Paleoecology reconstruction from trapped gases in a fulgurite from the late Pleistocene of the Libyan Desert

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ABSTRACT

When lightning strikes the ground, it heats, melts, and fuses the sand in soils to form glass tubes known as fulgurites. We report here the composition of CO_2, CO, and NO contained within the glassy bubbles of a fulgurite from the Libyan Desert. The results show that the fulgurite formed when the ground contained 0.1 wt% organic carbon with a C/N ratio of 10–15 and a $\delta^{13}C$ of –13.96‰, compositions similar to those found in the present-day semiarid region of the Sahel, where the vegetation is dominated by C_4 plants. Thermoluminescence dating indicates that this fulgurite formed ~15 k.y. ago. These results imply that the semiarid Sahel (at 17°N) reached at least to 24°N at this time, and demonstrate that fulgurite gases and luminescence geochronology can be used in quantitative paleoecology.

Keywords: fulgurite, thermoluminescence, lightning, Libyan Desert, Sahel, paleoenvironment, Pleistocene.

INTRODUCTION

Atmospheric lightning is a transient high-current electric discharge that dissipates ~10^9 J per flash (Uman and Krider, 1989) and occurs at a rate of ~65 lightning flashes per second worldwide (Mackerras et al., 1998). The sudden flow of electrons during a lightning strike through the atmosphere results in a rapid heating of the air to peak temperatures near 30,000 K (Orville, 1968). In this process, nitric oxide (NO) is formed by a chain reaction according to the Zel'dovich mechanism (Zel'dovich and Raizer, 1966):

$$O_2 \leftrightarrows O + O,$$
$$O + N_2 \leftrightarrows NO + N,$$
$$N + O_2 \leftrightarrows NO + O.$$

The site where NO is actually formed has been debated: suggestions include inside the lightning channel (Hill, 1979; Navarro-González et al., 2001a), or within the shock wave (Chameides, 1979). Although NO has never been observed in situ in a lightning flash, it has been detected as a final product in laboratory simulated lightning (Wang et al., 1998), in the vicinity of a lightning flash below a thundercloud (Noxon, 1976), and inside a thundercloud (Stith et al., 1999). The production of NO by lightning is the major natural source of reactive nitrogen oxides ($NO_x = NO + NO_2$) in the atmosphere (Lawrence et al., 1995). NO_x plays an important role in the Earth's atmosphere-biosphere system. In the atmosphere, NO_x participates in many important photochemical reactions and exerts a controlling influence on the atmospheric ozone concentrations (Crutzen, 1970). In the biosphere, molecular nitrogen cannot be incorporated directly into biomolecules except for certain bacteria (Raven and Yin, 1998). Therefore, nitrogen fixation by lightning is a source of reactive nitrogen for organisms (Lawrence et al., 1995). Lightning may have played a major role in the origin (Miller and Urey, 1959) and early evolution of life on Earth (Navarro-González et al., 2001b). However, there is no direct evidence to show how the properties of lightning and its frequency may have varied with time. The occurrence of lightning in the past can be indirectly inferred from the finding of Late Triassic fossil charcoal, which may have been produced by natural wildfires triggered by lightning (Jones et al., 2002). The first evidence of an ancient lightning strike was the discovery of a fulgurite within sandstone (Harland and Hackler, 1966). The age of the fulgurite was speculated as Permian on the basis of the fossiliferous Carboniferous rocks overlying host sandstone. Similarly, the age of fulgurites collected in Niger, the southern Sahara, was estimated as late Pleistocene–middle Holocene, on the basis of the landscape history (Sponholz et al., 1993). However, direct dating of a fulgurite has not been reported until now. We present here the first detailed chemical analyses of trapped gases in a fulgurite that was instantaneously created when lightning struck the ground near the contemporaneous Libyan Desert, currently under the hyperarid Saharan climate.

GEOLOGIC AND CLIMATIC SETTING

The fulgurites for this study were collected in 1999 by an expedition to the Libyan Desert by Louis Carion (Carion Minerals, Paris). Figure 1 shows the approximate sampling location and the contemporaneous lightning density map for northeast Africa. The lightning data are from the Lightning Imaging Sensor (http://thunder.msfc.nasa.gov/research.html), a space-based instrument that monitors the distribution and variability of total lightning in the tropics. Figure 1 shows the absence of lightning activity in the core of the Libyan Desert. Lightning activity is currently confined to the north of the Libyan Desert on the Mediterranean Sea, and to its southern part in the Sahel region, increasing significantly to the south, where the tropical rain forest and humid savannas are found. This implies that the fulgurites from the core region

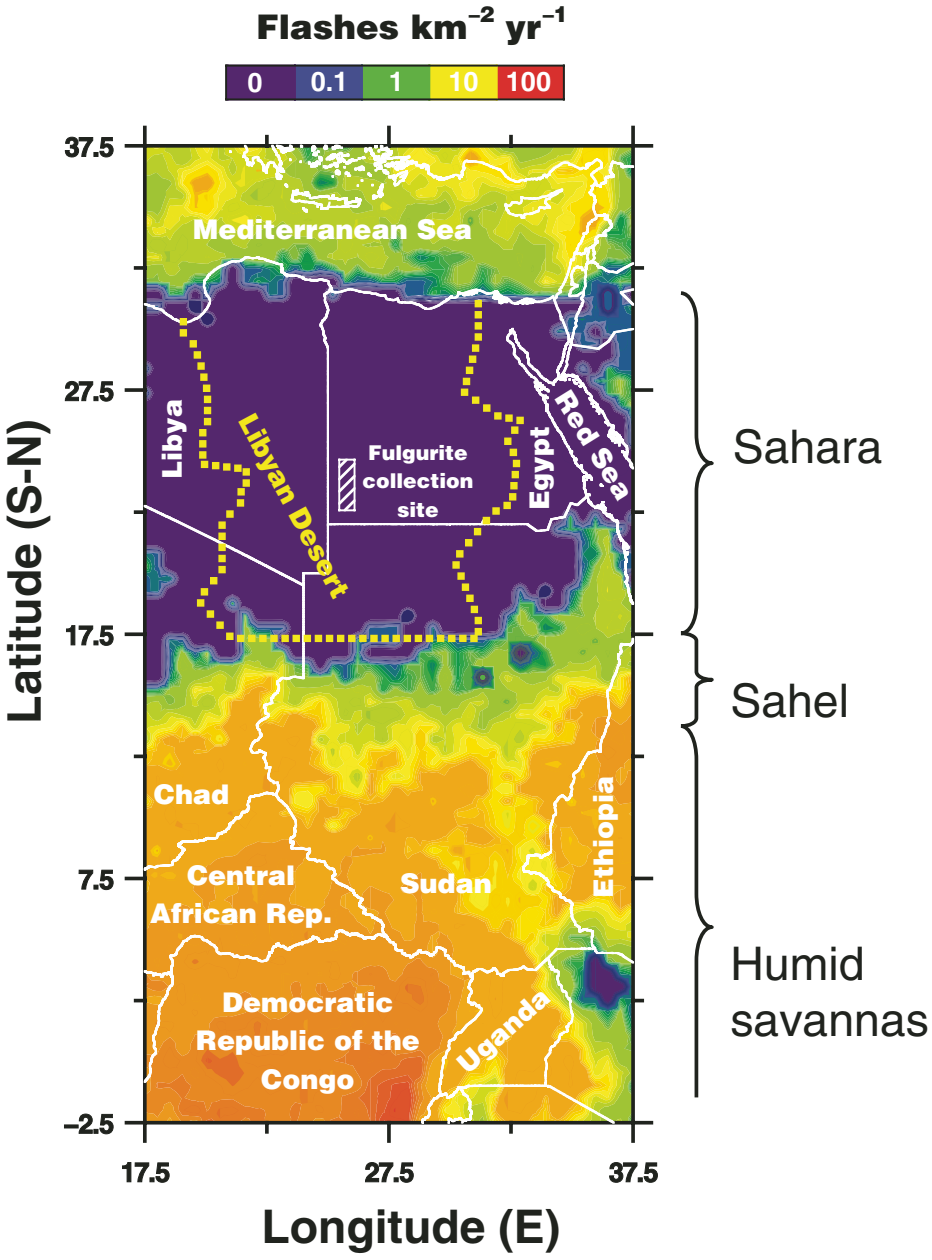

Figure 1. Contemporaneous lightning density in flashes per square kilometer per year is plotted for northeast Africa with 0.5° resolution. Lightning density was derived from average number of flashes detected per year between 1998 and 2005 in a 0.5° grid normalized to the fraction of Earth's area observed by the satellite per second (1.29×10^{-5}). From 1998 to 2005, 826,327 flashes were detected in this region.

of the Libyan Desert likely formed by thunderstorm activity under climatic conditions very different from the present.

CHEMICAL COMPOSITION OF FULGURITES

Figure 2 shows a cross section of a fulgurite rod ~3–4 cm in diameter, with thick walls and a narrow hollow center. The elemental composition as determined by X-ray fluorescence spectroscopy was 98.70% SiO_2, 0.65% Al_2O_3, 0.26% K_2O, 0.17% Fe_2O_3, 0.08% CaO, 0.07% Na_2O, ≤0.060% TiO_2, 0.02% MgO, and <0.005% P_2O_5 (see GSA Data Repository[1]). Scanning electron microscopy indicated that the fulgurite comprised silica (up to 98%) and 0.32%–0.20% Ca and K. A broad peak of SiO_2 in the X-ray diffraction spectrum indicated that the fulgurite

[1]GSA Data Repository item 2007039, materials and methods used in this study, is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

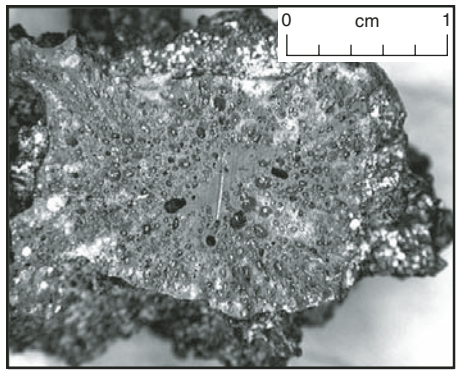

Figure 2. Cross section of fulgurite rod showing glass bubbles where gases are trapped.

was amorphous glass. Near the periphery and on the outside of the fulgurite, there were occasional scattered white grains resembling salt coating. These grains were determined to be a fine dust of quartz. Absence of a salt coating on the fulgurite implies no water or solute migration into the material since its formation.

ANALYSES OF THE TRAPPED GASES

The gases trapped in the glassy bubbles (Fig. 2) were released by breaking the glass walls using laser ablation under three different control atmospheres, and were analyzed using gas chromatography coupled to mass spectrometry. Table 1 summarizes the gases released under various conditions. For each atmospheric control setting, the experiments were replicated three times. In the presence of helium (He), the main gases released were carbon dioxide (CO_2), followed by carbon monoxide (CO) and NO, with traces of oxygen (O_2), methane (CH_4), hydrogen cyanide (HCN), and argon (Ar). In a reducing hydrogen atmosphere (H_2), the main gases released were CO, CO_2, formaldehyde (HCHO), and NO. In an oxidizing molecular oxygen atmosphere (O_2), the gases released were CO_2, followed by CO and NO.

The gases in the glass bubbles were chemically stable under normal environmental conditions and did not react with the silica of the fulgurite, having negligible diffusivities over glass below 430 °C and near atmospheric pressures (Mayer, 1915). These gases can remain in the glass structure for millions of years and thus provide insights into the chemical nature of the environment during their formation. Trapped gases in ancient glasses within 122 Ma basalts (Roberge et al., 2005) and glasses in 4500 Ma Martian meteorites have been documented (Pepin, 1985).

This paper reports the first observation of NO and other gases inside a lightning channel. The presence of NO in the glassy bubbles of a fulgurite supports the proposal that the NO formation occurs inside the lightning channel (Hill,

TABLE 1. TRAPPED GASES IN FULGURITE (WT%)*

Compound	Formula	Type of atmosphere used during ablation		
		He (wt%)	H_2 (wt%)	O_2 (wt%)
Carbon monoxide	CO	0.26	0.3	0.21
Carbon dioxide	CO2	1.09	0.28	1.5
Formaldehyde	HCHO	0	0.2	0
Oxygen	O_2	<0.02	<0.01	ND
Nitric oxide	NO	0.13	0.03	0.11
Methane	CH_4	<0.00001	<0.00001	<0.00001
Hydrogen cyanide	HCN	<0.00001	<0.00001	<0.00001
Argon	Ar	<0.01		

*Typical errors are <50%.
ND: Not determined

1979; Navarro-González et al., 2001a), and not in the shock wave (Chameides, 1979). The three ablation experiments indicate that the gas content in the fulgurite was ~1.3 ± 0.7 wt%. The puzzle is the source of these gases. Two possible scenarios are (1) atmospheric origin, and/or (2) volatile matter present in the soil at the time of the lightning strike. The detection of argon in the laser ablation experiment conducted in a helium atmosphere indicates the presence of trace levels of atmospheric gases. The expected ratio of CO_2/Ar in the atmosphere is 0.04; in contrast, the ratio of CO_2/Ar in the fulgurite gases is ≥109. Therefore, the source of these gases must be related to the volatile compounds present in the soil.

Because fulgurite comprises Si with very low Ca and Mg, it implies that little or no calcite or dolomite existed in the soil when fulgurite formed. Thus, the entire C content can be attributed to the soil organic matter, which was oxidized to CO_2 and CO during the lightning. The total C content is estimated to be ≈0.1%. The C/N ratio is 10 ≤ C/N ≤ 15, and C/O is ≈0.5. These values are comparable to current Sahelian soils on eolian sands from Niger with rainfall of 350–650 mm/yr (Wezel et al., 2000). In surface samples (0–10 cm) from southwestern Niger, the mean organic C content is ≈0.26%, similar to that found in the fulgurite. The C/N ratio in Niger soils is 12.

The $\delta^{13}C$ value of the carbon oxide species released by helium ablation was −13.96‰. This value is characteristic of organic matter following C_4 photosynthesis, and ranges from −9‰ to −17‰ with an average of −12‰ (Mariotti, 1991). C_4 plants have adapted to hot and arid zones of the Sahara-Arabian and/or Sudanian group. Under conditions of drought and high temperatures, C_4 plants have a competitive advantage over C_3 plants.

THERMODYNAMIC MODELING

Thermodynamic calculations were used to model the formation of a fulgurite glass with an initial chemical composition of 1 mol SiO_2, 0.3 mol H_2O, and 0.01 mol organic matter in the form of humic acid, with the elemental composition of $C_{12}O_8HN$ condensing from a hot vapor at 5500 K and 1 bar (Fig. 3). We used FactSage, a thermodynamic-based equilibrium speciation program (Bale et al., 2002). Humic acid was considered in the computations because it is a complex mixture of partially decomposed and otherwise transformed organic materials in the soil. As the gases and vapors cool down to 3100 K, liquid SiO_2 starts to form in the system. If the cooling rate of this system is sufficiently slow, liquid SiO_2 crystallizes into cristobalite at 1996 K, converts to tridymite at 1738.5 K, and to quartz at 1140 K. However, the fulgurite is principally amorphous silica and should have formed from rapidly quenched SiO_2. The freeze-out temperature of the fulgurite therefore should have been ~3100–2000 K. In this temperature range, carbon and nitrogen from the soil are thermodynamically locked as CO_2 and CO, and NO and N_2, respectively, and would have been trapped as such in the glassy structure of the fulgurite. The freeze-out temperatures of the fulgurites were very similar to that of NO inside the lightning channel in the atmosphere, estimated to be between 2700 and 2300 K (Navarro-González et al., 2001a). Therefore, our chemical studies also suggest that these fulgurites must have formed at a time when the soil in the region contained some organic matter (Fig. 3; Table 1).

CHEMICAL MECHANISMS OF GAS FORMATION

The CO_2/Ar ratio and the $\delta^{13}C$ data suggest that gases trapped in the fulgurites are not of atmospheric origin but are from the oxidation by water of the ambient soil organic during the lightening strike. Above 2400 K, the water molecules are decomposed to hydroxyl radicals and oxygen atoms, which then actively oxidize the organic molecules to generate carbon monoxide, carbon dioxide, and nitric oxide. Although the Zel'dovich mechanism (Zel'dovich and Raizer, 1966) does not account for the formation of NO in the fulgurite, it shows that under conditions that were likely to be present inside the lightning channel, the molecule is stable, and therefore supports the lightning channel mechanism for the formation of nitric oxide.

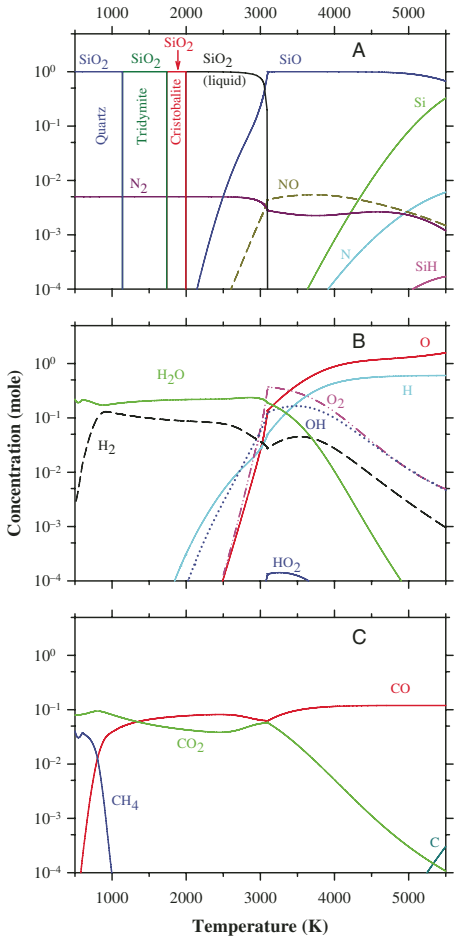

Figure 3. Thermodynamic model of simplified fulgurite composed of 1 mol SiO_2, 0.3 mol H_2O, and 0.01 mol organic matter ($C_{12}O_8HN$) at 1 bar pressure. A: Silicon and nitrogen species. B: Hydrogen and oxygen species. C: Carbon species.

AGE DETERMINATION

Because the fulgurites are mostly composed of silica, one approach to determine their age was to use thermoluminescence (TL) (Aitken, 1985, Singhvi and Wagner, 1986). This method uses the ability of quartz to serve as a sensitive radiation dosimeter of the natural radiation environment. The natural radiation environment arises from the decay of naturally occurring radionuclides, e.g., uranium, thorium, and potassium, along with a small contribution from cosmic rays. Irradiation causes ionization in the matrix and creates free charges, and some of these get trapped at lattice defects within the quartz crystal. The electronic configuration at some lattice defect sites ensures that charges in these defects reside over geological time scales. However, these are detrapped by a supply of external energy by using thermal or optical stimulation. Upon detrapping, the charges radiatively recombine to provide luminescence, the intensity of which is proportional to the radiation dose. In nature, the radiation dose is gener-

ally constant and the charges accumulate in a cumulative manner.

Thus, the ratio of the total luminescence (measured as paleodose in Grays [Gy]) to the annual radiation exposure (calculated using the concentration of radioelements as Gy/k.y.) provides the age. For fulgurites, the event dated is its formation. The multiple aliquot additive dose technique provided the paleodose. The annual radiation dose was based on the concentration of radioactive elements measured using instrumental neutron activation analysis. Given that the fulgurite formed via rapid cooling from 3100 to 2000 K, it can be assumed that the thermoluminescence of such a newly formed sample was ab initio zero. Two independent multiple aliquot age estimations using two different filter combinations transmitting in ultraviolet and blue windows yielded consistent ages of 14.3 ± 0.75 and 15.9 ± 1.59 ka, leading to an averaged approximate age of ca. 15 ka.

CONCLUSIONS

This is the first study in which trapped gases from a fulgurite were analyzed for their gas compositions and age. The presence of fulgurites in a region that today receives virtually no lightning indicates that lightning activity has changed at this location with time, and that lightning was common during the end of the late Pleistocene in the Libyan Desert region, where there was soil similar to current Sahelian sandy soils (i.e., 24°N). Our conclusions are consistent with literature on a wetter northern African climate ca. 15 ka (Hoelzmann et al., 1998), including a Sahara Desert that was almost covered by annual grasses and low shrubs, and the Sahel extending as far north as 23°N (Jolly et al., 1998; Kutzbach et al., 1996). This wet phase ended ca. 4.5–4 ka (Pachur and Altmann, 1997). These results also support the hypothesis that the dominant NO production is within the lightning channel. Our study reveals that the time of emplacement of the trapped gases in the fulgurites can be dated using TL. These analyses on fulgurites can thus be effectively used to quantitatively reconstruct the changes in African paleoecology

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