

1 **Physico-chemical study of an exogenic fulgurite from a thunderstorm**  
2 **on 10<sup>th</sup> August 2013 in Dallas, TX**

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18

19 **Abstract**

20 Droplet-like exogenic fulgurites comprise a minor grouplet of natural glasses resulting  
21 from powerful lightning strikes. Reports on such type-V fulgurites are scarce in the  
22 literature. In this work, a fulgurite specimen from the thunderstorm that took place on  
23 10<sup>th</sup> August 2013, in Dallas, TX, USA, has been analyzed using X-ray powder  
24 diffraction, X-ray fluorescence, scanning electron microscopy, energy-dispersive X-ray  
25 spectroscopy, and infrared and Raman spectroscopy techniques. X-ray diffraction

26 revealed the amorphous nature of the exofulgurite, and X-ray fluorescence showed a  
27 high Si, Al and Ca content. Infrared and Raman spectroscopy were key in revealing  
28 clear Si–O modes related signatures and a very significant presence of water (OH/H<sub>2</sub>O).  
29 A parallel with glassy silicate materials, but also with opal-A, was essential in the  
30 understanding of the fulgurite's characteristics. In particular, Raman data evidenced the  
31 exofulgurite to have a high degree of depolymerization.

32

33 **Keywords:** droplet fulgurite; FTIR; keraunology; natural glass; Raman spectroscopy;  
34 telluric

35

## 36 **1. Introduction**

37 High-energy events, such as impact cratering (Chao 1967; Golubev et al. 2020;  
38 Koeberl and Ferrière 2019; Maierhofer et al. 2019), nuclear detonations (Eby et al.  
39 2010; Roberts et al. 2019; Wannier et al. 2019), air bursts (Osinski et al. 2008; Silvia  
40 2017; Wasson 2003) (Fig 1), or lightning strikes (Block 2011; Feng et al. 2019; Martín-  
41 Ramos et al. 2019; Roberts et al. 2019; Sheffer 2007; Stefano et al. 2020) produce  
42 materials that are geochemically and morphologically comparable. These materials  
43 include, for instance, aerodynamically-shaped teardrops, beads and dumbbell glasses;  
44 high-temperature rapidly quenched microspherules and vesicular siliceous scoria-like  
45 objects; corundum, mullite, magnesioferrite, suessite (Fe<sub>3</sub>Si) or naquite (FeSi); and  
46 melted SiO<sub>2</sub> glass, or lechatelierite, which cannot be produced volcanically (Bunch et al.  
47 2012).

48 Fulgurites are formed when a lightning strike, which generates temperatures of over  
49 1,800 °C (3,270 °F), instantaneously melts silica, fusing grains together. A classification  
50 of fulgurites into four main types (Pasek et al. 2012; Pasek and Pasek 2018), considers

51 as type I those fulgurites whose target material is typically an almost pure quartz sand  
52 (over 90%); type II fulgurites originate from loose sediments or soil with variable  
53 amounts of clay, silt, quartz sand and/or small rock fragments; type III are associated  
54 with caliche; whereas type IV fulgurites originate when lightning strikes hit directly  
55 rock outcrops (or at least, when target material clast size is larger than the diameter of  
56 the resulting fulgurite glass). A minor fifth type corresponds to droplet-like exogenic  
57 fulgurites; they are morphologically different from the previous ones and they originate  
58 in a very particular way. Conventional fulgurites are hollow glass tubes formed in the  
59 quartzose sand, soil or rocks hit by the lightning strikes. On the other hand, exogenic  
60 fulgurites (i.e., type V fulgurites), which are commonly associated with type II or type  
61 IV fulgurites, show a morphology that is consistent with ejection from the fulgurite  
62 cylinder or the top soil and a subsequent landing and cooling on the ground surface  
63 (eventually with significant cooling in the air). Visually, they are amorphous and often  
64 “bubbly” in appearance, show different colors (e.g., green) than those found in  
65 conventional fulgurites (which are typically tan or brown) and have a smooth, glassy  
66 surface (unlike conventional fulgurites which have a gritty, sandy feel) (Pasek et al.  
67 2012).

68 The best documented cases of exogenic fulgurite occurrences took place in 2004 in  
69 Elko Hills, Northeastern Nevada, just south of the town of Elko (Mohling 2004) (Fig  
70 2a), and in Oswego, NY, on 2<sup>nd</sup> August 2008 (Walter 2011) (Fig 2b). The total number  
71 of reported occurrences of this type of fulgurites is scarce, and even more when it comes  
72 to their study. Sometimes, the discovery of fulgurite specimens does not follow  
73 immediately the occurrence of a thunderstorm; this may cast an initial doubt on their  
74 origin, which may be particularly the case for type V droplet fulgurites. The case under  
75 study here took place during a strong thunderstorm on 10<sup>th</sup> August 2013, when a

76 lightning bolt struck down a small tree in Mesquite, a suburban city located east of the  
77 city of Dallas, Texas. The next day, it was noticed that – apart from the charred remains  
78 of the tree – the ground was littered with bubbly, light and dark-green, “glass” pieces  
79 over a 4 m circular radius. The source of “glass emission” was traced to two small holes  
80 in the ground, from which molten liquid had apparently been shot up into the air in all  
81 directions. Specimens off the grass and nearby sidewalk were gathered before they were  
82 damaged by pedestrians and their discoverer began selling them online. The authors of  
83 this paper bought one of the specimens to study its composition (Fig 2*c,d*).

84 Even though several studies on fulgurites already exist, there is very limited data on  
85 the very particular case of exofulgurites, as previously mentioned, and questions arise  
86 about what type of geological object is created by a lightning strike in the particular  
87 circumstances of this one, and about the presence of singular features. Moreover, while  
88 several authors have already pointed to the importance of fulgurites’ investigation as a  
89 natural model for impact processes (Feng et al. 2019; Kochemasov 1985), the  
90 investigation of these natural glasses may have other relevant implications, namely as  
91 geological markers of paleoclimatic conditions (Carter et al. 2010a; Navarro-González  
92 et al. 2007; Pasek and Block 2009) and in telluric planetary studies. It is widely  
93 recognized that lightning strikes may have played an important role in Earth’s early  
94 stages, and the existence of lightning strikes has been recognized in Venus (Russell et  
95 al. 2007), and possibly in Titan (Petculescu and Kruse 2014). On other telluric planets,  
96 such as Mars, it is probable that at the time this planet had a thicker atmosphere,  
97 lightning strikes also occurred (Harrison et al. 2008). Fulgurites may thus be regarded as  
98 examples of such extreme environmental scenarios that need to be considered in a  
99 planetary geophysics context as well as in a terrestrial one.

## 100 **2. Geological setting**

101 The geology of Mesquite area, and in a broader way of Dallas County, is  
102 documented in general and more specific geological maps and memoirs on the region,  
103 including its soils (Barnes 1987; Coffee et al. 1980; Dallas Petroleum Geologists 1941;  
104 The University of Texas at Austin. Bureau of Economic Geology 1992; United States  
105 Geological Survey (USGS) 2014). The main geological unit in the area of Mesquite,  
106 and the one of interest herein, is the Ozan formation, which belongs to the Taylor Group  
107 (Late Cretaceous; Ku2 – Navarro and Taylor Groups, Fig 3). Navarro and Taylor groups  
108 strike regularly SSW-NNE for a few hundred kilometers, with an inflexion towards  
109 ENE in the extreme northeast of Texas. Ozan formation thickness shows values around  
110 150 m in Dallas County; rocks from this unit dip eastwards at a very low angle ( $< 1^\circ$ ).  
111 Lithologically, Ozan formation consists of a medium to dark-gray calcareous clay,  
112 poorly bedded, with variable amounts of silt; silt content tends to increase upwards,  
113 with possible occurrence of fine-grained sand. Clay is montmorillonitic; some  
114 glauconite, phosphate pellets, hematite nodules and pyrite nodules are present. At  
115 surface, clayey soils, dark gray to black in the upper part (thickness in the range 40-120  
116 cm) and dark gray to brown below, reflect the underlying lithology; total thickness may  
117 exceed 1.5 m.

118

## 119 **3. Methods**

120 The analytical approach to the study of the exogenic fulgurite sample included  
121 optical image and scanning electron microscopy (SEM) acquisition, as well as analyses  
122 by energy-dispersive X-ray spectroscopy (EDX), X-ray fluorescence spectroscopy  
123 (XRF), X-ray powder diffraction (XRPD), Fourier-transform infrared (FTIR)  
124 spectroscopy and Raman spectroscopy. In SEM acquisition, no sputter coating was

125 used, in order to be able to perform EDX analyses. In the remaining analyses (XRF,  
126 XRPD, FTIR and Raman spectroscopy), the sample was ground into fine powder in an  
127 agate mortar, homogenized, and analyzed «as is».

128 Optical microscopy was undertaken with an Avangard Optics (China) AN-E500  
129 iScope 500x USB digital microscope. SEM and EDX analyses were conducted with an  
130 EVO HD 25 (Carl Zeiss, Oberkochen, Germany) apparatus. Operative conditions are  
131 indicated in each SEM micrograph.

132 The elemental composition of the materials was determined by wavelength  
133 dispersive XRF spectroscopy with a Bruker S8 Tiger Series 2 apparatus, using the  
134 standardless analysis program QuantExpress to convert atoms of each element into  
135 oxides. Operative conditions: 60 kV Cu 200  $\mu\text{m}$  LiF200 0.23°. For comparison  
136 purposes, the analysis was repeated at the Research Technical Services of Universidad  
137 de Alicante, with a PW 2400 (Philips, Amsterdam, Netherlands) automatic sequential  
138 wavelength dispersive X-ray fluorescence spectrometer. The results were processed  
139 with the analytical software package SuperQ. In both cases, measurements were taken  
140 over the homogenized sample powder, with at least 3 measurements per analysis.

141 The X-ray powder diffractogram of the sample was obtained using a Rigaku (Tokyo,  
142 Japan) D/max 2500 diffractometer, in reflection geometry, with a  $\text{CuK}\alpha$  ( $\lambda=1.54 \text{ \AA}$ )  
143 radiation and using crystalline silicon as a standard. Operative conditions: 40 kV, 30  
144 mA;  $2\theta=5-80^\circ$ ; step=0.02°; t=1 s/step. The analysis was repeated at the facilities of the  
145 Universidad de Zaragoza with equal results.

146 The infrared spectra were collected using a Thermo Scientific (Waltham, MA, USA)  
147 Nicolet iS50 FTIR spectrometer, equipped with an in-built diamond attenuated total  
148 reflection (ATR) module. The spectra were collected in the 400-4000  $\text{cm}^{-1}$  region at  
149 room temperature, with a 0.5  $\text{cm}^{-1}$  spectral resolution; a total of 128 scans per spectrum

150 were co-added. Ten spectra were collected from subsamples in powder form, with no  
151 significant differences observed between them.

152 The Raman spectra were acquired at room temperature in the 133-3820  $\text{cm}^{-1}$  range at  
153 1  $\text{cm}^{-1}$  spectral resolution on a Jasco (Easton, MD, USA) NRS-5100 dispersive Raman  
154 system (532.11 nm laser line; 600 lines/mm dispersion grating; 50×1000  $\mu\text{m}$  slit;  
155 rejection filter 532.0 nm; resolution 6.83  $\text{cm}^{-1}$ , 3.60  $\text{cm}^{-1}/\text{pixel}$ ; objective lens MPLFLN  
156 20×; laser power 1.0 mW; attenuator OD0.6; 4-stage Peltier cooled CCD (UV-NIR  
157 range, 1024 × 255 pixel)). This characterization was also conducted at the Research  
158 Technical Services of Universidad de Alicante. In total, three powdered subsamples  
159 were analyzed, each with a minimum of three collected spectra.

160

## 161 **4. Results and discussion**

### 162 **4.1. *Optical examination and SEM analysis***

163 The droplet fulgurite specimen was light-green in color, and consisted of a main  
164 body, roughly spherical (diameter <1 cm), and minor spherical protuberances, some of  
165 them no bigger than 1-2 mm in diameter; the overall size was approximately 1.5 cm  
166 (Fig 2*c,d*). Optical microscope images (Fig 4) showed a material with glassy  
167 appearance, already observable in hand-specimen observation. Microscopic observation  
168 of some of the spherical protuberances revealed the presence of a very high number of  
169 light-halo vesicles; the existence of such vesicles was already observable  
170 macroscopically, some being bigger than 0.5 mm in diameter (Fig 2*d*). They are clearly  
171 indicative of the presence of rapid expanding volatiles leading to the formation of glass  
172 bubbles as a consequence of extreme heating associated to the lightning strike.

173 Scanning electron microscopy (SEM) micrographs of the surface of the  
174 microprotuberances (Fig 5) showed a body with a «crater-like» appearance, as it would  
175 be expected from above observations. The fulgurite appeared to be constituted by a

176 groundmass with an amorphous appearance, with no visible individual mineral grains. It  
177 did not show the flow textures characteristic of lechatelierite formed at >2,200 °C, such  
178 as those exhibited by the microspherules or SLOs from the Younger Dryas episode  
179 12.9KYrBP (Fig 6). This feature indicates that, in the formation of the exofulgurite  
180 from Dallas, this temperature was not reached.

181

#### 182 **4.2. X-ray fluorescence and EDX studies**

183 The exofulgurite originates from soil material. The main soil constituents are also  
184 those present in the underlying calcareous montmorillonitic clay. The soil is smectitic  
185 and calcareous, the very high shrink-swell potential of the soil being strongly indicative  
186 that the smectite is a main constituent of the soil (Coffee et al. 1980; Templin et al.  
187 1956). In this context, in a temperate climate with annual average precipitation over 900  
188 mm, usual soil evolution leads to a loss of alkalis; particularly in what concerns CaO, a  
189 loss in the carbonate content leads to a residual enrichment in the smectitic and silt  
190 fractions in the soil, and consequently to an enrichment in silica content.

191 Chemical composition from XRF and EDX analyses is presented in Table 1. It  
192 reflects the montmorillonitic clayey nature of local lithology and its soil, namely for  
193 MgO content. The high CaO content is clearly related to the clay/soil being calcareous;  
194 K<sub>2</sub>O can be linked to the occurrence of glauconite. The EDX analyses of the surface of  
195 one of the fulgurite's minor spherical protrusions indicated the existence of some local  
196 heterogeneity, the major difference being the absence of iron. Content of Fe<sub>2</sub>O<sub>3</sub>(total)  
197 for XRF results may be at least partially linked to the presence of iron-bearing nodules  
198 in the clay, which could account for an heterogeneous distribution of iron in the soil,  
199 and thus its absence in one minor protrusion. However, it is not clear that the nodules  
200 alone may account for Fe<sub>2</sub>O<sub>3</sub>(total), a fraction of this content being likely in connection



201 with montmorillonite, marginally also with glauconite; as such, a local compositional  
202 fractionation related with the fulgurite formation process is likely to have occurred (this  
203 will be further discussed below).

204 XRF analytical results for the bulk sample (Dallas fulgurite), together with chemical  
205 composition data for other fulgurites, are presented in Table 2<sup>i</sup>. This table gathers  
206 examples of fulgurites of the same type as the Dallas fulgurite (i.e., type V), but also of  
207 type II and type IV specimens (the ones with which exogenic fulgurites are commonly  
208 associated). The specimens from York, Vernal and Tiedra are droplet-type fulgurites.  
209 York and Vernal samples are associated with type II fulgurites, the parent material  
210 being a mica-schist derived soil and a loess, respectively (Pasek et al. 2012); Tiedra  
211 specimens are related to an archaeological site (Martín-Ramos et al. 2019). The  
212 Greensboro fulgurite is a type II specimen originated from a red-brown clayey soil  
213 (formed from the weathering of a diabase) (Carter et al. 2010a). The Viseu (Abrunhosa  
214 et al. 1995) and Mottarone (Elmi et al. 2017) fulgurites are both type IV, associated  
215 with granites. The Zacatecas type II fulgurite was found in a calcareous soil (Reyes-  
216 Salas et al. 2017).

217 Chemical composition data in Table 2 reflect two major influences: origin and  
218 chemical composition fractionation during the rapid heating/fusion/solidification  
219 process associated with a lightning strike (which is recognized in a number of works,  
220 including some cited in Table 2). The Viseu fulgurite shows little compositional  
221 differences towards the parent granite, whereas the Mottarone fulgurite is clearly more  
222 silica rich than the granite it derives from. A similar process of silica enrichment is clear

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<sup>i</sup> For additional XRF data from other type I, type II and type IV fulgurites, the interested reader is referred to the recent article by Roberts et al. (2019).

223 for the Greensboro diabase soil-related fulgurite. In the case of Zacatecas, the  
224 occurrence of a fractionation process is clear, with a silica-enriched and calcium  
225 depleted cover, and a high CaO content vitreous core. The same process of silica  
226 enrichment is present in the droplet-type fulgurites of Vernal and York, in respect to the  
227 type II fulgurites they are related with, along with an enrichment in K<sub>2</sub>O and a loss in all  
228 other major element oxides (those with values above 1% in Table 2). The wide  
229 occurrence of compositional fractionation in fulgurites, including exogenic fulgurites,  
230 makes it very probable that the same process took place in the case of the Dallas  
231 fulgurite; fractionation has already been discussed in what concerns iron, but the same  
232 process is likely to be more widespread, namely in what concerns silica enrichment.

233 Fulgurites are usually considered as mineraloids. However, the fusion-solidification  
234 process involved in their formation has a parallel in some volcanic rock-types. With this  
235 in mind, and in order to compare the Dallas fulgurite composition with those of other  
236 fulgurites, CIPW norms (Cross et al. 1912) were calculated (see Table 2); they show a  
237 clear difference between normative corundum + hypersthene fulgurites and normative  
238 diopside + wollastonite + titanite fulgurites. The Dallas fulgurite belongs to this last  
239 group, together with Tiedra and the core Zacatecas fulgurite.

240

#### 241 **4.3. X-ray powder diffraction study**

242 The X-ray powder diffractogram (Fig 7) showed no peaks associated with the  
243 presence of crystalline phases. Therefore, it confirmed that the fulgurite specimen was  
244 entirely constituted by vitreous material.

245 The amorphous nature of the Dallas fulgurite prevented any quantitative  
246 identification of potential mineralogical components by XRPD, making it necessary to

247 use complementary characterization techniques, namely FTIR and Raman  
248 spectroscopies.

249 Moreover, the extremely low number of reported occurrences of exogenic fulgurites,  
250 and even scarcer existence of corresponding analytical data, led us to look for a proxy.  
251 At this stage, emphasis was placed on the specimen composition and its crystallinity  
252 degree. Opal-A was chosen as a proxy, on the basis of its amorphous character, its  
253 siliceous composition and the presence of water (OH / H<sub>2</sub>O), which was expected to be  
254 also present in the exofulgurite under study (and later on confirmed). Silica glass (in a  
255 broad sense) was used as another proxy.

256 The exofulgurite X-ray powder diffractogram showed a main broad asymmetric  
257 peak, very similar to data of several specimens of opal-A (Drees et al. 1989; Eckert et  
258 al. 2015; Liesegang and Milke 2014; Smith et al. 2018) and of silica glass (Gerber and  
259 Himmel 1986; Kivi et al. 2016; Wan et al. 2016; Warren and Loring 1935). However,  
260 there was a minor difference in the  $2\theta$  (Cu  $K\alpha$ ) position of the diffuse peak:  $\sim 24.2^\circ$  for  
261 the fulgurite versus  $\sim 22.2^\circ$  for opal-A and  $\sim 21.3^\circ$  for pure silica glass. In the latter case,  
262 for soda-lime-silica glass, the  $2\theta$  value increases to  $\sim 23.5^\circ$  (12.4% CaO, 11.4% Na<sub>2</sub>O,  
263 76.3% SiO<sub>2</sub>; (Biscoe et al. 1941)) and  $\sim 23.9^\circ$  (8.1% CaO, 3.2% MgO, 13.2% Na<sub>2</sub>O,  
264 72.51% SiO<sub>2</sub>; (Chakraborty et al. 2010)).

265 The fact that the fulgurite's diffractogram (total sample) shows that the specimen is  
266 entirely amorphous strongly supports the absence of soil/sand grains being embedded in  
267 the matrix. As such, either the exogenic fulgurite did solidify in the air or at least it had  
268 cooled down enough, when it hit the ground, not to embed soil particles in the matrix.

269

#### 270 **4.4. FTIR spectroscopic studies**

271 For spectral interpretation and analysis, the infrared spectrum (Fig 8a) can be divided  
272 into two regions: 400 – 1500 cm<sup>-1</sup>, comprising of a number of bands common to all  
273 silicates with tetrahedrally coordinated silicon (Farmer 1974; Graetsch et al. 1994;  
274 Langer and Floerke 1974; Plyusnina 1979; Webb and Finlayson 1987); and the second  
275 region, 1500 – 4000 cm<sup>-1</sup>, which contains water-related (Efimov et al. 2003; Goryniuk  
276 et al. 2004) and organic matter-related C-H vibrational modes (Ganesh Kumar et al.  
277 2014; Garai et al. 2006). The infrared spectrum of the Dallas fulgurite is characterized  
278 by three bands at 460, 784 and 1069 cm<sup>-1</sup> attributed to a O-Si-O bending ( $\delta(\text{O-Si-O})$ ),  
279 symmetric ( $\nu_s(\text{Si-O})$ ) and asymmetric ( $\nu_{as}(\text{Si-O})$ ) Si-O-Si stretching vibrations,  
280 respectively (Farmer 1974; Smallwood et al. 1997; Webb and Finlayson 1987). The  
281 peak positions of these bands compared to pure silica glass (Bock and Su 1970), opal-A  
282 (Gemological Institute of America 2020), and calcium aluminosilicate glass (70 mol%  
283 SiO<sub>2</sub>, 10 mol% Al<sub>2</sub>O<sub>3</sub>, 20 mol% CaO; i.e., a composition similar to that of the Dallas  
284 fulgurite) (Huang and Behrman 1991) are found in Table 3. The positions of the  
285 characteristic vibrational modes of opal-A and the calcium aluminosilicate glass are  
286 very similar to those of the Dallas fulgurite.

287 Figure 8 presents an infrared spectrum of the Dallas fulgurite (solid line) together  
288 with the infrared spectra of quartz (black dotted line) and opal-A (red dotted line) for  
289 visual comparison. Of particular note is the  $\nu_{as}(\text{Si-O})$  band at 1069 cm<sup>-1</sup> which is  
290 significantly broader in the spectrum of the Dallas fulgurite compared to quartz and  
291 opal-A, a feature that is usually associated with amorphous materials. Additional  
292 spectral features, which appear as distinctive shoulders at ~965 and ~1175 cm<sup>-1</sup>,  
293 contribute to broaden this band. A similar pattern is observed in the infrared spectrum of  
294 calcium aluminosilicate glass with the band in the 1050–1100 cm<sup>-1</sup> region and the band  
295 at ~960 cm<sup>-1</sup> assigned to the stretching vibration of the Si–O bond of the [SiO<sub>4</sub>]

296 tetrahedra, with one corner shared with an aluminum or calcium polyhedron  
297 (Si(OA1/Ca) group) in the first case, or with two corners shared with aluminum-oxygen  
298 or calcium-oxygen polyhedra (Si(OA1/Ca)<sub>2</sub> group) in the second case (Huang and  
299 Behrman 1991). The number of non-bridging oxygens increases with excess CaO, these  
300 “modifiers” breaking the inter-tetrahedral bonds, a phenomenon also referred to as  
301 “depolymerization” of the glassy network (Khalil et al. 2010). In addition, the position  
302 of the  $\nu_{\text{as}}(\text{Si-O})$  band at  $\sim 1100 \text{ cm}^{-1}$  is an indicator of the three-dimensionality of the  
303 silica network, a shift towards lower wavenumbers indicating that the network is weaker  
304 or in lower three-dimensionality than fused pure silica glass (Kamiya et al. 2000). The  
305 band at  $\sim 1175 \text{ cm}^{-1}$ , responsible for a shoulder in the main  $1069 \text{ cm}^{-1}$  band, may also be  
306 attributed to  $\nu_{\text{as}}(\text{Si-O})$  (Anbalagan et al. 2010).

307 According to Drees et al. (1989), the intensity of the  $965 \text{ cm}^{-1}$  band decreases from  
308 opal-A to more crystalline silica polymorphs, such as opal-CT and quartz. In the  
309 spectrum of opal-A, the band is due to  $\nu(\text{Si-O})$  of Si-OH groups (Hiro and Sato 1971),  
310 and the band intensity weakens as the Si-OH groups condense to form Si-O-Si bonds  
311 (Moenke 1974). In Fig 8a,b, this band in the opal-A specimen is visible in the spectrum  
312 as an inflexion superposed on the lower side of the main band. A similar Si-OH band,  
313  $\sim 965 \text{ cm}^{-1}$ , is also observed in water-containing amorphous silica, as silica gel, which  
314 may remain (although subdued) even when the sample is heated to relatively high  
315 temperatures (up to  $400 \text{ }^\circ\text{C}$ , or – depending on the cases – even  $800 - 1000 \text{ }^\circ\text{C}$ )  
316 (Huffman and McMillan 1985; Perry et al. 1991; Uchino et al. 1991).

317 Both the calcium and water content of the Dallas fulgurite may contribute to the  
318 spectral features observed in the  $400\text{-}1500 \text{ cm}^{-1}$  region.

319 A broad band is centered at  $\sim 3400\text{ cm}^{-1}$  in the fulgurite spectrum and, together with  
320 features at 2000, 1880 and  $1631\text{ cm}^{-1}$ , indicates the presence of OH groups and/or  
321 bound  $\text{H}_2\text{O}$  (see Table 3 for specific band assignments).

322 The bands at 2358, 2855, 2926 and  $2961\text{ cm}^{-1}$  (Fig 8*a,c*; Table 3) are due to C-H  
323 stretching vibrations (Ganesh Kumar et al. 2014; Garai et al. 2006), which indicates the  
324 presence of organic matter.

325

#### 326 **4.5. Raman spectroscopic studies**

327 The Dallas fulgurite Raman spectrum (Fig 9), in the region up to  $1250\text{ cm}^{-1}$ , is  
328 dominated by two broad bands, centered at  $\sim 480$  and  $1014\text{ cm}^{-1}$ , typical of glassy  
329 silicate materials. The intense band at  $\sim 480\text{ cm}^{-1}$ , with the presence of additional weaker  
330 bands, is assigned to the twisting ( $\tau(\text{Si-O-Si})$ ) and bending ( $\delta(\text{Si-O-Si})$ ) modes of the  
331  $\text{SiO}_4$  tetrahedral units. Bands in the high wavenumber region –  $800$  and  $1014\text{ cm}^{-1}$  – are  
332 associated with  $\nu_s(\text{Si-O})$  of silica tetrahedra with one to four non-bridging oxygen atoms  
333 (Carter et al. 2010a; Colomban and Slodczyk 2009; White and Minser 1984). Figure 9  
334 presents the Raman spectra of the fulgurite together with the RRUFF database spectra  
335 of quartz and opal-A. The width of the  $\sim 480\text{ cm}^{-1}$  band is broader in the fulgurite  
336 spectrum than the corresponding band in the spectrum of quartz and opal-A, indicating  
337 that the fulgurite has a markedly amorphous character. The fulgurite's chemical  
338 analyses showed that its composition was mainly silica with high  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$   
339 content, which is likely linked to the presence of the two strong broad bands observable  
340 in the fulgurite's Raman spectrum.

341 The Raman spectrum of the fulgurite in the spectral range  $300\text{-}1250\text{ cm}^{-1}$  resembles  
342 results collected from a Ca-based glaze reported by Colomban (2005). In this work,  
343 within the high wavenumber region, spectral deconvolution revealed four bands

344 corresponding to four, three, two, one/zero non-bridging oxygen atoms per silica  
345 tetrahedra, at increasing Raman shift values. The position of the band attributed to the  
346 four non-bridging oxygen atoms was observed in the range of  $\sim 800\text{-}850\text{ cm}^{-1}$ , similar to  
347 the position of the band at  $\sim 800\text{ cm}^{-1}$  in the fulgurite spectrum. Colomban (2005)  
348 measured the degree of polymerization by calculating the ratio of the area of the Si-O  
349 bending modes to the area of the Si-O stretching modes ( $I_p = A_{500}/A_{1000}$ ). For the Dallas  
350 fulgurite this value was  $I_p = 1.12$ , which is outside the 1.3–2.5 interval defined for Ca  
351 glasses (Colomban and Slodczyk 2009) (the implications of these results will be  
352 discussed in section 5).

353 Further insight on the Raman data of the Dallas fulgurite can be achieved by  
354 comparing results with data from an investigation of White and Minser (1984) on  
355 natural glasses, which includes experimental work on synthetic glasses. An increasing  
356  $\text{Na}_2\text{O}+\text{Al}_2\text{O}_3$  (1:1) to  $\text{SiO}_2$  ratio in soda-alumina-silica glasses was noted to influence  
357 the Raman spectrum, with the maximum of the mid-wavenumber region intense band  
358 shifting closer to  $500\text{ cm}^{-1}$  (from  $470 \rightarrow 489\text{ cm}^{-1}$ ); and two broad bands at 995 and  
359  $1095\text{ cm}^{-1}$  merging into a single band centered at  $998\text{ cm}^{-1}$ . The Raman spectrum of the  
360 Dallas fulgurite is quite similar to the Raman spectrum collected from synthetic glass  
361 with the highest  $\text{Na}_2\text{O}+\text{Al}_2\text{O}_3$  (1:1) to  $\text{SiO}_2$  ratio. Similar to what happens in the side-  
362 area context of igneous rocks, aluminum would contribute to polymerize three-  
363 dimensional frameworks within the glass. On the other hand, alkali ions would  
364 depolymerize the three-dimensional framework with the creation of non-bridging  
365 oxygen atoms. Alkaline-earth ions would have a similar effect to the alkali ones;  
366 additionally, when their content is high, they would originate phase separation into  
367 silica-rich and silica-poor regions, with less and more than the expected number of non-

368 bridging oxygen atoms, respectively. For this reason, silica-poor regions would have a  
369 high contribution to the observed spectra (White and Minser 1984; Winter 2010).

370 The Raman spectra of tektites and obsidians in White and Minser (1984)'s study  
371 show similar lineshapes in the 300-1250  $\text{cm}^{-1}$  region, with two broad bands at  $\sim 437$ - $467$   
372 and  $\sim 990$ - $1151$   $\text{cm}^{-1}$ , and a band of low intensity at  $\sim 800$   $\text{cm}^{-1}$ , which is also the pattern  
373 observed for the Raman spectrum collected from the Dallas fulgurite. However, unlike  
374 the latter, along with a high intensity mid-wavenumber band, they all show a rather low  
375 intensity high wavenumber band, thus indicating a highly polymerized three-  
376 dimensional framework structure. Two particular samples may be highlighted: an  
377 Apollo 16 lunar glass (with a 42.7% silica; high Fe, Mg and Ca; and low alkalis  
378 content) and a synthetic «basalt» glass without iron; both show a band at  $\sim 1000$   $\text{cm}^{-1}$   
379 stronger than the one at  $\sim 500$   $\text{cm}^{-1}$ , indicative of a high depolymerization degree. The  
380 Dallas fulgurite is intermediate between the two groups, closer to the latter than to the  
381 former, with a broad strong band at  $\sim 1014$   $\text{cm}^{-1}$ , albeit not as intense as the band at  $\sim 480$   
382  $\text{cm}^{-1}$ . White and Minser (1984)'s NBO/T (non-bridging oxygen to bulk composition)  
383 index for the fulgurite shows a value between 0.27 (considering all Fe as  $\text{Fe}_2\text{O}_3$ ), 0.32  
384 (1:1) and 0.37 (considering all Fe as FeO) (0.02-0.07 for the tektites and obsidians, a  
385 maximum of 0.62 for the lunar glass and 0.74 for the «basalt»).

386 The fulgurite's Raman spectrum in the 1250-4000  $\text{cm}^{-1}$  region (Fig 9a) is dominated  
387 by a massif with a double maximum at  $\sim 2060$   $\text{cm}^{-1}$  and  $\sim 3080$   $\text{cm}^{-1}$ , which likely  
388 includes weaker bands. In this region, it closely resembles the spectrum of an  
389 amorphous specimen of opal-A, as shown in Ostrooumov et al. (1999). A band at 1680  
390  $\text{cm}^{-1}$  (not evident in the fulgurite's rising curve) is associated with H-O-H vibration  
391 (McMillan and Remmele 1986), and the band at 3080  $\text{cm}^{-1}$  is typical of molecular  $\text{H}_2\text{O}$   
392 groups (Walrafen 1964).



393

## 394 **5. Overall discussion**

395 The Dallas exofulgurite chemical composition, see Table 1 and Table 2, indicates  
396 that it belongs to a specific group with normative diopside + wollastonite + titanite. Its  
397 high CaO content, together with silica and alumina, proved to have a role in its  
398 properties. XRPD confirmed its amorphous character, but delivered little more  
399 information. FTIR and Raman spectra were key in understanding the fulgurite's  
400 characteristics. The use of opal-A and silica glass (in a broad sense) as proxies, for  
401 which a wider amount of data is available, proved to be the second key in the study of  
402 the Dallas exofulgurite.

403 The FTIR spectrum revealed characteristic bands in the higher wavenumber region  
404 attributed to OH and/or H<sub>2</sub>O-related modes and in the lower wavenumber regions bands  
405 related to Si-O bending and stretching vibration modes in silica tetrahedra. The band at  
406 965 cm<sup>-1</sup> ( $\nu$ (Si-O) of isolated Si-OH groups), characteristic of lower crystallinity degree  
407 silica polymorphs, was more intense in the Dallas fulgurite than in the opal-A specimen  
408 in Fig 8, as well as in other cases in the literature; this 965 cm<sup>-1</sup> band is present as a  
409 shoulder on the main 1069 cm<sup>-1</sup> band, both reflecting the significant calcium content of  
410 the specimen. Thus, the shoulder at 965 cm<sup>-1</sup> very likely corresponds to the  
411 superposition effect of Ca content and the presence of Si-OH groups. The overall  
412 indications from the FTIR spectrum were in the direction of the existence of some  
413 short-range silica tetrahedra structuration with relevant depolymerization, and the  
414 presence of water (OH / H<sub>2</sub>O), possibly in significant amounts.

415 The exofulgurite Raman spectrum contained bands within two distinct regions: from  
416 100 cm<sup>-1</sup> to 1250 cm<sup>-1</sup> and from 1250 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The two strong broad bands  
417 centered ~480 cm<sup>-1</sup> and ~1014 cm<sup>-1</sup> are characteristic of glassy silicate materials, and

418 are followed by a very broad high-intensity double maximum OH / H<sub>2</sub>O related massif.  
419 Raman spectra results for opals show that an increase in the structural disorder in opals  
420 is accompanied by a broadening and reduction of the number of bands, and a  
421 considerable increase in the intensity and width of OH and H<sub>2</sub>O related bands  
422 (Ostrooumov et al. 1999). By opal standards, the Raman spectrum of the exofulgurite in  
423 Fig 9 was indicative of a highly disordered material.

424 The fundamental factor was the possibility to evaluate the exofulgurite's  
425 depolymerization degree, from Raman data, on the basis that the Si-O  
426 bending/stretching modes are separately associated with the ~480 cm<sup>-1</sup>/~1014 cm<sup>-1</sup>  
427 massifs, the latter being related to the presence of non-bridging oxygen atoms in a  
428 material structure. The NBO/T index value for the fulgurite is in the range 0.27 to 0.37  
429 (the role of iron being unclear); in any case significantly above values for tektites and  
430 obsidians (0.02 to 0.07), a higher value indicating higher depolymerization.  
431 Additionally, the I<sub>p</sub> index value is low (I<sub>p</sub> = 1.12), below the 1.3 lower limit defined for  
432 Ca glasses (a lower value indicating higher depolymerization). The NBO/T index is set  
433 on the basis of the mole content for major component oxides; the I<sub>p</sub> index is calculated  
434 by determining the ratio of the areas under the ~500 cm<sup>-1</sup>/~1000 cm<sup>-1</sup> bands. Moreover,  
435 data from the fulgurite's FTIR and Raman spectra between 1250 and 4000 cm<sup>-1</sup>  
436 revealed the existence of an important water (OH/H<sub>2</sub>O) content (by opal standards).  
437 Strong indications in this direction came also from the highly vesicular character of the  
438 fulgurite's sample, as revealed by hand-specimen and optical microscope observation,  
439 as well as SEM images, indicative of an important volatile phase, and entirely  
440 compatible with a high water content near the soil surface during a thunderstorm.

441 OH groups and molecular water have a depolymerization effect that is not taken into  
442 account in the NBO/T index. The 1014 cm<sup>-1</sup> massif in Raman spectra is partly due to the

443 high CaO fulgurite's content; but a strong contribution most likely comes from OH  
444 groups and molecular water content. This would also explain the low  $I_p$  index value,  
445 below the 1.3-2.5 interval for Ca glasses. And, if the water effect was taken into  
446 account, the exofulgurite's NBO/T index should be higher, closer to the lunar Apollo 16  
447 sample maximum value of 0.62.

448 In the broader context of telluric planets, depolymerization of the silicate melts could  
449 also result from the solution of methane, associated with the formation of OH-groups, or  
450 from the solution of carbon monoxide (Eggler and Baker 1982; Mysen and Richet 2005;  
451 Taylor 1987). As an example, this could be interesting in the case of Titan, in which  
452 there would possibly be lightning strikes in combination with  $CH_4$ , both as gas in the  
453 atmosphere and in liquid form on the surface (Hörst 2017).

454 Some weak peaks in the exofulgurite's FTIR spectrum are indicative of the presence  
455 of C-H bonds. The presence of carbon compounds in the sample is not unlikely, owing  
456 to the presence of organic matter in the soil from which the exofulgurite originated. In  
457 this respect, the presence of organic matter in fulgurites has also been reported by Elmi  
458 et al. (2017), who found bands suggestive of polyaromatic hydrocarbon molecules  
459 (cyclic alkenes) in the Raman spectra of the rock fulgurites from Mt. Mottarone  
460 (Piedmont, Italy), and by Carter et al. (2010b), who found polyaromatic hydrocarbons  
461 in a type-II fulgurite found in Greensboro (NC, USA).

462 A precise temperature value determination for the exofulgurite's formation is not  
463 possible. However, it can be constrained. The absence of flow textures, characteristic of  
464 lechatelierite formed at temperatures  $>2,200$  °C, is indicative that this temperature was  
465 not reached. In fact, the  $I_p$  index value of 1.12 suggests much lower temperatures.  
466 Colomban (2005) indicates values of ca. 1,400 °C for  $I_p \sim 7$ ; 1,000 °C for  $I_p \sim 1$ ; and ca.  
467 600 °C or less for  $I_p \sim 0.3$ . Experimental petrology data for a dacite-like composition

468 (which is not very far from the fulgurite's chemical composition) points towards a dry  
469 solidus and liquidus temperature at surface pressure of 970 °C and 1020 °C,  
470 respectively (Gill 2010). On the basis of all these values, a temperature formation of ca.  
471 1,000 °C, or lower, is likely for the exofulgurite (which applies particularly to  
472 solidification temperature). In this respect, a high water content contributes to lowering  
473 the fusion/solidification temperature of the material.

474

## 475 **6. Conclusion**

476 Fulgurites are formed under very particular circumstances, and the droplet-type  
477 Dallas exofulgurite originated in an even more particular way. Its mode of occurrence  
478 indicates that the fused target soil hit by the lightning strike was projected upwards into  
479 the air. The joint features of lightning strike origin, with an extremely rapid  
480 heating/fusion/solidification process, plus the exofulgurite's chemical composition  
481 (especially its CaO content), the high water content and – in particular – the high  
482 depolymerization degree of its structure make it unique. This last singular feature  
483 represents a clear difference in comparison with terrestrial tektites and obsidians. While,  
484 at this stage, a possible role of this high depolymerization degree of the fused silicate  
485 remains uncertain, the study of these natural glasses may serve as an analogue for  
486 telluric planetary studies in extreme environmental scenarios involving water, methane  
487 or carbon monoxide.

488

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492

493 **Conflict of interest statement**

494 The authors declare no conflict of interest.

495

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721 **FIGURE CAPTIONS**

722 **Fig 1** (a) Libyan “desert glasses” from Dakhleh Oasis and other sites in the Great Sand  
723 Sea at the Egyptian-Libyan border, originated from sand melted by a meteorite. (b)  
724 Fallout melt debris and aerodynamically-shaped glasses in beach sands of Motoujina,  
725 Hiroshima Bay, Japan, related to the nuclear explosion in 1945. Reproduced with  
726 permission from Wannier et al. (2019). (c,d) Assortment of backlit teardrops (Bunch et  
727 al. 2012) and a trinitite sample from Trinity site, Alamogordo, NM, USA, generated  
728 after the explosion of the first atomic bomb in 1945. (e) Glassy impactite with multiple  
729 accretionary nodules from Meteor Crater, near Winslow, Northern Arizona, USA (as  
730 part of the Younger Dryas cooling episode 12.9KYrBP) (Bunch et al. 2012). (f,g)  
731 Desert glass sample and glassified ceramic slag from Tall el-Hammam area, Jordan,  
732 resulting from the 3.7KYrBP Kikkar Event.

733 **Fig 2** (a) Exogenic fulgurite from Elko Hills, Elko County, NV, USA (size: 27×19×16  
734 mm; weight: 5.32 g) (Mohling 2004); (b) exogenic fulgurite from Oswego, Oswego  
735 County, NY, USA (Walter 2011); (c,d) droplet fulgurite with protuberances from  
736 Dallas, TX, USA. The space between two adjacent unit-and-value hatch marks in (c)  
737 represents a millimeter.

738 **Fig 3** Left: Mesquite area geologic map (data from U.S. Geological Survey (United  
739 States Geological Survey (USGS) 2014)); right: Geology of Texas map (The University  
740 of Texas at Austin. Bureau of Economic Geology 1992).

741 **Fig 4** Optical microphotographs (at 500× magnification) of the small spherical  
742 protuberances (1-2 mm diameter) on the surface of the droplet fulgurite: (a,b) adjacent  
743 light-halo craters on the surface of microprotuberance #1; (c) surface of  
744 microprotuberance #2; (d) nipple and scratches/stretch marks on microprotuberance #3.

745 **Fig 5** SEM micrographs of the surface of the microprotuberances on the exogenic  
746 fulgurite specimen. Operative conditions: (a) magnification=203X, acceleration  
747 voltage=15 kV, working distance=11 mm, probe current=44 pA, stage at Z=25 mm; (b)  
748 magnification=223X, acceleration voltage=15 kV, working distance=11.6 mm, probe  
749 current=10 pA, stage at Z=25 mm; (c) magnification=207X, acceleration voltage=15  
750 kV, working distance=10.5 mm, probe current=11 pA, stage at Z=25 mm.

751 **Fig 6** SEM-BSE image of a spherule from Abu Hureyra (product of Younger Dryas  
752 episode 12.9KYrBP) that shows high-temperature flow lines or *schlieren* (reproduced  
753 with permission from Bunch et al. (2012))

754 **Fig 7** X-ray powder diffraction pattern of the exogenic fulgurite from Dallas, TX, USA.

755 **Fig 8** FTIR spectrum of the exofulgurite specimen from Dallas, TX, USA (black solid  
756 line): (a) full spectral range; (b) 1600–400  $\text{cm}^{-1}$  region; (c) 4000-1400  $\text{cm}^{-1}$  region.

757 Spectra from quartz (dotted black line) and opal (dotted red line) are also shown for  
758 comparison purposes. The inset in (a) shows the bands in the 3100–2200  $\text{cm}^{-1}$  region in  
759 higher detail.

760 **Fig 9** Raman spectrum of the exofulgurite specimen from Dallas, TX, USA (black solid  
761 line): (a) full spectral range; (b) 100–1300  $\text{cm}^{-1}$  region. Spectra from quartz (dotted  
762 black line) and opal (dotted red line) are also shown for comparison purposes.



## TABLES

**Table 1.** Analysis of major and minor elements as oxides for the exogenic fulgurite sample from Dallas, TX, USA.

Oxide	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	SrO	Y <sub>2</sub> O <sub>3</sub>
XRF	62.43	0.89	11.41	8.21	0.25	0.86	14.09	0.34	1.35	0.16	-	-	-
XRF	64.83	0.58	16.30	3.70	0.14	1.15	11.78	0.36	1.09	0.02	0.047	0.026	0.012
EDX	69.72	-	18.10	-	-	1.90	8.58	-	1.69	-	-	-	-

**Table 2.** Bulk abundance (wt%) of major oxides in fulgurites from different origins.

Oxide	Dallas, TX, USA		York, PA, USA	Vernal, UT, USA	Greensboro, NC, USA	P° do Vasco, Viseu, Portugal		Tiedra, Valladolid, Spain		Mottarone, Baveno, Piedmont, Italy		“San José de Lourdes”, Zacatecas, México	
	Avg.	(min-max)				Avg.	(min-max)	Avg.	(min-max)	Avg.	(min-max)	core	cover
SiO <sub>2</sub>	63.63	(62.43-64.83)	55.49	67.60	81.30	68.93	(68.13-69.72)	61.45	(59.1-63.8)	73.90	(71.97-75.79)	60.84	71.83
TiO <sub>2</sub>	0.73	(0.58-0.89)	1.23	0.51	1.15	0.80	(0.77-0.83)	0.65	(0.5-0.8)	0.04	(0.03-0.05)	0.28	0.42
Al <sub>2</sub> O <sub>3</sub>	13.86	(11.41-16.30)	25.75	13.91	8.32	16.14	(15.97-16.30)	8.40	(8.1-8.7)	7.70	(7.54-7.79)	10.13	14.17
Fe <sub>2</sub> O <sub>3</sub> *	5.95	(3.70-8.21)	6.36	3.69	8.48			10.00	(9.4-10.6)			2.47	4.04
FeO*						3.09	(2.50-3.67)			0.38	(0.22-0.51)		
MnO	0.19	(0.14-0.25)	0.07	0.65	0.28	-		0.45	(0.4-0.5)	0.06	(0.02-0.10)	0.04	0.09
MgO	1.01	(0.86-1.15)	1.63	2.58	0.10	0.29	(0.19-0.39)	2.40	(2.0-2.8)	0.24	(0.20-0.26)	1.33	1.31
CaO	12.94	(11.78-14.09)	1.71	5.20	0.15	-		11.80	(10.5-13.1)	0.80	(0.75-0.83)	18.56	3.82
Na <sub>2</sub> O	0.35	(0.34-0.36)	0.75	3.74	0.04	3.40	(3.39-3.40)	-	-	0.05	(0.04-0.07)	0.47	0.85
K <sub>2</sub> O	1.22	(1.09-1.35)	4.35	2.92	0.18	7.43	(7.30-7.56)	3.90	(3.3-4.5)	0.20	(0.12-0.28)	2.80	3.35
P <sub>2</sub> O <sub>5</sub>	0.09	(0.02-0.16)	0.08	0.76	0.01	-		0.70	(0.5-0.9)	0.25	(0.07-0.50)	0.07	0.07
Total	99.97		97.42	101.56	100.01	100.08		99.75		83.61		96.99	99.95
Ref.	This work		(Pasek et al. 2012)		(Carter et al. 2010a)	(Abrunhosa et al. 1995)		(Martín-Ramos et al. 2019)		(Elmi et al. 2017)		(Reyes-Salas et al. 2017)	
<b>CIPW Norm (wt %)</b>													
<i>q</i> **	34.57		28.61	29.30	79.94	25.15		28.88		71.14		21.89	44.12
<i>an</i>	32.62		7.96	3.52	0.68					2.34		17.26	18.49
<i>ab</i>	2.96		6.35	31.65	1.34	23.95		11.40		0.42		3.98	7.19
<i>or</i>	7.21		25.71	17.26	1.06	43.85		23.05		1.18		16.55	19.80
<i>c</i>			16.89	3.31	7.81	2.75				6.55			2.37
<i>di</i>	5.70							12.90				7.15	
<i>hy</i>			4.06	6.43	0.25	0.82				1.34			3.26

<i>wo</i>	9.11					10.66		26.87	
<i>ru</i>		1.15		0.83	0.47				0.32
<i>il</i>	0.41	0.15	0.97	0.60		1.07	0.08		0.19
<i>mt</i>			0.64						
<i>hm</i>	5.95	6.36	3.25	8.48	3.09	10.00		2.47	4.04
<i>ap</i>	0.21	0.19	1.76	0.02		1.62	0.58	0.16	0.16
<i>tn</i>	1.27					0.34		0.58	

\* Fe<sub>2</sub>O<sub>3</sub>(total) and FeO(total)

\*\* *q, an, ab, or, c, di, hy, wo, ru, il, mt, hm, ap* and *tn* stand for quartz, anortite, albite, orthoclase, corundum, diopside, hypersthene, wollastonite, rutile, ilmenite, magnetite, hematite, apatite and titanite, respectively (Cross et al. 1912). Cells highlighted in green and yellow indicate fulgurites belonging to the normative corundum + hypersthene group and to the diopside + wollastonite + titanite group, respectively.

**Table 3.** Main bands in FTIR and Raman spectra (in  $\text{cm}^{-1}$ ) and their assignments for the exogenic fulgurite sample from Dallas, together with some proxies used for comparison purposes.

Spectroscopic technique	Fulgurite	Opal-A*	Pure silica glass	Calcium aluminosilicate glass	Assignment	
FTIR		3640–3650			Isolated silanol group vibrations	
		3400	3410/3421		$\nu_{\text{as}}(\text{O-H})$ , H-bound Si–OH	
			3230–3250		Stretching modes of liquid water (physisorbed $\text{H}_2\text{O}$ )	
		2961 (w)			$\nu_{\text{as}}(\text{C-H})$ of $-\text{CH}_3$	
		2926 (w)			$\nu_{\text{as}}(\text{C-H})$ of $>\text{CH}_2$	
		2855 (w)			$\nu_{\text{s}}(\text{C-H})$ of $>\text{CH}_2$	
		2358 (w)			$\delta(\text{Al-OH})+\nu(\text{O-H}) / \nu(\text{O=C=O})$ , $\text{CO}_2$	
		2000	1996/2007		$\text{H}_2\text{O}$ , $\text{OH}^-$ overtone vibration	
		1880	1880/1883			
		1631	1631/1636		$\delta(\text{H-O-H})$	
		1175			$\nu(\text{Si-O})$	
		1069	1061	1110	1065	$\nu_{\text{as}}(\text{Si-O})$
		965	965		960	$\nu(\text{Si-O})$ , isolated Si–OH and/or $(\text{Si}(\text{OA1}/\text{Ca})_2)$
		784	793	805	780	$\nu_{\text{s}}(\text{Si-O})$
		460	453	452–468	464	$\delta(\text{O-Si-O})$
Raman	235					
	480	463.5			$\tau(\text{Si-O-Si})$ and $\delta(\text{Si-O-Si})$	
	800					
	1014	962			$\nu_{\text{s}}(\text{Si-O})$ , silica tetrahedra	
		1066				
		2060				
	3080				$\nu(\text{O-H})$ , molecular $\text{H}_2\text{O}$ groups	

\* (Adamo et al. 2010; Aines and Rossman 1984; Eckert et al. 2015; Gemological Institute of America 2020; Ilieva et al. 2007; Langer and Floerke 1974)























