

Reactive phosphorus via simulated lightning discharge: A role for fulgurites in pre-biotic chemistry

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ABSTRACT

Apatite is the most common phosphorus-bearing mineral in primary igneous rocks. Despite its early and ubiquitous presence in such rocks at the Earth's surface, its phosphorus exhibits a low reactivity in prebiotic chemosynthesis. This situation may change radically upon the transformation of phosphorus from orthophosphates to pyrophosphates or phosphides which are, in contrast, highly reactive in such scenarios. Pyrophosphates and phosphides are today however, scarce on Earth, generally not being stabilized in rock-forming processes. Noticeable exceptions are lightning-struck rocks (i.e., fulgurites). Here, we present the first evidence of reactive phosphorus (P) in a fulgurite which has been experimentally generated under controlled conditions from natural apatite. Crushed apatite was transformed into a fulgurite through the application of controlled high voltage electrical discharges. We document both the apatite (pre-experiment) and the fulgurite (post-experiment) texture, state, and chemistry. ³¹P and ¹⁹F nuclear magnetic resonance spectroscopy reveals the presence of a reactive P phase (pyrophosphate) in the fulgurite. Our results support the speculation that frequent lightning activity under early Earth conditions may have provided more than 100–10,000 kg/yr of reactive P on early Earth through the generation of reactive P-bearing fulgurites. Their presence may have enabled the chemosynthesis of vital prebiotic components such as RNA and lipids for the emergence of life on Earth.

1. Introduction

Phosphorus (P) is a key element in the evolution of life because it is pivotal in the biological coding of information (DNA and RNA), in metabolism (as ATP), and in cellular structure (as phospholipids). In magmatic systems from the Hadean up to today, the minor element P is present virtually exclusively in the oxidized state (orthophosphate: PO₄^{3−}) in phases such as apatite, monazite, and whitlockite (Hazen, 2013). Apatite is also known as the highest P crustal reservoir (Smith, 1981; Walton et al., 2021). Thus, phosphate minerals on Earth have almost certainly been witnesses to the prebiotic path to life. The common phosphate minerals are however highly stable and relatively

unreactive, leading to the so-called *phosphate problem* (Orgel, 1968; Benner et al., 2012; Pasek, 2017). Reduced P compounds (e.g., phosphites, hypophosphites) have, in contrast, been proposed as a source of P for primitive biological systems (White and Metcalf, 2007). This is because phosphide minerals (e.g., schreibersite, (Fe, Ni)₃P) are thermodynamically unstable on the Earth's surface and thus more reactive than phosphate minerals, reacting with water to yield phosphites (Pasek and Lauretta, 2005; Bryant and Kee, 2006; Pasek et al., 2007; Gull et al., 2015). Phosphides are common accessory phases in chondritic meteorites, interplanetary dust particles, and comets (Buchwald, 1984; Papike, 1998) but extremely rare on the Earth's surface (c.f., Disko Island, Greenland (Pedersen, 1981), Sulu terrain, China (Yang et al., 2005),

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Hatrurim formation in Levant (Britvin et al., 2015)). It has been postulated that reactive P phases might be readily available on the early Earth due to (i) heavy meteorite bombardments (Pasek and Lauretta, 2005; Bryant and Kee, 2006; Pasek et al., 2007; Bryant et al., 2009), (ii) low-temperature metamorphic heating (Herschly et al., 2018) and (iii) the reduction of phosphate to phosphite via lightning discharge (Essene and Fisher, 1986; Pasek and Block, 2009; Pasek et al., 2012; Hess et al., 2021). Here we concentrate on the latter.

To date, studies on the lightning discharge origin of reactive P compounds have been based almost exclusively on the analysis of natural fulgurite samples composed of non-prebiotic materials (i.e., sand) (Essene and Fisher, 1986; Pasek and Block, 2009; Pasek et al., 2012; Hess et al., 2021). Exceptions are provided by Glindemann et al. (1999) and De Graaf and Schwartz (2000), who exposed powdered apatite placed in a quartz tube sealed with a tungsten wire to a low-power electric current in a domestic microwave oven.

Here, we present the first successful generation of a reactive P phase in fulgurite generated experimentally by lightning discharges on natural apatite. Importantly, in the controlled environment of the experiments presented here we employ a continuing current effect, a crucial component of natural fulgurite genesis. The experimental apparatus used in this study has been designed and constructed to ensure compliance with the lightning research community's recommendations for lightning strike studies (e.g., waveforms IEC 62305) and thus can be easily compared and reproduced by other groups. We document experimentally for the first time the lightning-induced generation of reactive P phase in generated fulgurite using ^{31}P solid/liquid-state nuclear magnetic resonance (NMR) spectroscopy. The results demonstrate the feasibility of the fulgurite hypothesis for a repository of a reactive P-bearing phase on the early Earth.

2. Methods

2.1. Fulgurite synthesis experiment

The fulgurite sample was experimentally generated via a DC source with a trigger-pulse setup in the high voltage laboratory at the Universität der Bundeswehr (UniBw), Germany (Supplementary Video S1). A schematic diagram of the setup can be seen in Supplementary Fig. S1.

The laboratory setup was built considering the similarity of natural lightning currents, and the study procedure was based on the electrical inputs developed for standard lightning tests. Lightning currents are essentially unidirectional and are studied as a sum of different component effects. The main current components are first return stroke, subsequent return stroke and long-duration continuing current. The first return strokes have the highest current amplitudes, typically of the order of 10^3 A, lasting up to several hundred microseconds. The subsequent return strokes are lower in amplitude and duration, but often with a significantly higher current steepness di/dt of up to a few 100 kA/ μs . The long-duration continuing currents exhibit much lower current amplitudes of just a few 100 A, but last much longer (in the range of 100 to 500 milliseconds).

Our experiment setup consists of a Marx-generator, DC-source system, circuit breaker, inductor and cylindrical sample container (Supplementary Fig. 1). The Marx-generator is used as a trigger-pulse to override the dielectric field strength of the target material, producing currents with a 500–5000 A peak over ca. 100 μs , in a first stroke effect. Next, the DC-source produces a long-duration continuing current (60 batteries of 12 V, 720 V). These modules are connected to a cylindrical sample container (Fig. 1), yielding lightning strikes in a highly-controlled environment. A circuit breaker is used to control the currents flow at pre-determined conditions in accordance with lightning standards.

In our setup, the inner tube is filled with approx. 250 g of crushed powder. The dielectric field strength of the material is overridden with the help of a Marx generator, igniting the arc channel to start the melting

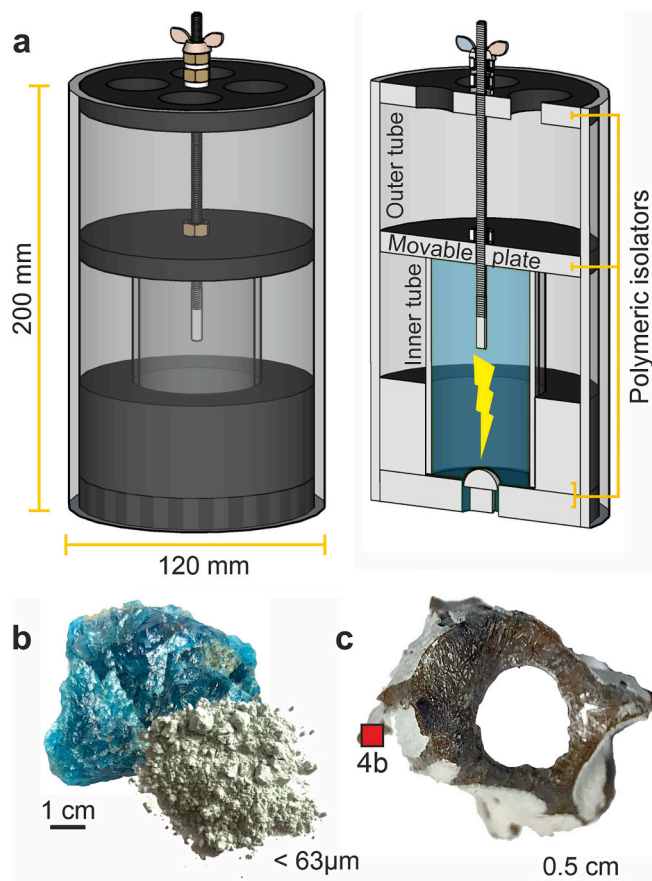


Fig. 1. Experimental apparatus, natural apatite (target material), and experimentally generated fulgurite. (a) 3D image and sectional view of the sample container. The outer plexiglass tube is used as a protective shell against a possible explosion, and the inner tube holds a controlled volume of the target material. (b) Hand specimen of apatite and its crushed powder. (c) Experimentally generated fulgurite; the red square represents the area sampled for ^{19}F MAS NMR analysis (Fig. 4b).

process, with an impulse duration of around 100 μs . Next, a DC-source generator produces a long-duration continuing current on the material in pre-set time – 500 ms, which is within the limits of natural lightning, to melt more mass around the arc. All melted mass are rapidly cooled down and create ca. 4 g of fulgurite. The long-duration continuing current characteristic used for the experimentally generated fulgurite is presented in Supplementary Fig. S2.

2.2. Sample preparation

250 g of natural apatite were ground in an agate mortar in a vibration mill down to 63 μm for lightning discharge experiment. Additionally, a sample of natural apatite (length / width: 3 cm / 3 cm) was embedded in an epoxy mount for further analysis.

Generated fulgurite sample was impregnated with Crystalbond 509, a semi-permanent transparent mounting medium, to prevent possible mechanical disruption of the fulgurite sample during cutting. To quantify the morphological properties of the fulgurite, the sample was cut perpendicular to its long axis using a precision diamond wire saw. After cutting the specimen, it was heated to 80 $^{\circ}\text{C}$ for ca. 1 min to remove most of the Crystalbond, followed by immersion in acetone for ca. 30 s to complete the cleaning process. Next, the surface was checked with a binocular microscope to verify that the Crystalbond was removed completely. A mount (epoxy resin) was prepared from one half of the fulgurite.

2.3. Laser scanning confocal microscopy

The fulgurite was examined under a Keyence 3D Laser Scanning Confocal Microscope (LSCM) VK-X1000 with 5× objective lens (WD 22.5) in the Department of Earth and Environmental Sciences at Ludwig-Maximilians-Universität (LMU), Munich - Germany in order to examine the inner and outer surfaces of the tube-like fulgurite sample.

2.4. X-ray fluorescence spectroscopy

Major and trace element analyses on natural apatite were conducted using a Malvern Panalytical Axios Fast X-ray fluorescence spectrometer (XRF) at University of Mainz, Germany. The major element analyses were carried out on fused glass discs whereas the trace element analyses were carried out on compacted powder pellets. Typical accuracy of the analyses of the standard references was nearly 1% relative (RMS) for major elements and around 4% relative (RMS) for trace elements.

2.5. Scanning electron microscopy

The natural apatite and experimentally generated fulgurite were analyzed using a Hitachi SU 5000 Scanning Electron Microscope (SEM) at LMU Munich. Backscattered electron images (BSE) of representative portions of the apatite and fulgurite were acquired at 100× magnification. Data collection was conducted by Oxford Instrument (AZtechEnergy Advanced EDX-System) Aztech software.

2.6. Electron probe microanalysis

The quantitative chemical compositions of the apatite and the fulgurite were analyzed using a Cameca SX 100 electron microprobe at LMU Munich. The apatite and fulgurite samples were examined under the same conditions and standards for accurate comparison of these two samples. The operating conditions were an accelerating voltage of 15 kV and an electron beam diameter of 10 µm with a current of 20 nA. The following standards were used: orthoclase (Al, K), albite (Na, Si), Durango fluorapatite (P, Ca, and F), anhydrite (S), vanadinite (Cl), thorium oxides (Th), rutile (Ti), LaPO₄ (La), CePO₄ (Ce), NdPO₄ (Nd), copper (Cu), tungsten (W).

2.7. X-ray diffraction spectroscopy

Qualitative phase determinations of natural apatite and fulgurite were obtained using a GE X-ray diffractometer (XRD 3003 TT) at LMU Munich. In order to determine the amorphous content (glass), approximately 17 wt% of silicon (Alpha Aesar Silicone powder, –325 mesh, 99.5%) was added as internal standard and mixed in agate mortar until well mixed visually homogeneous powder was obtained. Mineral indexing patterns were interpreted using Profex 10.13 software.

2.8. ³¹P and ¹⁹F NMR spectroscopy

³¹P and ¹⁹F NMR experiments were conducted on a solid-state NMR spectrometer at TU-Darmstadt. Direct-polarization (DP) and ¹⁹F/³¹P cross-polarization (CP) experiments were conducted under magic angle spinning (MAS) conditions. The spectrometer was equipped with a 400 MHz wide-bore Magnet, Bruker Avance II+ console, and a Bruker 3.2 mm H/F/X/Y MAS probe. Samples were spun in 3.2 mm zirconia rotors. MAS frequencies were set to 18 kHz for DP experiments, ³¹P and ¹⁹F, and to 10 kHz for CP experiments, respectively. Background suppression was utilized for ¹⁹F DP spectra (Bruker zgbs sequence), with 90° pulse of 3.9 µs. The relaxation delay was set to 10 s to ensure thermal equilibrium conditions for each scan. The tip angle for ³¹P DP was set to 22°, relaxation delay to 9 s, and ¹⁹F decoupling was applied during data acquisition. The parameters for the ¹⁹F/³¹P cross CP. Experiments were; a 3.5 ms contact time for long-range cross-polarization, 100 µs for short-

range cross-polarization, VACP sequence with 50% ramp on the ¹⁹F channel, 10 s relaxation delay, and ¹⁹F decoupling during data acquisition. External standards for referencing were phosphoric acid (0 ppm) for ³¹P spectra and solid Barium Fluoride (–14.3 ppm to CFCl₃) for ¹⁹F spectra, respectively.

Solutional ³¹P NMR spectroscopy was performed on a Unity INOVA spectrometer at the University of South Florida (operating at 161.84 MHz). 200 mg samples of the unaltered powdered apatite and the artificial fulgurite were separately extracted by a Na₄EDTA (0.025 M) solution for one week in closed vials, and the resulting supernatant was then filtered and dried down and rehydrated in D₂O. NMR then analyzed the solutions for 5000 scans using previously described methods (Gull et al., 2020).

3. Results

3.1. Starting material

Crushed natural apatite from Ipirá Complex, Bahia (Brazil) (<63 µm mesh size) was used as a starting material for our experiments instead of a rock containing apatite to avoid mineral interactions. The natural apatite and crushed powder are illustrated together in Fig. 1b. The apatite was analyzed for bulk composition using XRF (Table 1). The morphology and state of the apatite were investigated using SEM, EPMA, XRD, and ³¹P solid/liquid-state NMR.

In terms of morphology and mineral chemistry, the apatite sample represents a typical polycrystalline blue apatite specimen from the Ipirá complex (Fig. 1b). Its mineral formula has been calculated using the method provided by Ketcham (2015) as (Ca_{5.133}Sr_{0.002}Ce_{0.014}La_{0.009}Mn_{0.002}Fe_{0.002})(P_{2.824}Si_{0.130}O₁₂)(F_{0.857}Cl_{0.033}OH_{0.108}). The presence of minor uranium and thorium was also detected. The EPMA data are confirmed by “bulk” XRF analyses (Supplementary Table S1). The apatite sample contains minor microscopic subhedral to anhedral calcite grains (<5 µm) (Fig. 2a, b, and c). It can be classified as a fluorapatite in composition and crystalline structure, as confirmed by a XRD analysis (Fig. 2d).

As expected, a complete absence of any amorphous material in the structure of the pristine apatite has been confirmed by ¹⁹F magic-angle spinning (MAS) NMR spectroscopy (Fig. 2e). According to Vyalikh et al. (2015), –88 and –100 ppm peaks may be attributed to isolated water in this spectrum.

Table 1

Major and trace element composition of natural apatite from Ipirá Complex, Bahia (Brazil), determined using XRF.

Major elements (wt%)		Trace elements (ppm)	
SiO ₂	1.49	Sc	2
Al ₂ O ₃	0.01	Co	2
Fe ₂ O ₃	0.04	Ni	28
MnO	0.04	Zn	7
MgO	bd	Ga	3
CaO	54.76	Sr	566
Na ₂ O	bd	Y	bd
K ₂ O	bd	Zr	bd
TiO ₂	bd	Nb	bd
P ₂ O ₅	38.14	Cs	94
F	3.1	Ba	7
Cl	0.229	La	2500
Cr ₂ O ₃	bd	Ce	3800
NiO	0.0012	Nd	1800
SO ₃	1.034	V	32
LOI	0.29	Rb	bd
Total	99.229	Cu	6
		Cr	15
		W	33
		Pb	85
		Th	3251
		U	118

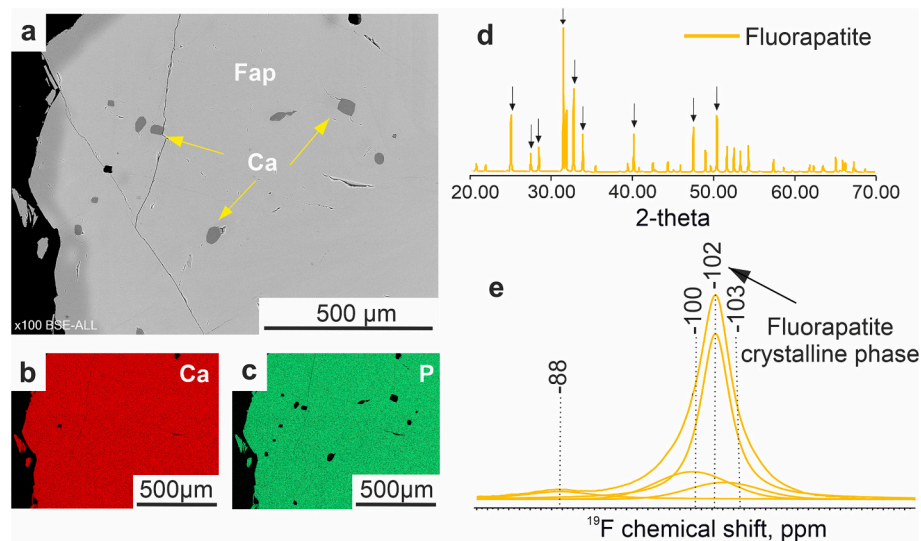


Fig. 2. Morphological and chemical properties of natural apatite. (a) BSE image revealing calcite (Ca) crystals in a fluorapatite (Fap) mass. (b) EDS element mapping of Ca (c) EDS element mapping of P. (d) XRD pattern of the natural apatite. Fitted spectra show the crystalline fluorapatite phase and some of the main peaks are indicated by arrows. (e) ^{19}F MAS (18 kHz) NMR spectrum of natural apatite. Y-axis shows intensity (a.u.).

3.2. Experimentally generated fulgurite

The experimentally generated fulgurite is dark brown in color, and its outer surface is finely dusted by a loose greenish powder of pristine apatite (Fig. 1c). It is nearly 1.5 cm in length and 2 cm in width (Fig. 3a) and displays a 0.7 cm diameter longitudinal central void, a common feature of natural fulgurites. Despite having been melted, the fulgurite exhibits a high degree of crystallinity, which clearly represents a recrystallized apatite mass wholly different in texture to the natural apatite. This is in contrast to the common observation of a glassy state of silicate fulgurites (Purdom, 1966; Frenzel and Ottemann, 1978; Merrill, 1886; Frenzel and Stähle, 1982, 1984; Frenzel, 1989; Clocchiatti, 1990;

Pasek et al., 2012) and likely results from the poor glass-forming ability of molten oxyfluorides. Newly-formed euhedral semi-transparent apatite crystals (ca. 0.4 mm) were detected via LSCM (Fig. 3b). The size of the newly recrystallized apatite crystals increases to ca. 0.6 mm at the inner surface of the fulgurite (Fig. 3c). Pristine crystals adhering to the outer surface exhibit sub-rounded edges, a morphological modification generated during the high temperature excursions of the experimental lightning strikes (Fig. 3d). XRD data confirm that the bulk of this crystalline mass is fluorapatite (Fig. 4a) and coherent with common fluorapatite spectrum (Silva et al., 2021).

^{19}F MAS NMR has been performed to examine the state of fluorine in the fulgurite. A single peak dominates the NMR spectrum at -102 ppm

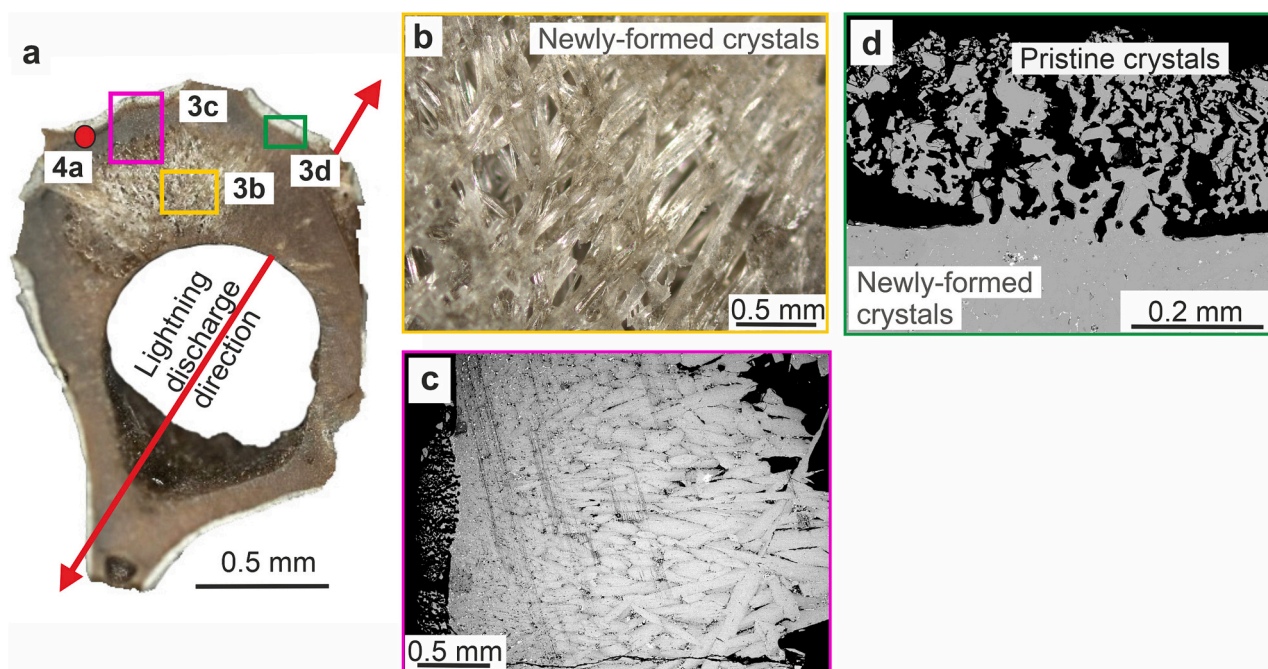


Fig. 3. Morphological properties of experimentally generated fulgurite. (a) Transverse image of fulgurite in the 3D LSCM. The double arrow shows lightning discharge direction, which indicates that lightning can initiate from the upper or lower electrodes. The red circle represents the sampled area for XRD analysis (Fig. 4a). (b) Optical image of newly-formed semi-transparent fluorapatite crystals via 3D LSCM and (c) BSE image. (d) A BSE image of pristine crystals and newly-formed crystals on the outer edge of the fulgurite.

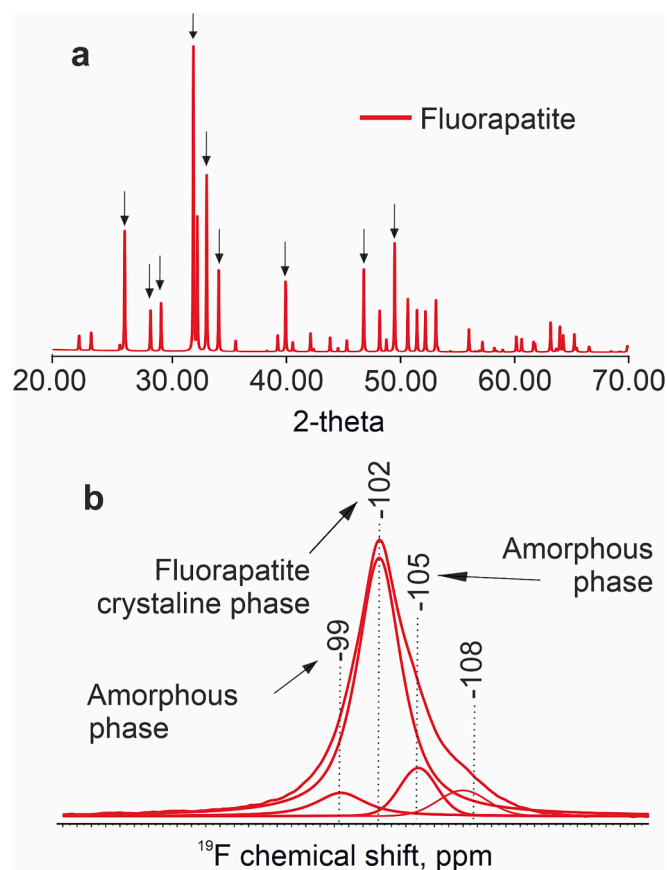


Fig. 4. Chemical properties of experimentally generated fulgurite. (a) XRD pattern of the studied area on the fulgurite. Fitted spectra show the crystalline fluorapatite phase. Some major peaks are indicated by arrows. (b) ^{19}F MAS (18 kHz) NMR spectrum of fulgurite detected using direct polarization. Y-axis shows intensity (a.u.).

attributed to PO_4^{3-} groups in crystalline fluorapatite. Additional peaks have resolved at -99 ppm, -105 ppm, and -108 ppm. The -99 ppm and -105 ppm peaks can be assigned to amorphous phases. The -108 ppm peak might be assigned as $\text{Ca}\cdots\text{F}$ interactions (-108 ppm) like in crystalline CaF_2 (Massiot et al., 2001) or Ca_3F by Vyalikh et al. (2015). However, we could not identify the presence of CaF_2 and Ca_3F in corresponding to our XRD data (Fig. 4b). Further, the phase diagram of apatite – fluorite, contains thermal maxima that would appear to exclude the formation of CaF_2 from an apatite starting material. The EPMA data of the fulgurite reveal a homogeneous chemical composition for the fluorapatite. The pristine crystals on the outer surface of the fulgurite show slight morphological differences, presumably due to thermal effects, but no major shifts in chemical composition. The newly-formed apatite crystals are depleted in F. Increased concentrations of W and Cu at trace levels are also observed in the newly-formed crystals and the interstitial phases. The interstitial phases also appear to be enriched in Th and REEs. Unfortunately, point measurements via EPMA involve an excitation volume significantly exceeding the size of the interstitial phases, and thus, there may be some convolution of the volumes of minor phases whose dimensions are ca. $3\text{ }\mu\text{m}$. All chemical data are summarized in Supplementary Table S2.

^{31}P solid/liquid-state NMR have been performed to examine the structural differentiation between natural apatite and experimentally generated fulgurite (Fig. 5 a and b). The main difference between pre- and post-experimental samples is the presence of the phosphate dimer pyrophosphate ($\text{P}_2\text{O}_7^{4-}$, PPI) in the fulgurite sample at a -4.5 ppm peak. This finding thus confirms the presence of a reactive P-bearing phase at a concentration of 5% at a 4 ppm peak via ^{31}P solid-state MAS NMR

measurement (Fig. 5c). This is the first experimental evidence for the presence of a reactive phase of P in an experimentally generated fulgurite composed of natural fluorapatite.

4. Discussion

Based on the observations presented above, we interpreted the synthesis process of this experimental fulgurite, generated from natural apatite, as one in which the entire sample within the domain of fulgurite generation has wholly melted and then massively recrystallized to a variably fine-grained apatite upon cooling. This recrystallization generates F- (and possibly Cl-) depleted apatite crystals accompanied by the nucleation and growth of interstitial phases, which presumably capture some of the F, together with Th and REEs. Phosphide minerals (e.g., schreibersite, $(\text{Fe}, \text{Ni})_3\text{P}$) have yet to be explicitly detected in these fulgurites. It must, however, be noted that our attempts at detection using XRD, EPMA, and SEM were likely complicated due to the low Fe and Ni content of the initial material and the nano-crystallinity of potential phosphide phases. Despite these potential analytical limitations, minor amorphous phase was detected in the bulk of fulgurite by ^{19}F MAS NMR (Fig. 4b).

The rate of fulgurite-forming lightning discharge and the phosphorus content of the sample in which the lightning strike plays a crucial role in the estimation of the reactive phosphorus source from fulgurite in the early Earth. Hess et al. (2021) estimate the amount of reduced phosphorus created by each strike by assuming an average fulgurite mass (250 g), average phosphorus contents (0.0065–0.044 wt%), and the per cent of phosphorus that is reduced (10–20% highly reduced, 25–50% mildly reduced). Based on these values, the amount of reactive phosphorus is calculated as 0.224% to 3.08%:

$$(0.0064 \text{ to } 0.044) \times [(0.1 + 0.25) \text{ to } (0.2 + 0.5)] = 0.224\% \text{ to } 3.08\%.$$

In this work, we measured the total amount of reactive phosphorus in the fulgurite to be around 5% by NMR analysis, which is higher than the upper limit (0.224% to 3.08%) based on the assumed values by Hess et al. (2021). Apatite as a monomineralic rock is rare in nature and hence in the presence of further rock-forming phases may be different in detail. Our work here should be viewed as an important basis on which to build towards multiphase rocks. Multi-phase rocks might behave differently under lightning discharge and the possible reactive phosphorus amount may vary depending on the phosphorus content of the rock (Yamagata et al., 1991). Additionally, the rate of the cloud-to-ground lightning discharge during the early Earth environment and target material physical features are other significant factors. It has been observed in our unpublished study that the target material with small grain size supports the formation of fulgurite. It is thought that the presence of suitable target material with the higher lightning discharge fraction may increase the reactive phosphorus source.

The importance of abiotic P redox changes, such as those demonstrated here in the lightning-generated reactive phase of P in experimentally generated fulgurite, for prebiotic chemosynthesis is since decades a central point of discussion (Gulick, 1995; Schwartz and Chittenden, 1977; Glindemann et al., 1999; De Graaf and Schwartz, 2000; Pasek and Lauretta, 2005; Pasek, 2008; Pasek and Block, 2009; Pasek et al., 2012; Pasek et al., 2013; Pasek et al., 2017; Herschy et al., 2018; Hess et al., 2021). The thermodynamic study of Pasek and Block (2009) indicates that phosphate (as CaHPO_4) can be reduced to phosphite (as CaHPO_3) at about 2000 K and oxygen fugacity of about 10^{-5} in natural fulgurites. In local environments, the proportion of the reduced P species may also exhibit enrichment under reduced atmospheric condition (De Graaf and Schwartz, 2000). Here, the newly-formed crystals are proof that we have exceeded the melting point of fluorapatite (around 1644 °C) and that the minimum temperature of the simulated plasma is close to the reduction temperature range (about 2000 K) referred to by Pasek and Block (2009). The temperature might be significantly higher; however, we cannot measure the temperature in

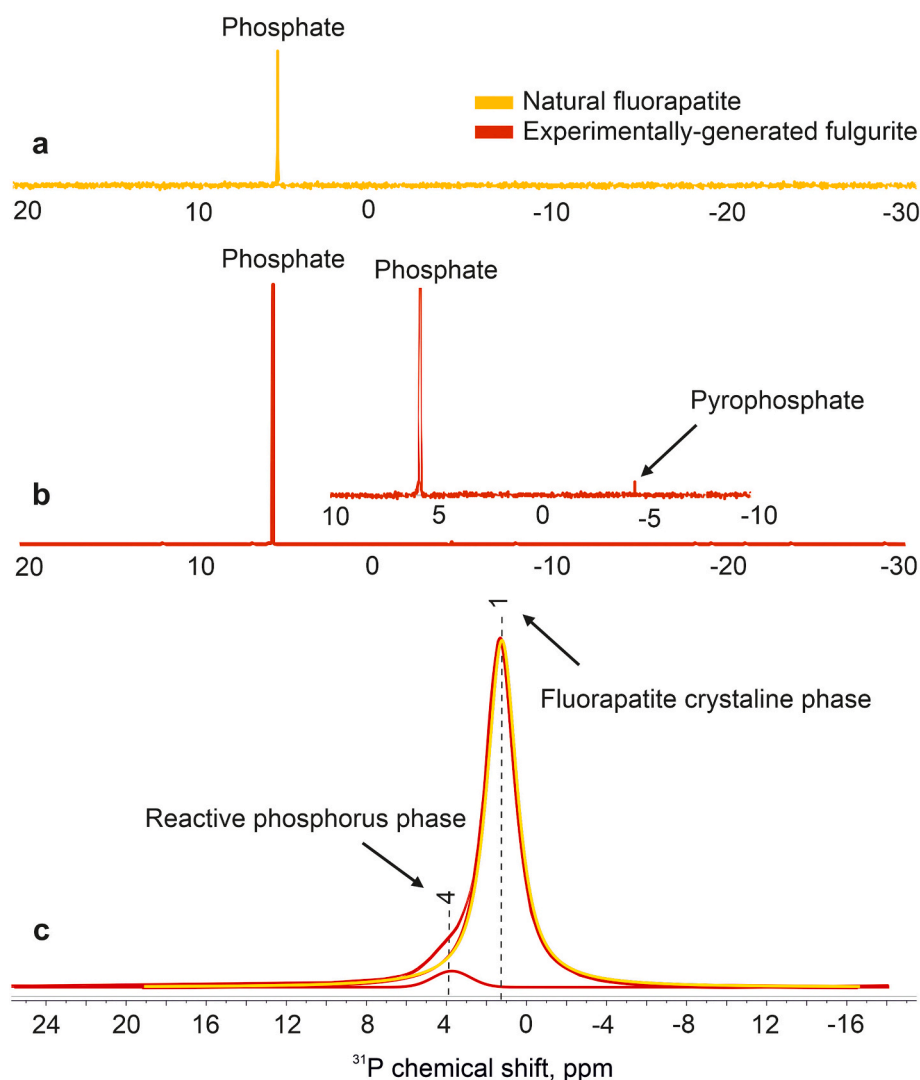


Fig. 5. ^{31}P NMR spectra of natural fluorapatite and experimentally generated fulgurite extract. (a) A solution state natural fluorapatite sample exhibits a single phosphate peak. (b) A solution state experimentally generated fulgurite displays an additional peak at -4.5 ppm consistent with the presence of pyrophosphate. (c) ^{31}P solid-state MAS NMR spectrum presents approx. 5% reactive phosphorus on the 4 ppm peak in the bulk of experimentally generated fulgurite. Spectra are normalized to a maximum intensity. Y-axis shows intensity (a.u.).

the experiment setup due to current technical limitations.

The formation of reduced P requires high energy inputs. Meteorite impacts may have delivered substantial quantities of P to the early Earth system (Russell et al., 2014; Pasek, 2017; Ritson et al., 2020). However, we note that its relatively chaotic environment may have destroyed potential prebiotic reagents and would have generally created inappropriate conditions for prebiotic synthesis. Further, some P species (e. g., phosphide minerals) carried to Earth by meteorite impacts also require survival through delivery followed by aqueous alteration to generate a reactive P phase.

As noted at the outset, lightning strikes have also been suggested as a terrestrial source of reduced P species in natural fulgurites (Essene and Fisher, 1986; Pasek and Block, 2009; Pasek et al., 2012; Hess et al., 2021). Notably, these previously-studied fulgurites are all modern and bear a lithology influenced by modern biogeochemistry. For instance, Essene and Fisher (1986) link the production of phosphides and other reduced phases in their fulgurite to the combustion of a tree root during a lightning strike. In the absence of biologically-derived concentrated carbon for reduction, we show that lightning discharge still facilitates phosphate activation through the formation of pyrophosphate. While not a reduced oxidation state P species, pyrophosphate still bears appreciable phosphorylating power and can phosphorylate sugars and other simple substrates to generate critical organophosphates (Pasek, 2020). Lightning strikes at the Earth's surface might generate environments in which prebiotic reagents can survive once generated and

participate in the crucial formation steps of proto-life. On the early Earth lightning activity may have been far more common than today. The successful generation of reactive P-bearing species in experimentally generated fulgurite under controlled conditions represents a crucial step in constraining the P problem, providing a readily reactive P source on the early Earth.

5. Conclusions

We have experimentally demonstrated that fulgurite formed by lightning discharge can generate activated phosphate forms from apatite. Lightning strikes were likely a common occurrence at the surface of the early Earth. This process may have provided an organophosphate source for pre-biotic chemical assembly. Thus, realistic simulation of natural lightning discharge in a controlled experimental environment, as achieved here for the first time, may provide an essential element for reproducing such synthesis.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2023.121343>.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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