A Raman spectroscopic study of a fulgurite

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A Raman microspectroscopic study of several fulgurites has been undertaken. A fulgurite is an amorphous mineraloid, a superheated glassy solid that is formed when a lightning bolt hits a sandy or rocky ground and thermal energy is transferred. The Raman spectra revealed several forms of crystalline and fused silica and also the presence of polyaromatic hydrocarbons found in an interfacial zone of a glass bubble. This, together with the presence of anatase, a low-temperature polymorph of TiO2, suggested that some regions of the fulgurite specimen were not subjected to temperatures of 1800°C, which are attained when lightning hits the surface of sand or a rock.

Keywords: Raman spectroscopy; fulgurite; lechatelierite; polyaromatic hydrocarbons; shocked quartz; anatase

1. Introduction

There are several terrestrial phenomena that result in the formation of glassy geological materials (Rakov 1999), including air-to-ground lightning strikes (about 30% of the lightning discharges that occur), volcanic eruptions, meteorite impacts and nuclear explosions. The glassy formation on rocks at, or near, the summit of mountains has also been attributed to lightning strikes and is termed exogenic fulgurite. When a lightning bolt hits the surface of sand or a rock, a large amount of thermal energy exchange estimated at up to 1 GJ is transferred, with peak temperatures of 30,000°C in the air and attaining 1800°C in the superheated rock matrix (Uman 1964; Krider & Dawson 1968). The resulting fusion of the siliceous components of the rock and sand forms a fragile hollow tube in which often a glassy froth is found containing bubbles of entrapped air and gases from the surrounding area (Jones et al. 2005). The phenomenon was first reported

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by Herman in 1706 (Rakov 2008), who recognized two forms of the amorphous, mineraloid fulgurite (Lat. fulgur, lightning), also referred to as lightning stone, petrified lightning or lechatelierite.

The formation of fulgurites is accompanied by mineralogical and sometimes compositional changes, and may record information about the environment in which they were formed. Fulgurite specimens from a sand strike in South Amboy, NJ, USA, were analysed using wet chemical methods by Myers & Peck (1925), who determined that the three main chemical components were silica, comprising 99 per cent of the geological material, with alumina and iron oxide the remaining 1 per cent. The existence of glassy regions in the fulgurite specimens was observed and a refractive index measurement of 1.462 ± 0.003 was reported to be typical of fused silica. It was suggested that the silica component comprised of fused quartz, and cristobalite and possibly mullite, a mineral containing alumina and silica in the ratio of 3 : 2. Essene & Fisher (1986) investigated a fulgurite from Winans Lake, MI, USA, finding iron silicides and native silicon in the glassy matrix, which resulted from extreme reduction of the starting material. Navarro-Gonzalez et al. (2007) analysed a fulgurite specimen collected from the Libyan Desert, which was dated using thermoluminescence measurements up to 15 kya. Analysis of gas bubbles trapped within glassy regions reveal the presence of carbon dioxide, carbon monoxide and nitric oxide, which were related to the palaeoclimate in this region of the Sahara at that time. Recently, Pasek & Block (2009) reported reduction of phosphate in fulgurites to phosphites and phosphides, suggesting that lightning may play a role in the global P biogeochemical cycle.

Raman spectroscopy is a non-destructive analytical technique that has been used to investigate a range of glassy geological materials including obsidian (White & Minser 1984; Bellot-Gurlet et al. 2004; Shimoda et al. 2004; Arias et al. 2006; Di Muro et al. 2006; Carter et al. 2008), tektites (White & Minser 1984; Faulques et al. 2001; Wondraczek et al. 2003) and fulgurites (White & Minser 1984; Champagnon et al. 1997). The Raman spectra of glassy silicate materials are characterized by a number of broad features that reflect the connectivity of the SiO$_4$ polymeric units within the three-dimensional framework of the silicate structure. In the low-wavenumber region (600–400 cm$^{-1}$), bands arise from the twisting and bending modes of the Si–O–Si bonds within the tetrahedral units, and at higher wavenumbers (1250–800 cm$^{-1}$), the bands originate from symmetric Si–O stretching modes (White & Minser 1984). In addition, it has been shown that the ratio of the areas under the broad bending and stretching bands centred at approximately 500 and 1000 cm$^{-1}$ ($A_{500}/A_{1000}$) can be used to elucidate glass nanostructure, composition, as well as temperature of formation. Typical values of this ratio, also known as the polymerization index ($I_p$), range from approximately 7 to 0.3 and are obtained from glasses formed at temperatures ranging from approximately 1400–600°C or less, respectively (Colomban 2000, 2001; Colomban & Slodczyk 2009).

The aim of this work is to use Raman spectroscopy to investigate a number of individual fulgurite fragments that originated from the one specimen. The characterization of these types of natural materials is of fundamental importance in order to understand the mineralogical and compositional information contained within these geological markers of palaeoclimatic conditions.
2. Experimental

(a) Fulgurite samples

Four individual pieces of a fulgurite from Greensboro, NC, USA, were collected for molecular spectroscopic analysis; each comprising dark heterogeneous glassy material containing several white and greyish-brown areas (figure 1). Optical microscopy revealed that the black glassy areas contain spherical bubbles with inclusions. This fulgurite was found in a red-brown clayey soil, which is classified as an ultisol by the United States Department of Agriculture soil taxonomy. Organic materials, such as roots and leaf debris, were present throughout the topsoil. The total mass of the fulgurite was estimated to be greater than 20 kg, with two to three pieces greater than 1 kg in mass, and over 50 individual pieces recovered. On the basis of its physical attributes, it was classified as a type II fulgurite by Pasek & Block (2009).

(b) Elemental analysis

A 2 g specimen of the fulgurite was crushed and powdered for analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine Al, Fe, Mg, Ca, P, Sr, Ti, Na, K, Mn, Cr, Ba, Zr, Y and Si abundances. A 0.2 g sample of the powdered fulgurite was mixed with 0.8 g of LiBO2 flux in a graphite crucible. The sample was then fused at 1050°C for 15 min, and the resulting glass bead was dissolved in 50 ml of 10 per cent HNO3 solution with a Ge standard. A 2.5 ml aliquot of the sample solution was diluted again into a 47.5 ml 10 per cent HNO3 solution, then analysed using a Perkin–Elmer 2000DV optical emission spectrometer. The sample was calibrated and compared with samples of certified United States Geological Survey and Japanese Geological Survey standards G-2, JA-2, GS-N, JR-1, JG-2 and JG-3. These samples represent bulk compositions of the fulgurites, including glassy interior and grey fusion crust.

(c) Raman spectroscopy

Spectra were collected using a Renishaw Raman inVia Reflex Microscope (Renishaw plc, Wotton-under-Edge, UK), equipped with an air-cooled charge-coupled device camera. The spectrometer is fitted with holographic notch filters and two gratings (1200 mm per line (visible), 2400 mm per line (near infrared)). The attached microscope is a Leica DM LM and is equipped with three objectives (×50/0.75 NA, ×20/0.40 NA, ×5/0.12 NA) and a trinocular viewer that accommodates a video camera, allowing direct viewing of the sample.

Sample excitation was achieved using an Argon ion laser (Modu-Laser, UT, USA) emitting at 514.5 nm. Daily calibration of the wavenumber axis is required and is achieved by recording the Raman spectrum of silicon (one accumulation, 10 s) for both static and extended modes. If necessary, an offset correction is performed to ensure that the position of the silicon band is 520.50 ± 0.10 cm⁻¹. Spectra were not corrected for instrument response. The spectrometer was controlled using a PC with instrument control software (Renishaw WiRE 2.0 Service Pack 9).
Multiple regions within a sample were investigated with a minimum of three spectra collected within each region. Spectra were collected using a 50× objective, with a 10 s exposure time using the extended collection mode and an accumulation number varying between 1 and 10 depending on the signal-to-noise ratio of the data. The laser power at the sample varied, and was approximately between 1 and 2 mW.
3. Results and discussion

Figure 1 presents a photograph of the cross-sectioned fulgurite specimen, which is composed of dark heterogeneous glassy material containing several white and greyish-brown regions. The elemental composition as determined by ICP-OES is presented in Table 1. The fulgurite has low abundances of Na, K, P, Ca, and Mg, and relatively high abundances of Si, Fe, Al, and Ti. These abundances are consistent with the composition of the target material of the fulgurite, a soil formed from a weathered Mesozoic diabase intrusion. The compositional and mineralogical data reported here are the first for a fulgurite formed primarily of SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$ and TiO$_2$ oxides.

The Raman spectra of glassy silicate materials are characterized by a number of broad features that reflect the multiple coordination of Si–O bonds. Colomban (2000, 2001) has described this complex picture in an elegant way, invoking several types of chain, sheet and three-dimensional structures labelled Q$^0$–Q$^4$, which can be assigned as follows: Q$^0$, representing monomer SiO$_4$ units, with bands in the region 850–800 cm$^{-1}$; Q$^1$, representing Si$_2$O$_7$ groups, with a band near 950 cm$^{-1}$; Q$^2$, silicate chains with bands in the region of 1100–1050 cm$^{-1}$; Q$^3$, silicate sheets with a band near 1100 cm$^{-1}$; and Q$^4$, representing SiO$_2$ and tectosilicates with a band in the range of 1250–1150 cm$^{-1}$. Additionally, spectral features may arise from crystalline quartz and its modifications caused by pressure or temperature extremes, for which the parent Si=O band occurs at 465 cm$^{-1}$ (Jayaraman et al. 1987; McMillan et al. 1992; Schmidt & Ziemann 2000; Enami et al. 2007).

Figure 2 presents a typical spectrum collected from a glass bubble within a fulgurite specimen. The spectrum consists of a number of broad features arising from the silicate vibrations described above, with the dominant band at approximately 440 cm$^{-1}$ being assigned to the bending Si–O modes. The inset is an expansion of the 1400–700 cm$^{-1}$ spectral region and contains broad features centred at approximately 1188, 1057, 930, and 796 cm$^{-1}$. These bands are attributed to the symmetric Si–O stretching modes, and the positions are characteristic of tetrahedral units with four, three, one and zero bridging oxygen atoms, respectively. The polymerization index was used to estimate the glass formation temperature, which was greater than 1400$^\circ$C ($I_p \sim 10$) for this particular region of the sample (Colomban 2000).

Several spectra indicate the presence of crystalline regions within the fulgurite matrix with an intense Raman band at approximately 464 cm$^{-1}$ ($A_1$ mode) indicative of α-quartz. Figure 3 presents the spectra collected from within a glass bubble, with the inset showing an expansion of the Si–O bending region from 490 to 430 cm$^{-1}$. Of particular note is the shift in the position of the $A_1$ modes from 464 to 460 cm$^{-1}$, 354 to 355 cm$^{-1}$ and 204 to 189 cm$^{-1}$. A shift is also observed in the $E$ modes from 127 to 123 cm$^{-1}$ and from 1159 to 1162 cm$^{-1}$ (data not shown). This phenomenon has been reported in the Raman spectra of shocked crystalline quartz. The shifts observed in Figure 3 are consistent with the shocked quartz subjected to shock pressures of between 22 and 30 GPa (McMillan et al. 1992).

In one of the specimens (specimen (d), figure 1) an interfacial zone of a dark glassy bubble was found to yield a series of Raman spectra, which bore no resemblance to any of the spectra obtained from the glass and the surrounding matrix. This area was sampled at several points, and these spectra are shown in Figure 4. A series of sharp Raman bands are observed within three spectral

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Figure 2. A representative Raman spectrum of the fulgurite matrix exhibiting the characteristic vibrational modes of silicates.

Table 1. Bulk abundances (wt%) of major oxides in the fulgurite. Abundances are normalized to 100 wt%.

<table>
<thead>
<tr>
<th>oxide</th>
<th>bulk abundance (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>81.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.32</td>
</tr>
<tr>
<td>Fe₂O₃(total)</td>
<td>8.48</td>
</tr>
<tr>
<td>MnO</td>
<td>0.28</td>
</tr>
<tr>
<td>MgO</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.04</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.18</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.01</td>
</tr>
</tbody>
</table>

regions, namely 1650–1500 cm⁻¹, 1300–1000 cm⁻¹ and 420–300 cm⁻¹; these are superimposed upon a number of much weaker, broader Raman bands, which can be attributed to the glassy matrix in which the inclusion is contained.

The spectra can be broadly assigned to polyaromatic hydrocarbons (PAHs), where the higher wavenumber bands arise from C=C modes, those in the mid-wavenumber region arise from C–C and aromatic rings, and those in the low-wavenumber region can be associated with ring-deformation modes.
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Figure 3. Raman spectra collected from several regions within a fulgurite containing crystalline \(\alpha\)-quartz. The shifts in the various vibrational modes are indicative of shocked quartz subjected to shock pressures ranging from 22 to 30 GPa.

Figure 4. (a,b) Raman spectra collected from an interfacial zone of a dark glass bubble in a fulgurite (specimen (d), figure 1) containing a region attributed to organic material. The spectra exhibit features that are attributable to PAHs superimposed on broad glassy matrix bands.
Figure 5. Raman spectra collect from inclusion areas within the fulgurite glassy matrix showing the presence of (a) quartz and PAHs; (b) anatase.

(Frank et al. 2007). It is relevant to consider the origin of this carbonaceous inclusion in the glassy fulgurite matrix. The lightning bolt impacting upon a ground target would be expected to carbonize any organic material residues, and it is not unrealistic to presume that small amounts of carbonized material could be trapped within the glassy matrix. An important point to consider in this context is that the polyaromatic material is actually trapped within the interfacial zone of a glass bubble. This removes the possibility of extraneous contamination issues that could otherwise have arisen if, for example, the identification had been made in an external crust of the specimen. In addition, it is proposed that the temperature of glass formation is lower than anticipated within this region of the fulgurite specimen, as is evidenced by the spectra presented in figure 5.

Figure 5a is a spectrum that reveals the heterogeneous character of the fulgurite sample. The spectrum has the combined features of a PAH, together with some weak amorphous glass bands on which is superimposed a very intense $A_1$ mode of $\alpha$-quartz at 464 cm$^{-1}$. The existence of the PAH in the vicinity of amorphous glass implies that a temperature gradient was present within the sample during its formation. The characteristic spectrum of anatase with bands at 639, 512, 296 and 142 cm$^{-1}$, as seen in figure 5b, provides more compelling evidence to support this proposed temperature gradient. Anatase is one of the three polymorphs of TiO$_2$ that transforms from anatase to rutile at temperatures within the range of 1100–800°C (Coloban & Mazerolles 1990; Kim et al. 1998). This phase transition can be influenced by a number of factors including the heating rate, size of TiO$_2$ particles and presence of other materials within the sample (Zhang & Banfield 2000). Finding anatase within the fulgurite specimen provides further evidence to suggest that the temperature of
the glass formation was lower in some regions within the sample than the reported 1800°C attained, when lightning hits the surface of sand or a rock (Uman 1964; Krider & Dawson 1968).

Daly et al. (1993) previously reported fullerenes in a fulgurite, though the pathway of fullerenes production could not be definitively linked to the fulgurite formation process (Heymann et al. 2003). Graphite has also been observed in fulgurite glasses, presumably resulting from the reduction of organic compounds in the precursor soil (Essene & Fisher 1986). A previous study investigating the gases in a bubble inside a fulgurite reports finding carbon dioxide and carbon monoxide, the origin of these gases were attributed to the plant matter at the point of a lightning strike (Navarro-Gonzalez et al. 2007). Similarly, Steele et al. (2006) have reported that they identified polyaromatic compounds from a glassy region of the Shergottite, Nakhtie, Chassignite Martian meteorite Alan Hills 84001 and from a volcanic basalt specimen from the Svalbard Arctic Mars analogue site.

Clearly, the presence of polyaromatics, albeit unidentified on a molecular basis, in a meteorite and a volcanic glass (Steele et al. 2006) lends credence to the assertion that PAHs could also have survived the thermal shock of a terrestrial lightning strike. This is the first observation, as far as we can ascertain, of the non-destructive detection, identification and location of organic material incorporated into the matrix of a fulgurite.

4. Conclusions

In this study, we report a molecular spectroscopic study of the composition of a fulgurite and reveal novel information about these little-understood geological markers of palaeoclimatic conditions. A non-destructive, non-invasive protocol has been used to determine the composition of a geological material modified by biological colonization, with the creation of novel geobiological compounds at the surface and subsurface, and especially at quartz crystal interfaces in the body of the rock at the microscopic level.

The Raman spectra collected from these fulgurites have produced some interesting findings, including the presence of PAHs together with anatase, a polymorph of titanium oxide that converts to rutile at temperatures greater than 1100–800°C. This suggests that the fulgurite sample was subjected to a range of temperatures during formation. In addition, Raman spectra collected from various areas within the fulgurite resembled the spectra of shocked crystalline quartz, and shifts in numerous bands indicated that these crystalline regions are subjected to shocked pressures ranging between 22 and 30 GPa.

The implications of this discovery for extraterrestrial and planetary exploration are also far reaching. Astrophysicists and astrobiologists have postulated that violent electric storms would have been a major feature of the evolutionary development of planets and their satellites and that these can now be still observed, for example, on Titan. The preservation of an early record of organic material inside glasses synthesized in developing evolutionary systems from electric storms provide yet another novel example of an extreme environmental scenario that needs to be considered in an astrobiological context as well as a terrestrial one.

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