditions [49]. Therefore, they would be degradation products and the oleic acid would have been completely 303 degraded on Earth since no Raman spectra have been identified in the LDGs. Oleic acid 304 305 could not be conserved within the LDG. However, they were located in inner inclusions of the LDG, so they could have been also trapped during the impact. 306

307 Other authors have also identified those compounds in Darwin glasses but using gas308 chromatography after destroying the samples [16].

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310 **4.** Conclusions

311 SEM/EDS allowed us to identify the candidate inclusions to be analyzed by Raman 312 spectroscopy in the search of organic compounds due to the identification of carbon, not 313 correlated with any other element.

314 Despite Raman spectroscopy has not been employed till now to detect organic 315 compounds in DG and LDG, this work has demonstrated its ability to provide a huge 316 amount of information about organic compounds as well as the pressures and temperatures at which samples were subjected. Moreover, this technique preserves the 317 samples unlike other ones, which destroy the specimens. Organic compounds such as 318 phytoliths, oxalates, palmitic acid, myristic acid, oleic acid, 4-methyl phthalic acid and 319 320 S-H stretching vibrations of amino acids residues containing sulfhydryl groups were identified in some inclusions of the LDGs and DGs. Moreover, quartz, fullerene, 321 amorphous carbon, calcite and amorphous calcite were also found. 322

Nowadays the lack of knowledge lies within the origin of the organic compounds in the 323 324 LDGs and DGs. The only work describing the presence of organic compounds in DGs suggests that such organic components inside DGs were trapped into the impact melt, 325 326 avoiding its decomposition since the impact [16]. In addition, the presence of phytoliths, palmitic acid, myristic acid, oleic acid, 4-methyl phthalic acid and S-H stretching 327 vibrations of amino acids residues found in this work can be related to plant or bacterial 328 329 life, suggesting an active interaction of the LDG and DG with the surrounding environment. They would be in the impact glasses due to terrestrial weathering 330 331 processes.

332 The identification of oxalates in the exterior of the specimens could indicate the colonization of the LDGs by microorganisms, novel information in this type of 333 materials. However, the identification of shocked oxalate in the inner inclusions could 334 335 suggest that terrestrial oxalates were trapped during the LDG formation. The identification of palmitic acid and myristic acid, oleic acid and 4-methyl phthalic acid in 336 337 the inner inclusions of the impact glasses could also suggest an initial trapping process into the impact melt and its preservation when the melt quenched to glass. However, the 338 339 conservation of some compounds in the LDGs, such as the oleic acid, could have been 340 altered, since some by-products were detected (palmitic acid and myristic acid). That situation was not observed in the DGs, where it was only identified oleic acid, not their 341 342 degradation products. Thereby, it is remarkable that there are differences between the 343 presence of organic compounds in the LDGs and DGs, probably due to they were 344 formed by different extraterrestrial bodies and in different locations (Libyan Desert and Tasmania respectively). 345

In addition, the identification of a special fullerene indicated that LDG could have
reached temperatures in the range of 670 -1900 K and pressures of 15 GPa. These facts

display that samples could reach different temperatures during their formation, in agreement with the temperature data from other inorganic compounds found in the same specimens by us [13, 22]. Thus, we mainly consider such compounds were trapped during the impact melt formation, remaining unaltered for millions of years in the inner inclusions of the impact glasses. Moreover, some partially-polar organic compounds found in the outer inclusions could have been also added to the samples subsequently by terrestrial weathering.

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364 Conflict of Interest: none

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367 [1] Cooper G, Horz F, Spees A, Chang S. Highly stable meteoritic organic compounds
368 as markers of asteroidal delivery. Earth Planet Sci Lett. 2014; 385: 206-215.

369

370 [2] Pizzarello S, Shock E. The Organic Composition of Carbonaceous Meteorites: The

371 Evolutionary Story Ahead of Biochemistry. Cold Spring Harbor Perspect. Biol., 2,

a002105; 2010.

³⁶⁶ **References**

- [3] Sephton MA, Wright IP, Gilmour I, de Leeuw JW, Grady MM, Pillinger CT. High
 molecular weight organic matter in martian meteorites. Planet Space Sci. 2002; 50: 711716.
- 377
- [4] Bailey MJ, Howard KT, Kirkby KJ, Jeynes C. Characterisation of inhomogeneous
 inclusions in Darwin glass using ion beam analysis. Nucl Instrum Methods Phys Res B
 2009; 267: 2219-2224.
- 381
- [5] Barrat JA, Jahn BM, Amossé J, Rocchia R, Keller F, Poupeau GR, Diemer E.
 Geochemistry and origin of Libyan Desert glasses. Geochim Cosmochim Ac. 1997; 61:
 1953-1959.
- 385
- [6] Pratesi G, Viti C, Cipriani C, Mellini M, Geochemistry and origin of Libyan Desert
 glasses. Geochim Cosmochim Ac. 2002; 66: 903- 911.
- 388
- 389 [7] Greshake A, Koeberl C, Fritz J, Reimold WU. Brownish inclusions and dark streaks
- in Libyan Desert Glass: evidence for high-temperature melting of the target rock.
 Meteorit Planet Sci. 2010; 45 : 973-989.
- 392
- 393 [8] Giuli G, Paris E, Pratesi G, Koeberl C, Cipriani C. Iron oxidation state in the Fe-
- rich layer and silica matrix of Libyan Desrt Glass: A high- resolution XANES study.
- 395 Meteorit Planet Sci. 2003; 38: 1181- 1186.
- 396

397	[9] Swaenen M, Stefaniak EA, Frost R, Worobiec A, Van Grieken R. Investigation of
398	inclusions trapped inside Libyan Desert Glass by Raman microscopy. Anal Bioanal
399	Chem. 2010; 397: 2659- 2665.

401 [10] Howard K.T. Physical distribution trends in Darwin glass. Meteorit Planet Sci.
402 2009; 44: 115-129.

403

[11] Lo CH, Howard KT, Chung SL, Meffre S. Laser fusion argon-40/argon-39 ages of
Darwin impact glass. Meteorit Planet Sci. 2002; 37: 1555- 1562.

406

407 [12] Aramendia J, Gomez-Nubla L, Fdez-Ortiz de Vallejuelo S, Castro K, Murelaga X,
408 Madariaga JM. New findings by Raman micro spectroscopy in the bulk and inclusions
409 trapped in Libyan Desert Glass. Spectrosc Lett. 2011; 44: 521- 525.

410

411 [13] Gomez-Nubla L, Aramendia J, Alonso-Olazabal A, Fdez-Ortiz de Vallejuelo S,

412 Castro K, Ortega LA, Zuluaga MC, Murelaga X, Madariaga JM. Darwin impact glass

413 study by Raman spectroscopy in combination with other spectroscopic techniques. J

414 Raman Spectrosc. 2015; 46: 913- 919.

- 415
- [14] Kramers JD et al. Unique chemistry of a diamond-bearing pebble from the Libyan
 Desert Glass strewnfield, SW Egypt: Evidence for a shocked comet fragment Earth
 Planet Sci Lett. 2013; 382: 21-31.

419

- 420 [15] Meisel T, Koeberl C, Ford RJ. Geochemistry of Darwin impact glass and target
- 421 rocks. Geochim Cosmochim Ac. 1990; 54: 1463-1474.

423 [16] Howard KT et al. Biomass preservation in impact melt ejecta. Nat Geosci. 2013; 6:
424 1018-1022.

425

426 [17] Sapers HM, Osinski GR, Banerjee NR. Preston LJ. Enigmatic tubular features in
427 impact glass. Geology 2014; 42: 471-474.

428

[18] Schultz PH, Harris RS, Clemett SJ, Thomas-Keprta KL, Zarate M. Preserved flora
and organics in impact melt breccias. Geology 2014; 42: 515-518.

431

432 [19] Sapers HM, Banerjee NR, Osinski GR. Potential for impact glass to preserve
433 microbial metabolism. Earth Planet Sci Lett. 2015; 430: 95-104.

434

[20] Marshall CP, Edwards HGM, Jehlicka J. Understanding the Application of Raman
Spectroscopy to the Detection of Traces of Life. Astrobiology 2010; 10: 229-243.

437

438 [21] Bost N et al. Testing the ability of the ExoMars 2018 payload to document
439 geological context and potential habitability on Mars. Planet Space Sci. 2015; 108: 87440 97.

441

[22] Gomez-Nubla L, Aramendia J, Fdez-Ortiz de Vallejuelo S, Alonso-Olazabal A,
Castro K, Zuluaga MC, Ortega LA, Murelaga X, Madariaga JM. Multispectroscopic
methodology to study Libyan desert glass and its formation conditions. Anal Bioanal
Chem 2017; 409: 3597-3610.

- 447 [23] Castro K, Pérez-Alonso M, Rodríguez-Laso MD, Fernández LA, Madariaga JM.
- 448 On-line FT-Raman and dispersive Raman spectra database of artists' materials (e449 VISART database). Anal Bioanal Chem. 2005; 382: 248-258.
- 450
- 451 [24] Lafuente B., Downs, R.T., Yang, H., Stone, N. The power of databases: the
- 452 RRUFF project. In: Highlights in Mineralogical Crystallography (eds. T. Armbruster
- 453 and R. M. Danisi), Berlin; 2015. pp. 1-30.
- 454
- 455 [25] Adar F. Resonance Enhancement of Raman Spectroscopy: Friend or Foe?.
 456 Spectroscopy 2013; 28(6).
- 457
- [26] Tourwe E, Baert K, Hubin A. Surface-enhanced Raman scattering (SERS) of
 phthalic acid and 4-methyl phthalic acid on silver colloids as a function of pH. Vib.
 Spectrosc. 2006; 40, 25-32.
- 461
- 462 [27] Thomas A. Fats and Fatty Oils. Ullmann's Encyclopedia of Industrial Chemistry

463 14, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; 2012.

- [28] Albaigés J, Frei RW, Merian E. Chemistry and Analysis of Hydrocarbons in the
 Environment 5, Gordon and Breach Science Publishers, Glasgow; 1983.
- 467
- 468 [29] Summons RE et al. Preservation of Martian Organic and Environmental Records:
- 469 Final Report of the Mars Biosignature Working Group. Astrobiology 2011; 11: 157-
- 470 181.
- 471

472	[30] Huang Y, Aponte JC, Zhao J, Tarozo R, Hallmann C. Hydrogen and carbon
473	isotopic ratios of polycyclic aromatic compounds in two CM2 carbonaceous chondrites
474	and implications for prebiotic organic synthesis. Earth Planet Sci Lett. 2015; 426: 101-
475	108.

- 476
- 477 [31] Gallagher KL, Alfonso-Garcia A, Sanchez J, Potma EO, Santos GM. Plant growth
 478 conditions alter phytolith carbon. Front Plant Sci. 2015; 6, Article753.
- 479

[32] Frank O, Jehlicka J, Edwards HGM. Raman spectroscopy as tool for the
characterization of thio-polyaromatic hydrocarbons in organic minerals. Spectrochim
Acta A 2007; 68: 1065-1069.

483

484 [33] Socrates G. Infrared and Raman characteristic group frequencies, John Wiley and485 sons edition, England; 2001.

486

487 [34] Burckle LH, Delaney JS. Terrestrial microfossils in Antarctic ordinary chondrites.
488 Meteorit Planet Sci. 1999; 34: 475-478.

489

[35] Blank VD et al. Synthesis of superhard and ultrahard materials by 3Dpolymerization of C60, C70 fullerenes under high pressure (15 Gpa) and temperatures
up to 1820 K. Zeitschrift für Naturforschung 2006; 61b: 1547-1554.

- 494 [36] Kuznetsov VL, Butenko YV. Nanodiamond graphitization and properties of onion-
- 495 like carbon (eds: Gruen, D.M., Shenderova, O.A. and Vul, A.Y.) in Synthesis,

496 Properties and Applications of ultracrystalline diamong, Amsterdam, The Nederlands;497 2005. pp. 199-216.

498

- 499 [37] Obraztsova D, Fujii M, Hayashi S, Kuznetsov VL, Butenko YV, Chuvilin AL.
 500 Raman identification of onion-like carbon. Carbon 1998; 36: 821-826.
- 501
- [38] Elsila JE, de Leon NP, Plows FL, Buseck PR, Zare RN. Fullerenes in extracts of
 impact breccia samples from Sudbury, Gardnos, and Ries impact craters and the effects
 of aggregation on C₆₀ detection. Geochim Cosmochim Acta 2005; 69: 2891-2899.
- 505
- [39] Heymann D, Chibante LPF, Brooks RR, Wolbach WS, Smalley RE. Fullerenes in
 the K/T boundary layer. Science 1994; 265: 645-647.
- 508
- 509 [40] Heymann D, Jenneskens LW, Jehlička J, Koper C, Vlietstra E. Fullerenes in
- 510 extracts of impact breccia samples from Sudbury, Gardnos, and Ries impact craters and
- the effects of aggregation on C60 detection. Fuller Nanotub Car N. 2003; 11: 333-370.
- 512 [41] Miura Y, Kobyashi H, Kedves M, Gucsik A. Carbon source from limestone target
- 513 by impact reaction at the K/T Boundary. 30th Lunar and Planetary Science Conference
- 514 Proceedings, Houston, abs.#1522; 1999.
- 515
- 516 [42] Abate B, Koeberl C, Kruger FJ, Underwood Jr. JR. BP and Oasis impact structures,
- Libya, and their relation to Libyan Desert Glass. Geol. Soc. Am. 1999; 339: 177-192.

- 519 [43] Wang Y, Alsmeyer DC, McCreery RL. Raman Spectroscopy of Carbon Materials:
- 520 Structural Basis of Observed Spectra. Chem Mat. 1990; 2: 557-563.

[44] Frost RL, Weier ML. Thermal decomposition of humboldtine - a high resolution
thermogravimetric and hot stage Raman spectroscopic study. J Therm Anal Calorim.
2004; 75: 277-291.

525

526 [45] Frost RL. Raman spectroscopy of natural oxalates. Anal Chim Acta. 2004; 517:
527 207–214.

528

- 529 [46] Mishra AK, Murli C, Garg N, Chitra R, Sharma SM. Pressure-Induced Structural
- 530 Transformations in Bis (glycinium) oxalate. J Phys Chem B 2010; 114: 17084-17091.

531

[47] Czamara K, Majzner K, Pacia MZ, Kochan K, Kaczor A, Baranska M. Raman
spectroscopy of lipids: a review. J Raman Spectrosc. 2015; 46: 4-20.

534

[48] Kumar R, Sripriya R, Balaji S, Senthil Kumar M., Sehgal PK. Physical
characterization of succinylated type I collagen by Raman spectra and MALDITOF/MS and in vitro evaluation for biomedical applications. J Mol Struct. 2011; 994:
117–124.

539

[49] Lalman JA, Bagley DM. Anaerobic degradation and methanogenic inhibitory
effects of oleic and stearic acids. Water Res. 2001; 35: 2975-2983.

542