

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

Rafael Navarro-González, Shannon A. Mahan, Ashok K. Singhvi, Rafael Navarro-Aceves, Jean-Louis Rajot, Christopher P. McKay, Patrice Coll, and François Raulin

### **MATERIAL AND METHODS**

The fulgurite studied in this work was collected in the 1999 expedition to the Libyan Desert by Mr. Louis Carion (Carion Minerals, Paris). The sample was kept in a dark plastic bag within a dark room since collection.

**ELEMENTAL COMPOSITION.** The elemental composition of the fulgurite was determined by X-ray fluorescence spectroscopy and scanning electron microscopy. A small piece of fulgurite was broken and put in an ultrasonic bath with de-ionized water for 5 minutes to remove adhering soil and/or sand. The sample was then oven dried at 80°C and crushed in agate mortar. An aliquot of the powder was put in an ultrasonic bath with de-ionized water to ensure good dispersions of the powder. The suspension was then filtered on 0.4 µm polycarbonate filter. Three aliquots were analyzed directly on the filters for each sample. A blank was prepared by filtration of the same quantities of de-ionised water as used for samples filtration.

**ANALYSIS OF GASES.** A cross section of the fulgurite (about 2 cm thick) was mounted on a stainless steel plate and inserted into a Pyrex flask reactor equipped with 50mm O-ring seal joints and a high vacuum stopcock. The air inside the reactor was pumped out and the vacuum pressure was maintained at 0.001 mbar for two days to remove any gases and humidity absorbed in the fulgurite. Then the reactor was filled with a control atmosphere composed of either helium (99.9998%), oxygen (99.98%) or hydrogen

(99.9998%) to 1000 mbar and the system was allowed to equilibrate for 24 hrs. The procedure was repeated two times with the same atmosphere. Finally the reactor was filled to 600 mbar and the surface of the fulgurite was ablated with a pulsed Nd:YAG laser operating at 1064nm for 2 hrs to release the gases inside the glassy bubbles of the fulgurite. The gases released were quantitatively analyzed by gas chromatography using a PoraPlot Q fused-silica column (25 m long  $\times$  0.32 mm I.D. with a 2.5 m particle trap) coupled to electron impact mass spectrometry (MS) operating at 10-200 m/z with a scan rate of 4.4 scan/s at 70 eV. The column program temperature was isothermal at 60°C for 2 min, and then a rate of 10°C min<sup>-1</sup> up to 240°C, and finally isothermal for 35 min. The carrier gas used was helium with a flow of 1.2 ml min<sup>-1</sup>. After the gas analysis, the weight loss of the fulgurite was recorded by an analytical balance with a precision of 0.01 mg. Each atmosphere was run in triplicate and the experiment sequence was first helium, followed by oxygen and finally hydrogen. For each experiment, a different surface area of the fulgurite was ablated, usually about 0.5 mm  $\times$  0.5 mm with a depth of 2-5 mm.

For the analysis of stable carbon isotopic Analysis, the gases were directly injected into a mass spectrometry (Finnigan Delta Plus XL with dual inlet) equipped with an Elemental Analyzer (Flash 1112EA) with ConFlo III as interface and an autosampler A200S. The reference gas CO<sub>2</sub> with a purity of 99.998% from Praxair ( $\delta^{18}\text{O}_{\text{VSMOW}} = -7.16$  and  $\delta^{13}\text{C}_{\text{VPDB}} = -11.29$ ), which was calibrated with an Oztech tank of CO<sub>2</sub> ( $\delta^{18}\text{O}_{\text{VPDB}} = -9.78$  and  $\delta^{13}\text{C}_{\text{VPDB}} = -10.99$ ). The  $\delta^{13}\text{C}_{\text{VPDB}}$  for the CO<sub>2</sub> gas samples were calculated by the following expression:

$$\delta^{13}\text{C} = \left[ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} - 1 \right] \cdot 10^3$$

The result of  $\delta^{13}\text{C}_{\text{VPDB}}$  were normalized with NBS-22, PEF 1 and Sucrose ANU to check the VPDB scale. The estimation of the precision and accuracy of the whole set of samples was checked using a sucrose reference sample which was analyzed every six samples. For this technique the standard deviation reported is 0.2 ‰ for carbon.

**SOIL ORGANIC MATTER.** Soil samples were freeze-dried and then were finely ground and homogenized with an agate mortar mill. Then the organic matter was quantitatively oxidized by titration with permanganate according to the following procedure: To one gram of soil, 10 ml of 30% sulfuric acid and 4 drops of 0.1 M  $\text{AgNO}_3$  (to eliminate chlorides) were added, and then the mixture was sonicated for 5 min and then centrifuged for 5 min at 2000 rpm. The supernatant containing the dissolved organic matter was then titrated at 60°C with 0.001 M  $\text{KMnO}_4$  (previously standardized with oxalic acid).

**THERMOLUMINESCENCE.** The age of the fulgurite was determined by thermoluminescence (TL). While careful handling was done post collection, the choice to use high temperature TL was made to minimize adverse effects from any light exposure during the storage of sample in the field. Use of TL also ensured that a thermal stimulation signal was used to date a thermal event. The outer skins (2mm to 3mm) were removed under red light using a diamond saw. A piece was saved for scanning electron microscope (SEM) and instrumental neutron activation analysis (INAA). The cut sample of the fulgurite was then prepped in a dark lab. Gentle crushing was done with a mortar and pestle followed by a 2 hour 2N HCl rinse, 2 hour 30%  $\text{H}_2\text{O}_2$  rinse and a very mild HF etch of 5% to 10% for 10 minutes to remove surface defects. Although SEM analysis of “bright spots” (possible feldspar rich phase) found these grains could contain K percentages from 0.20 to 0.32%, overall K-spar contamination was small, as indicated by a near background photon yield for infrared stimulation. Because of the low concentration of a feldspathic phase in this sample, it was assumed that the essential

signal was contributed by the dominant silica rich phase. We suggest that this silica rich phase was closer in composition to quartz than glass, as the shape of the TL glowcurve was similar to that found for normal crystalline quartz which is typically used for TL dating purposes. The quartz grains behave as paleodosimeters, with the measured luminescence intensity being proportional to the total absorbed ionizing radiation dose since burial or after the system was reset via a heating event above 500°C. This intensity divided by the radiation dose rate, (the luminescence-derived post-burial dose or equivalent dose) yields a TL age. The radiation dose rate measured in Gray (1 Gray (Gy) is equivalent to the absorption of 1 joule of energy per kilogram of material) for the environment of the sample was calculated from INAA measurements of naturally occurring radionuclides of the surrounding sand ( $0.25 \pm 0.08\%$  K,  $0.48 \pm 0.1$  ppm U, and  $1.31 \pm 0.1$  ppm Th), as well as from the fulgurite ( $0.20 \pm 0.06\%$  K,  $0.46 \pm 0.1$  ppm U, and  $1.26 \pm 0.1$  ppm Th), and combined with estimates of local cosmic-ray dose rates ( $0.2526 \pm 0.08$  Gy/ka for 500 m elevation and 25 cm depth). The radiation dose rate was derived to be  $0.92 \pm 0.02$  Gy/ka. Given that a sample had a homogenization due to melting, the annual dose rate was computed as a fine grain dose with a value of 0.04. Initial TL glow curves were run on aliquots between 4 to 11 microns (silt-size fraction) to look for photon yields and to check for the 110°C TL curve, which indicated a minimum detectable dose of about 1.5 Gy. The TL was stimulated by heating up to 500°C at a rate of 5°C/sec. Emissions were measured under blue filters Schott BG-39 and Kopp 7-59 using a Daybreak 1100 Automated TL System. After these preliminary analyses, the multiple aliquot additive dose method was performed using 20 aluminum discs plated with the silt-size grains and exposed to a beta source with energy of 0.04 Gy/sec for 2.4

Gy, 4.8 Gy, 9.6 Gy and 19.2 Gy. A set of discs were kept as naturals. All the discs were then preheated  $\approx 240^{\circ}\text{C}$  for one minute, followed by an Infrared Stimulated Luminescence “wash” at 100 second count kept at  $30^{\circ}\text{C}$ -SAM. Data indicated an equivalent dose of  $13.2 \pm 0.22$  Gy. The age plateau spanned a temperature region of  $290^{\circ}\text{C}$  to  $410^{\circ}\text{C}$ , which is considered to be an optically hard-to-bleach region. The plateau was remarkably lengthy and precise. In an attempt to duplicate these results, the lab used some of the same parameters (multiple aliquots, additive dose, preheat, silt-size grains) while making two changes. These changes were that the TL was detected under emissions from two Hoya U-340 UV filters and these were fitted to a Riso DA-TA-15A/B reader. The data from this run closely matched the original run and averaged an equivalent dose of  $14.6 \pm 1.3$  Gy. A supralinearity correction of about 1.2 Gy was assumed. The second equivalent dose data comes from the region of  $330^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ , which was of a shorter duration than the first analyses, but still considered stable.

## **CHEMICAL ANALYSES OF SOIL SURROUNDING THE FULGURITES**

Elemental analyses of surface soil sampled at Banizoumbou, near Niamey, with  $\leq 500$  mm annual rainfall, gave results very close to those for the fulgurite samples (Rajot, et al., 2003): 97.51%  $\text{SiO}_2$ , 1.28%  $\text{Al}_2\text{O}_3$ , 0.12%  $\text{K}_2\text{O}$ , 0.17%  $\text{Fe}_2\text{O}_3$ , 0.29%  $\text{CaO}$ ,  $\leq 0.02\%$   $\text{Na}_2\text{O}$ , 0.15%  $\text{TiO}_2$ , 0.02%  $\text{MgO}$ , and 0.07%  $\text{P}_2\text{O}_5$ . Similar to the fulgurite, Si is dramatically dominant in the soil, with the content of the other elements also in the soil in the same order of proportion as those in the fulgurite.

The sand collected in the vicinity of the fulgurites was also analyzed for organic material and other volatile molecules by chemical wet methods and flash pyrolysis

coupled to GCMS (Navarro-González et al., 2003). The results indicated that the sand contains extremely low levels of organics (0.003–0.007% carbon) that could not account for the gases trapped in the fulgurite.

## AGE DETERMINATION

The uranium-thorium isochron dating method (Teichert *et al.*, 2003) was also attempted, in order to provide another independent age for the fulgurites; however, despite a careful determination of the range of values for  $^{234}\text{U}/^{232}\text{Th}$  and  $^{230}\text{Th}/^{232}\text{Th}$ , they were too small to obtain a isochron, implying that that the fulgurites could not be dated by this technique.

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