

Fried Phosphate and Organic Survival: Lightning in Biogeochemical Cycles. M.A. Pasek¹, T.P. Kee², E.A. Carter³, M.D. Hargreaves⁴, H.G.M. Edwards⁴, and Z. Atlas¹. ¹mpasek@cas.usf.edu. Department of Geology, University of South Florida, 4202 E Fowler Ave, Tampa, Florida FL, 33620, USA. ²School of Chemistry, University of Leeds, Leeds LS2 9JT, UK. ³Vibrational Spectroscopy Facility, School of Chemistry, The University of Sydney, NSW 2006, Australia. ⁴Centre for Astrobiology and Extremophiles Research, School of Life Sciences, University of Bradford, Bradford BD7 1DP, UK.

Introduction: Since early experiments in prebiotic chemistry, lightning has long been associated with the origin of life on the earth. Lightning also provides one of the few means of abiotically fixing nitrogen breaking the strong N-N triple bond, and hence may have played a role in the enrichment of the early earth in bioessential elements.

When lightning strikes the ground, the target material undergoes mineralogical, morphological, and chemical changes. Cloud-to-ground lightning is accompanied by the formation of a glassy tube known as a fulgurite which follows the path of lightning. Temperatures often exceed the vaporization point of silica during the formation of a fulgurite, leaving a central void through which gases and other volatiles escape.

Here we present the results of two studies of fulgurites from around the world and discuss their implications for the speciation of bioessential elements. Recent work has shown that phosphates are reduced during fulgurite formation to form metal phosphides and calcium phosphite compounds, effectively changing the redox state of phosphorus from +5 to +3-0 [1]. Additionally, organic compounds have been shown to survive being struck by lightning to form PAHs. The formation of these PAHs also decreases the local temperature regime of the fulgurite.

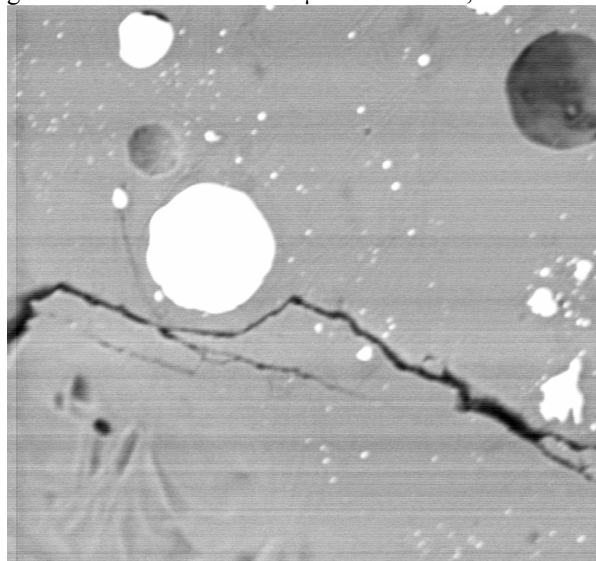
Methods: A series of ten fulgurites were analyzed to constrain phosphorus chemistry by ³¹P NMR spectrometry and by electron microprobe point analysis. These methods are outlined elsewhere[1]. Additionally, one of these fulgurites, from Greensboro, NC, USA, was analyzed by Raman spectroscopy to investigate the molecular composition, and by ICP-OES to determine major element abundances.

Spectra were collected using a Renishaw Raman inVia Reflex Microscope (Renishaw plc., Wotton-under-Edge, UK), equipped with an air-cooled charge-coupled device (CCD) camera. Sample excitation was achieved using an Argon ion laser (Modu-Laser, Utah, USA) emitting at 514.5 nm. Daily calibration of the wavenumber axis is required and is achieved by recording the Raman spectrum of silicon (1 accumulation, 10 seconds) for both static and extended modes. If necessary, an offset correction is performed to ensure that the position of the silicon band is $520.50 \pm 0.10 \text{ cm}^{-1}$. Spectra were not corrected for instrument

response. The spectrometer was controlled by PC with instrument control software (Renishaw WiRE™ 2.0 Service Pack 9).

A 2g specimen of the fulgurite was crushed and powdered for analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine major element abundances. These samples represent bulk compositions of the fulgurites including glassy interior and grey fusion crust.

Figure 1. Back-scattered electron image of Metal grains in a fulgurite from York county, PA, USA. The grain at the center left is 20 μm in diameter,



Results: Phosphorus-rich iron metal grains (Figure 1) are common in many types of fulgurites. The extraction procedure used for analysis by ³¹P NMR resulted in the production of reduced P species, formed by a process similar to those formed by corrosion of meteoritic phosphides [2,3]. Further, unusual Ca-H₃PO₃-SiO₂ minerals were formed in fulgurites formed in caliche from the Sonora desert, with as much as 70% of the total extracted phosphorus reduced from phosphates to lower oxidation state species.

The fulgurite from Greensboro NC, USA formed from a weathered diabase intrusion and hence its major elemental composition consists of primarily SiO₂ (81.3% by weight), Fe₂O₃ (8.5%), Al₂O₃ (8.3%), and TiO₂ (1.2%), with the remainder (<1%) comprised of other major elements.

Organic material from the soil in which the fulgurite formed is shown to convert to PAHs as demonstrated by Raman spectroscopy (Figure 2).

Discussion: These results show that lightning can influence phosphorus redox chemistry in ways not usually seen at the surface of the Earth. Additionally, lightning can cause distinct changes to the chemical structure of organic compounds, and it does result in their complete oxidation.

Implications for Phosphorus Biogeochemistry: The amount of phosphorus compounds reduced by lightning per year is approximately 3,000 kg/yr across the globe [1]. Hence reduced oxidation state phosphorus compounds originating during a lightning strike are unlikely to be a major portion of the total phosphorus flux on the Earth.

However, on the early earth, reduced P compounds may have comprised a larger portion of the total P available for reactions [3,4]. Further, recent results have shown that reduced P compounds can also originate from geothermal waters [5]. These results highlight the efficacy of P redox chemistry, and suggest that prior results demonstrating the production of prebiotic

polyphosphates [6] may in fact be the result of oxidation or reduced P compounds [7].

Implications for Carbon Compound Chemistry: The presence of organic compounds within a fulgurite suggests that organic compounds can survive high energy events. By analogy, meteoritic organic compounds may transform to PAHs during ablation or impact, which may alter the inventory of organic material that reached the surface of the early Earth. Further work with fulgurites may detail the types and speciation of compounds that survive or are created during high energy events.

References: [1] Pasek, M.A., and Block, K. (2009) *Nature Geoscience*, 2, 553-556. [2] Pasek, M.A. et al. (2007) *GCA*, 1344-1345. [3] Bryant, D.E., et al. (2009) *Int. J. Astrobio.*, 8, 27-36. [4] Pasek, M.A. (2008) *PNAS*, 105, 853-858. [5] Pech, H. et al. (2009) *EST* 43, 7671-7675. [6] Yamagata, Y. et al. (1991) *Nature*, 352, 516-519. [7] Pasek, M.A. et al. (2008) *ACIE*, 47, 7918-7920.

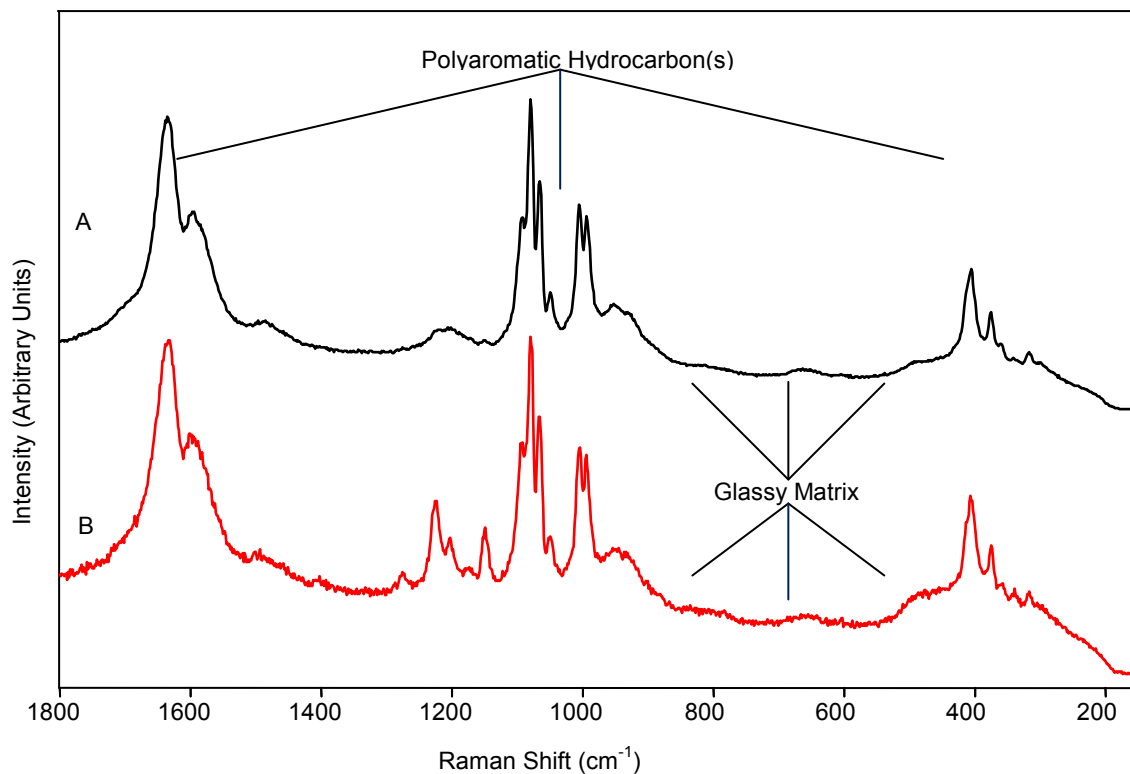


Figure 2. Raman spectra collected from an interfacial zone of a dark glass bubble in a fulgurite containing a region attributed to organic material. The spectra exhibit features that are attributable to polyaromatic hydrocarbons superimposed on broad glassy matrix bands.