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## **Constraints on Iron Silicide Formation from a Fulgurite from Southwick Massachusetts**

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### **Abstract**

Fulgurites are natural glasses that form when lightning strikes sand, soil, or rock and fuses the individual grains together to generate what is usually a tubular structure that follows the path of the strike. During this process, localized reducing conditions are conducive to forming rare minerals including iron silicides. This paper examines a fulgurite formed in Southwick, Massachusetts (USA), that displays an iron silicide that has a clearly defined reaction rim. The reaction rim demonstrates the production of a more silicon-rich rind consisting of  $\text{Fe}_5\text{Si}_3$  on a core of  $\text{Fe}_2\text{Si}$ , and the most likely route to forming this material is by reaction of silicon gas with  $\text{Fe}_2\text{Si}$  at high temperature ( $>1000^\circ\text{C}$ ), with a reaction timescale of about one second. This reaction suggests the high temperature, reducing conditions of a lightning strike favor reactions of condensed matter (e.g., liquid or solid iron minerals) with gas that occurs rapidly during the lightning strike. The conditions necessary to form these minerals suggest that the fulgurite became more reducing over time, as more Si entered the solid phase,

perhaps as oxygen left the system, either as CO<sub>2</sub> or from the breakdown of SiO<sub>2</sub> gas.

Keywords: Fulgurites, Silicides. Reduced Minerals, Reduction

## 1. Introduction

Lightning is a ubiquitous natural process, and an individual strike can produce a peak power of  $10^{13}$  W and a peak temperature of  $>30000$  K all within about a millisecond (Krider *et al.*, 1968). When lightning strikes soil, sand, or rock, the resulting rapid change in temperature can lead to the formation of a natural glass known as a fulgurite. This temperature change consists of an extremely rapid temperature increase due to the formation of the plasma channel ( $<1$  second), followed by a slower, but still relatively rapid decrease as the heat dissipates conductively ( $\sim$ minutes). A fulgurite is a glassy and usually tubular structure that follows the path of the strike. Fulgurites can be natural or artificial in origin. Artificial fulgurites are formed when a downed electric power line discharges into soil, often over periods of minutes to hours. In contrast natural fulgurites form under much shorter timescales ( $<1$  second) with much higher power (megawatts to gigawatts) (Pasek and Pasek, 2018).

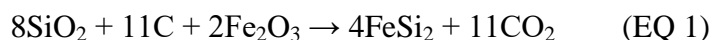
Lightning strikes produce extremely high temperatures and through this rapid deposition of energy are capable of generating a highly reducing local environment (Sheffer, 2007). Due to the reductive environment formed when lightning strikes a material, Hess *et al.* (2021) argued that fulgurites could have played a role in supplying a source of reactive reduced phosphorus on the early Earth surface. Fulgurites were one of the first modern rock type in which reduced phosphorus was discovered (Pasek and Block, 2009), present likely as both phosphides and phosphites, including solid CaHPO<sub>3</sub> (Bindi *et al.*, 2023a). The process of fulgurite formation (high temperature, high energy, and highly reducing) leads to the

formation of rare materials such as iron silicides, phosphides, phosphites (Pasek *et al.*, 2012), and even more complex alloys (Bindi *et al.*, 2023b).

Iron silicides are a group of rare minerals that form under reducing conditions. Silicides have been invoked as a possible solution to the presence of a light element in the earth's core (Lin *et al.*, 2002; Kuwayama *et al.*, 2009; Hsieh *et al.*, 2020), and in general are rare in surficial rocks. Essene and Fisher (1986) were the first to investigate iron silicides in fulgurites, specifically the Winans Lake fulgurite. The Winans Lake fulgurite contains metallic spherules inside a glassy matrix, consisting of intergrowths of phosphides, metals, and silicides. The silicides included compositions such as  $\text{Fe}_3\text{Si}_7$ ,  $\text{FeSi}$ , and  $\text{FeTiSi}_2$ . The Winans Lake fulgurite displays no signs of the spherules mixing with the matrix leading to the conclusion that the spherules were contemporaneous with the formation of the fulgurite. The cause of silicate reduction within the fulgurite was attributed to concurrent carbon oxidation, likely produced by combustion of a nearby tree root, as evidenced by the presence of graphite within the fulgurite.

Since Essene and Fisher's study (Essene and Fisher, 1986), there have been several more reports of iron silicides in fulgurites (see review by Feng *et al.* 2021). Iron silicide minerals include fersilicite/naquite ( $\text{FeSi}$ ), ferdisilicite/linzhiite ( $\text{FeSi}_2$ ), gupeiite ( $\text{Fe}_3\text{Si}$ ), hapkeite ( $\text{Fe}_2\text{Si}$ ), luobusaite ( $\text{Fe}_{0.84}\text{Si}_2$ ), xifengite ( $\text{Fe}_5\text{Si}_3$ ) and suessite ( $(\text{Fe}, \text{Ni})_3\text{Si}$ ). Several of these have been found in fulgurites (Essene and Fisher, 1986; Sheffer and Dyar, 2004; Cardona *et al.*, 2006; Block, 2011; Pasek *et al.*, 2012; Roberts *et al.*, 2019; Bindi *et al.*, 2023a). The formation of iron silicides within fulgurites likely depends on the presence of reductants such as organic carbon to drive the removal of O from  $\text{SiO}_2$ , though Sheffer (Sheffer, 2007) argued that carbon oxidation alone could not provide enough of a reducing environment to form iron silicides in all observed instances.

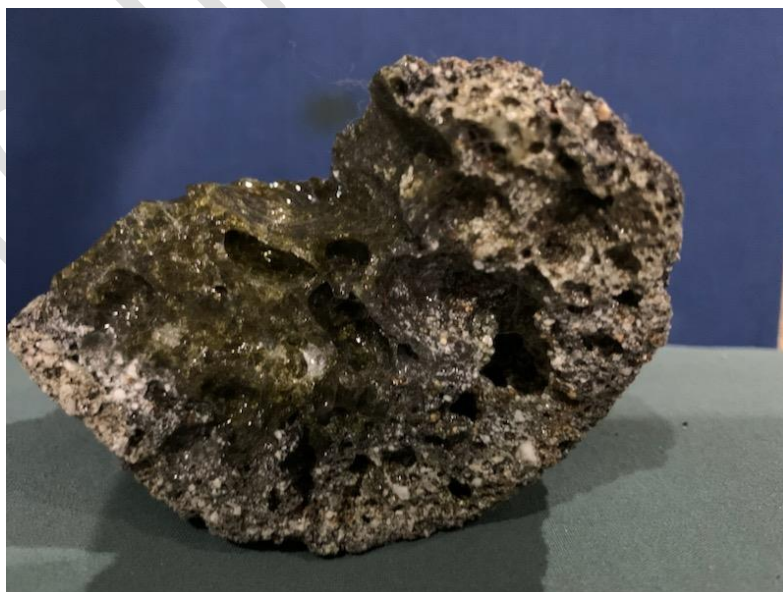
Iron silicides have been produced industrially for over 125 years to remove oxides from melted steel during casting processes (Brack *et al.*, 2015; Chepkasov *et al.*, 2020; Rappenglück, 2022). Industrially, the production of FeSi<sub>2</sub> follows the reaction:



An alternative route to production of iron silicides utilizes a process called electrodeposition. (Hovestad *et al.*, 1997; Popovici *et al.*, 2005; Liang *et al.*, 2006; Saidin *et al.*, 2011; Delekar, 2022).

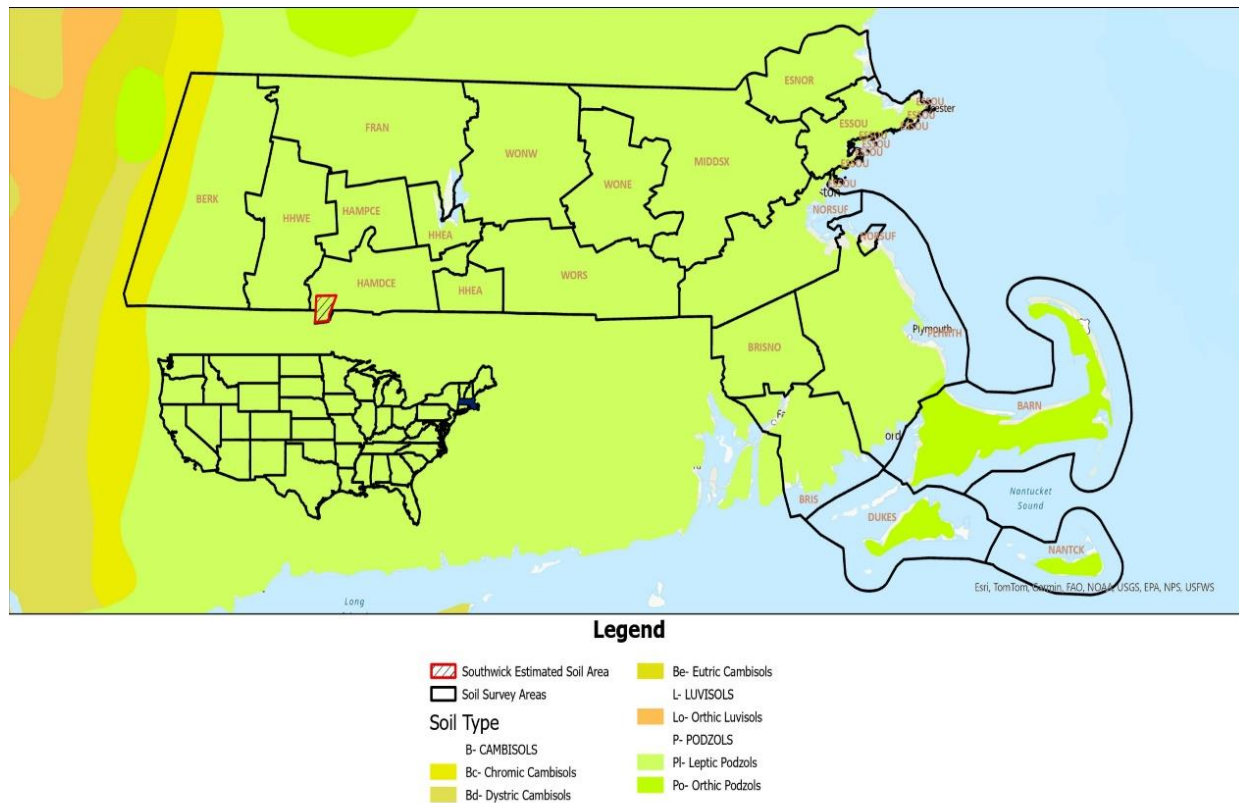
Building on the generation of silicides from industry, and noting the formation of silicides within some rocks, here we present data on an iron silicide within a Type II (Pasek *et al.* 2012) fulgurite from Southwick, Massachusetts, USA. We investigate a particular occurrence of iron silicides in this fulgurite to better constrain how these materials form under geologic settings, and especially in a lightning strike.

## 2. Methods and Materials



**Figure 1.** Picture of the fulgurite from Southwick Massachusetts in cross section. Width is 7 cm.

The Southwick, Massachusetts (USA) fulgurite (Figure 1) was obtained from the finders who sold the sample on eBay to one of the authors (M.A.P.) in 2015. The finders described the location only by the nearest town where it was found (See Figure 2), hence we will discuss the general geology of the Southwick area of Massachusetts (Schnabel, 1973), and contrast this sample with another nearby fulgurite to confirm its origin site. According to the Southwick geologic quadrangle, the surficial area of Southwick is predominantly composed of reddish brown or light olive gray till forming on sediments dated to the Triassic (252-201 million years ago). The fulgurite was said to have formed in 2010 after a thunderstorm.



**Figure 2.** Map of Massachusetts with Southwick highlighted in red. The legend shows the various soil types present in Massachusetts and the surrounding area. In particular, the area of Southwick is comprised of Leptic Podzols (PI) which are typically found within 200 cm from surface and comprised of appreciable clay mineralogy (Kitagawa, 2005).

The proximity of the Southwick fulgurite to another fulgurite discussed by Sheffer et al. (2003) in Farmington Connecticut (30 km) is noted. The target material of the Farmington fulgurite was sand and basalt gravel berm with oxide compositions listed in Table 1 and may have had a portion of aluminum conductor melted into the fulgurite. We believe in contrast that the Southwick fulgurite is fully natural whereas the Farmington fulgurite is a mix of natural and anthropogenic target materials. We highlight the Farmington fulgurite here mainly

to show that the similarities between the Southwick and Farmington bulk compositions shows that these fulgurites were formed from similar materials. Since samples of the surrounding soil were not available for confirmation of the Southwick fulgurite's formation site, such a comparison helps verify that the fulgurite was indeed found in its stated region.

**Table 1.** Oxide weight percentages of Farmington Connecticut fulgurite as per Sheffer (2007).

Contrast with Table 2.

	Bulk glass	SiO <sub>2</sub>	Lower, homogenous glass
SiO <sub>2</sub>	55.83	98.85	76.35
FeO	6.32	0	4.026
TiO <sub>2</sub>	19.92	0	0.48
Al <sub>2</sub> O <sub>3</sub>	2.91	0	10.35
MgO	6.00	0	1.45
K <sub>2</sub> O	1.48	0	1.35
CaO	5.09	0	2.46
Na <sub>2</sub> O	3.53	0	0.80
Total	101.08	98.85	97.266

Samples were analyzed using a Zeiss-EVO MA15 Scanning Electron Microscope with attached Oxford INCA250 Energy-Dispersive Spectrometer (EDS). The operating parameters were a probe current of 500 pA, counting time of 500 s, average count rate of whole spectrum of 2500 cps, and operating accelerating potential of 25 kV. A 30-nm carbon film was sputter-

coated onto the samples.

The Fe-Si phases were analyzed with a Bruker D8 Venture equipped with a Photon II CCD detector single crystal X-Ray Diffractometer. The instrument utilized graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), detector to sample distance of 7 cm, and an exposure time of 30s per frame. Intensity data was integrated for adsorption and Lorentz-Polarization with software packages from Bruker. Both XRD and SEM were performed at the CRIST, Centro di Studi per la Cristallografia Strutturale, Department of Chemistry, Università di Firenze, Italy

We used thermodynamic data to investigate the formation of iron silicides within the Southwick fulgurite. Specifically, the Gibbs free energy ( $\Delta G$ ) and equilibrium constant ( $K_{eq}$ ) of three potential reactions investigating the transformation of one iron silicide into another were calculated using a range of temperatures from 298.15 K – 1773.15 K increasing at increments of 25 K. The specific heat capacity ( $c_p$ ),  $\Delta H$  (change in enthalpy), and  $\Delta S$  (change in entropy) of  $\text{Fe}_5\text{Si}_3$  were calculated using HSC chemistry workbench (a thermodynamic equilibrium modeling program from Outokompu Research Oy; for more details see Pasek and Greenberg [2012]).  $S^0$ ,  $\Delta H$ , and  $c_p$  values at 298.15 for  $\text{SiO}_2$ ,  $\text{O}_2$ , Fe, and Si were obtained from NIST chemistry webbook (Linstrom, 1998). For all subsequent values past 298.15 K, a midpoint formula was used where thermodynamic values of the enthalpy (H) and entropy (S) were estimated at the 25 K incremental steps.

$$H_T^0 = \Delta H_{298.15}^0 + \int_{298.15}^T c_p dT \quad (\text{EQ 2})$$

$$S_T^0 = \Delta S_{298.15}^0 + \int_{298.15}^T \frac{c_p}{T} dT \quad (\text{EQ 3})$$

Using the  $c_p$  of  $\text{Fe}_5\text{Si}_3$  the  $c_p$  for  $\text{Fe}_2\text{Si}$  was calculated by multiplying the  $c_p$   $\text{Fe}_5\text{Si}_3$  by 3/8ths as  $c_p$  follows the number of atoms for related species. The  $\Delta c_p$  of  $\text{Fe}_2\text{Si}$  was calculated

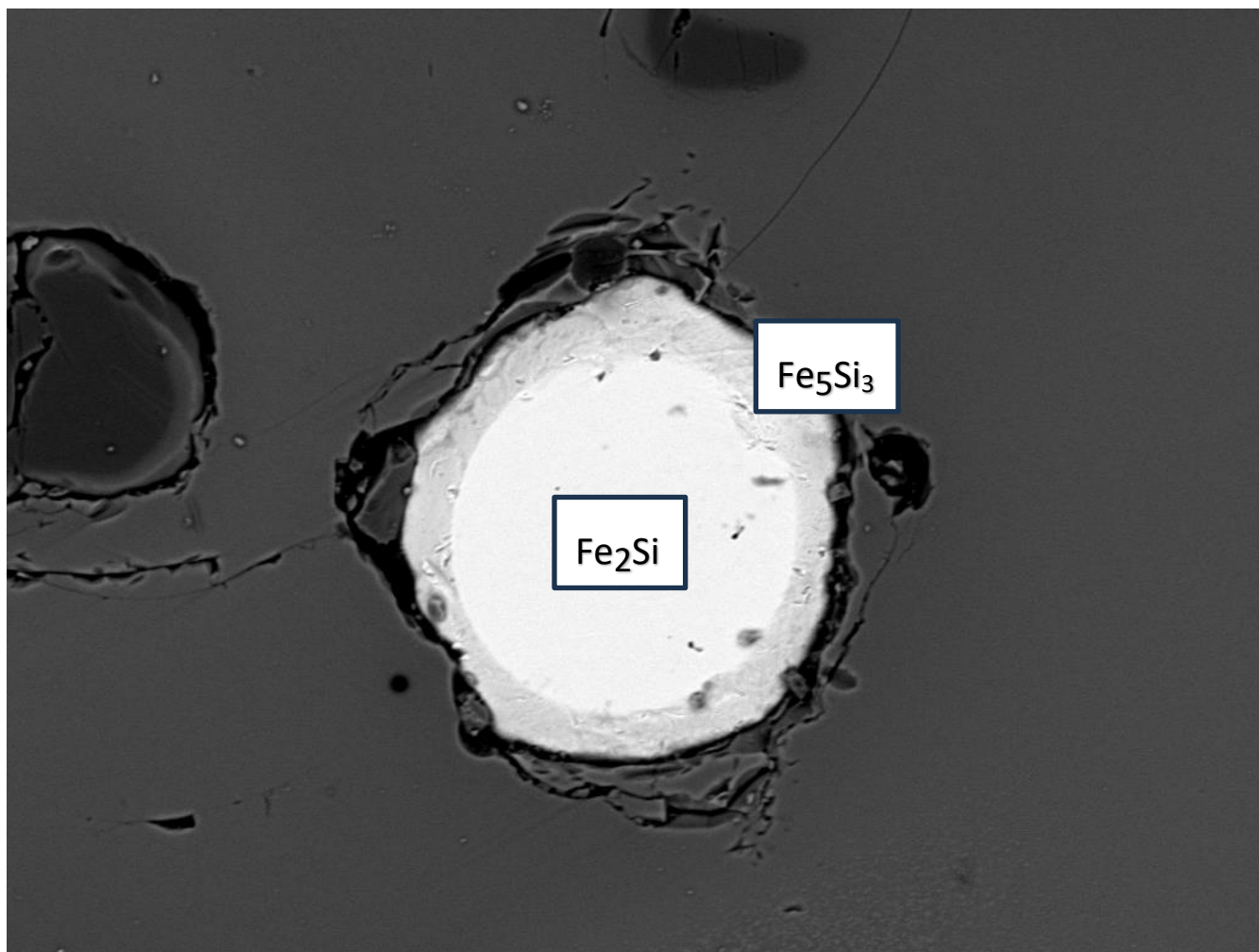


by obtaining an  $c_p$  value by taking an average of  $c_p$  at 298.15 K gathered from Cui and Jung (2017) for  $\text{Fe}_5\text{Si}_3$  (Cui and Jung, 2017) and subtracting the summation of iron and silicon  $c_p$  and dividing the result by 2. The  $\Delta H$  value for temperatures past 298.15 K for  $\text{Fe}_2\text{Si}$  was calculated using EQ 2. The  $\Delta H$  of  $\text{Fe}_2\text{Si}$  at 298.15 K was obtained through an averaging of values obtained from Cui and Jung (2017).

Using equation 3, the  $S^0$  for  $\text{Fe}_2\text{Si}$  were calculated for subsequent temperature past 298.15 K.  $\Delta S$  of  $\text{Fe}_2\text{Si}$  was calculated using the average  $S^0$  value at 298.15 K obtained from Cui and Jung 2017 (Cui and Jung, 2017) and subtracting the summation of iron and silicon  $S^0$  values.

The  $\Delta G$  and  $K_{eq}$  were then calculated for equations 4, 5, and 6.

### 3. Results



**Figure 3.** Back-scattered electron image of grain of Southwick Massachusetts fulgurite exhibiting a reaction rim. The outer rim is made up of  $\text{Fe}_5\text{Si}_3$  and the core is  $\text{Fe}_2\text{Si}$ . Sphere diameter is 95  $\mu\text{m}$ , including rim.

The Southwick Massachusetts fulgurite consists primarily of a groundmass of oxide glass (65%) with lechatelierite (200-400  $\mu\text{m}$  in diameter, compositionally >99%  $\text{SiO}_2$ ) dispersed throughout (35%). Accessory phases include spinel and metal grains. The groundmass of the fulgurite was analyzed by SEM to constrain its composition (Table 2) and investigate any unusual minerals within the glassy matrix. The general composition of the fulgurite seems to match with the information gathered from the Southwick quadrangle, but

the composition is like the nearby Farmington CT fulgurite, specifically the ‘lower’ glass, albeit with more Al<sub>2</sub>O<sub>3</sub> in the Southwick fulgurite. (Table 1). The predominant composition of protolith of the Southwick fulgurite is a clayey till which tracks with higher Al<sub>2</sub>O<sub>3</sub> percentages in contrast to the Farmington fulgurite. The two fulgurites are compositionally similar if the SiO<sub>2</sub> of the Farmington fulgurite is reduced from 75 to 61 wt.%, and all other oxides are increased by 50% by weight (Figure S1).

Notably, in general the composition of the protolith for most fulgurites closely tracks the composition of the outer glass (a ‘baked’ material), especially of Type II fulgurites (see description below), as the temperature of this ‘baked’ zone does not exceed the temperature of vaporization of the major rock-forming elements. Volatiles such as organic carbon and water are both depleted during the fulgurite-forming process, however (e.g., the Winans lake fulgurite, despite forming along a tree root, contained only trace quantities of graphite, see Essene and Fisher 1986).

**Table 2:** Oxide weight percentage of Southwick Massachusetts fulgurite groundmass glass.

Oxide:	Weight %:
SiO <sub>2</sub>	61.06
FeO	7.73
TiO <sub>2</sub>	1.16
Al <sub>2</sub> O <sub>3</sub>	15.11
MgO	3.43
K <sub>2</sub> O	1.50
CaO	6.76
Na <sub>2</sub> O	3.26

One spherical grain (~95  $\mu\text{m}$  in diameter) was found to exhibit a reaction rim (Figure 3) with an outer rim of  $\text{Fe}_5\text{Si}_3$  and a core of  $\text{Fe}_2\text{Si}$ . It was the only metal spherical grain noted within this section of the fulgurite. Based on SEM EDS data of this grain, the outer rim has an iron atomic percentage of around 62% while the core is close to 67%. For a correct identification, the two phases were handpicked from the polished section and analyzed by means of single-crystal X-ray diffraction. The outer rim turned out to exhibit a hexagonal symmetry, with  $a = 6.76(2)$   $\text{\AA}$ ,  $c = 4.72(2)$   $\text{\AA}$ , closely resembling the mineral xifengite,  $\text{Fe}_5\text{Si}_3$ . On the other hand, the core corresponds to the mineral hapkeite,  $\text{Fe}_2\text{Si}$ , with cubic symmetry and cell value of  $a = 2.85$   $\text{\AA}$ .

#### 4. Discussion:

The iron silicide phases seen in the Southwick Massachusetts fulgurite include an external rind of  $\text{Fe}_5\text{Si}_3$  and an internal core of  $\text{Fe}_2\text{Si}$ . This section will discuss the potential routes of formation of iron silicides as well as the potential significance of this grain. Following the fulgurite classification system, this fulgurite best fits the Type II archetype of clayey soil being struck by lightning (Pasek *et al.*, 2012). Iron silicide in fulgurites generally fall into two groups: iron-rich and silicon-rich, and most fulgurites bear silicon-rich silicides ( $\text{Si} > \text{Fe}$  by atomic fraction), if any are even present. Iron-rich silicides are more common in extraterrestrial material (Feng *et al.*, 2021), but do occur in fulgurites. The fulgurite from Southwick Massachusetts falls within the iron-rich category, with iron metal potentially reacting with all reduced silicon prior to the formation of more Si-rich silicides or even elemental silicon.

To further understand the mechanisms behind this reaction rim thermodynamic data

( $\Delta G$  in kJ/mol) for three possible equations were calculated (Table 3, with full range of values available in SI). Note that for these calculations we assume a pressure of 1 atm, and since some fulgurites may experience high pressure conditions, that is a limitation of the current model. We also acknowledge that applying thermodynamics to a system that may not have time to reach equilibrium necessarily means that the results predicted from thermodynamics are at best a prediction of reaction direction, and not a direct reflection of reality.

**Table 3:** Selected  $\Delta G$  values for the three equations in questi

Temperature (K)	$\Delta G$ equation 4	$\Delta G$ equation 5	$\Delta G$ equation 6
298.15	1852.8	-116.84	-31.753
673.15	1407.8	-280.52	-166.22
1048.15	896.41	-591.56	-405.87
1423.15	219.03	-974.28	-698.47
1773.15	265.30	-1570.1	-1152.2

on

We tested three potential routes for the formation of a  $\text{Fe}_5\text{Si}_3$  rind from  $\text{Fe}_2\text{Si}$  to see which may be the most plausible. In the first reaction, the internal  $\text{Fe}_2\text{Si}$  core may be reacting with  $\text{SiO}_2$  melt (as either  $\text{SiO}_2$  melt that later formed lechatelierite, which comprises 35% of the fulgurite by volume, or as a component of the groundmass melt), and expelling  $\text{O}_2$  to the environment.

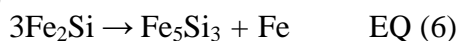


The second potential route of formation would follow the reaction:



In this reaction, the  $\text{Fe}_2\text{Si}$  core is reacting with silicon gas, through a silicidation reaction. This would parallel the known sulfidation of metals in meteorites (IMAE, 1994) and the phosphidation of metals, for example within Lunar impact rocks (Gooley *et al.*, 1973; Pasek, 2015). Notably, this reaction requires the presence of  $\text{Si}(\text{g})$ , which must have originated from reduction of the soil (e.g., as per Essene and Fisher 1986). In addition, EQ (5) is similar to EQ (4), inasmuch as  $\text{SiO}_2$  may break down to Si and  $\text{O}_2$  gases, through a thermodynamically unfavorable reaction. However, in the presence of organic carbon, the generation of CO and  $\text{CO}_2$  gas may push the reaction towards products.

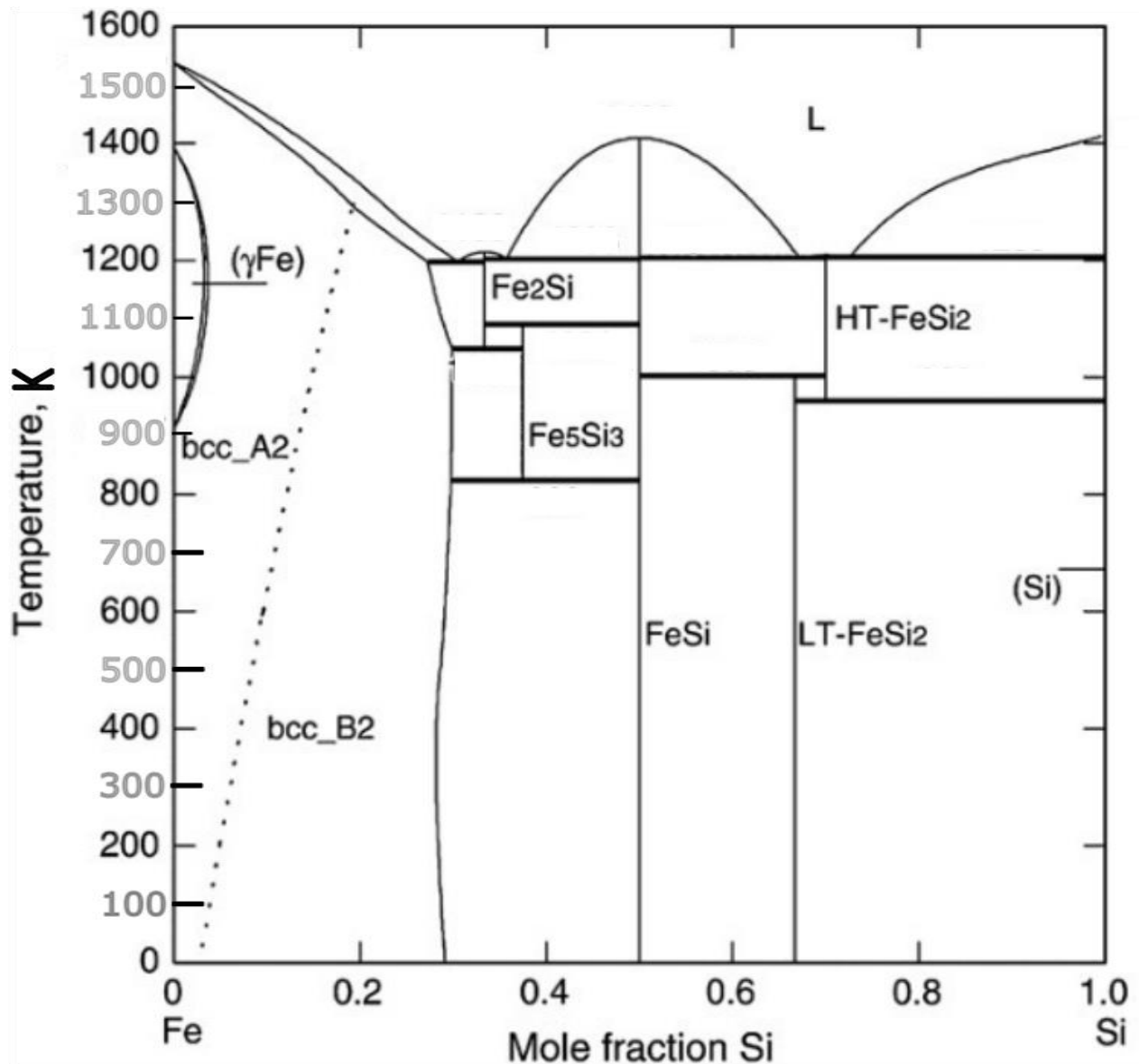
The third potential route of formation would be by incongruent melting, but this seems to be the least likely option as a more reduced phase comes from an oxidized phase, and is inconsistent texturally with the sample. That said, such a disproportionation reaction is expected from some reducing environments, such as the formation of awaruite (Bird and Weathers, 1975, 1979). Incongruent melting of minerals within fulgurites has also been reported for zircons (Kenny and Pasek, 2021).



The rind we see is more appropriately termed a reaction rim. A reaction rim signifies a secondary mineral that forms a rim around a primary grain. Possible causes of formation of these reaction rims are: (1) early formed crystal reactions with a melt, (2) solid state reactions with an intergranular fluid such as gas, (3) magmatic accretion from a different liquid, (4) solid state reactions between grains adjacent to primary during thermal or regional metamorphism (Spry, 2013).

Reaction rims can be found as a simple single layer surrounding a grain. A prime example of this is the serpentinization process where serpentine minerals form through water/rock interaction and begins encrusting olivine grains in peridotite (Cuthbert, 1990). Reaction rims can also form in a complex process with an assemblage of minerals. For example, one clearly defined rim from Griffin et al. (Griffin and Heier, 1973) showed an olivine grain (rimmed by accessory minerals such as orthopyroxene, clinopyroxene, garnet and spinel) next to a plagioclase grain. Following the initial growth structure, garnet began to propagate outward and enveloped the previous rims (with previous grains becoming inclusions) with clinopyroxene forming. The final stages of this reaction rim combine the reactions of water, garnet, and clinopyroxene to form a hornblende layer.

Seemingly, the closest mechanism that describes this fulgurite's reaction rim is a reaction between adjacent grains during thermal metamorphism. The thermal aspect could be attributed to the intense heat from the lightning strike. As such, this lightning-induced melting may be similar to prior reports of lightning-struck rocks (Castro *et al.*, 2020). It may also be possible that the lightning strike created a reducing environment further promoting the reduction from core to rim species. Based on thermodynamic data, the most likely reaction is the silicidation reaction in Equation 5. This reaction requires a very low  $fO_2$  (Essene and Fisher, 1986) estimate an  $fO_2$  between  $10^{-18}$  to  $10^{-13}$  at 1700 K).



**Figure 4.** Calculated Fe-Si phase diagram according to the modeling by Lacaze & Sundman (Lacaze and Sundman, 1991) and modified from Liang et al. (Liang *et al.*, 2011)

We favor EQ5, in which silicon gas reacts with iron silicides to generate new iron silicides. EQ5 is an exergonic reaction (Table 3), and we also expect increasing silicidation with higher pressure as temperatures increase (which results in a favoring of the products as gas is a reactant in EQ5, vs. a product in EQ4). Pressure may also increase due to shock (Chen et al. 2017). We base this on the Fe-Si phase diagram for these phases (Figure 4). From this figure it is apparent that Fe<sub>2</sub>Si is a higher



temperature phase than  $\text{Fe}_5\text{Si}_3$ , with  $\text{Fe}_2\text{Si}$  being stable from 1317-1476 K, whereas  $\text{Fe}_5\text{Si}_3$  is stable from 1093-1364 K. Given that the other major occurrence of rinds due to incongruent melting in fulgurites is on zircon with rinds of baddeleyite ( $\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2$ ) (e.g., (Pasek *et al.*, 2012; Kenny and Pasek, 2021)), these rinds form because of the high temperature phase forming a rind on the low temperature phase. The occurrence of  $\text{Fe}_5\text{Si}_3$  as a rind on  $\text{Fe}_2\text{Si}$  is the opposite.

As a ‘sanity check’ we contrast the sphere in Figure 3 to known metal gas-solid kinetics (e.g., oxidation, see SI). Metals generally follow a parabolic rate law during gas-solid reactions (Monceau and Pieraggi 1998), where the mass gained per surface area is proportional to the square root of the reaction time. If we assume a reaction time of one second, then for a sphere with a 100  $\mu\text{m}$  diameter, we find a requirement of a parabolic rate constant of about  $5 \times 10^{-6} \text{ kg}^2/\text{m}^4\text{s}$ . This rate constant matches measurements of the parabolic rate constant for iron phosphidation (Sasaki, 1985) at high temperature and likely under high pressure (see SI), as unfortunately metal silicidation rates have not been measured as robustly. However, the silicidation of metal should be reasonable under these timescales.

## 5. Conclusions

Iron silicides have been known from fulgurites since their discovery by Essene and Fisher (1986) in the Winan’s Lake fulgurite. These materials clearly indicate highly reducing conditions during the formation of a fulgurite from a lightning strike, usually from combusting organic matter. The likely driver of the reduction in the Southwick fulgurite is likewise combusting organic matter, which drives the oxidation state to extreme reduction, though no organic material was found within the Southwick fulgurite. Organic material has however been observed in other fulgurites, in the form of graphite (Essene and Fisher 1986), fullerenes (Daly *et al.*, 1993), polycyclic aromatic hydrocarbons (Carter *et al.*, 2010, Elmi *et al.* 2017) and partially graphitized carbon (Feng *et al.*, 2019). It seems

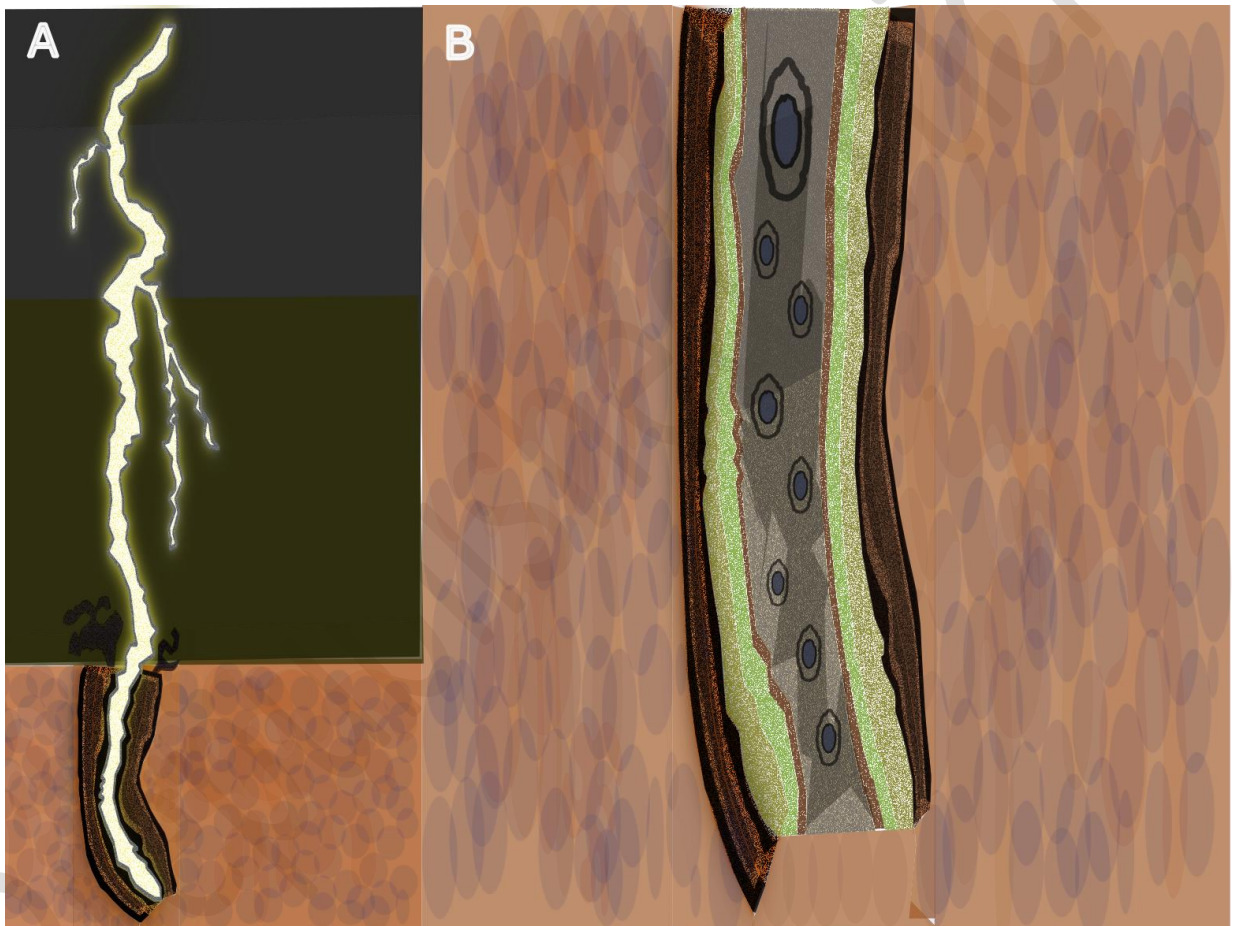
likely that a similar organic driver promoted reduction of the matrix to  $\text{Fe}_2\text{Si}$  and  $\text{Fe}_5\text{Si}_3$  in the Southwick fulgurite.

The fortuitous discovery of a  $\text{Fe}_5\text{Si}_3$  rind on an  $\text{Fe}_2\text{Si}$  core within the Southwick, MA fulgurite may give clues as to how these minerals are generated during a lightning strike. We note that, since only one grain was observed within this fulgurite, silicides may form by an assortment of other processes, but for this grain, we propose that the most likely pathway for formation of this grain is through silicidation of existing iron silicides. This sphere likely formed through gas-solid reactions in the cooling lightning plasma channel. Silicides are unstable at the peak temperatures of lightning forming a fulgurite ( $>1800\text{K}$ ), and hence they had to form as the fulgurite cools. The initial  $\text{Fe}_2\text{Si}$  phase likely formed under extremely reduced conditions somewhere between the iron-wustite and the silicon-silica buffers, and likely favored this composition due to the lower  $\text{SiO}_2$  abundance of the protolith. For example, Feng et al. (2021) track Fe-Si composition in fulgurites compared to groundmass composition, finding that fulgurites with  $\sim 60$  wt.% or less  $\text{SiO}_2$  tend to have more Fe-enriched silicides (where  $\text{Fe} > \text{Si}$  by atomic fraction), whereas those with  $>70\%$   $\text{SiO}_2$  tend to have Si-enriched silicides.

We present a simple illustration of the likely formation process for these grains (Figure 5). In this process, lightning strikes and propagates through soil (Figure 5A), vaporizing a portion of the soil. As this gas cools, iron-metal rich grains, possibly as  $\text{Fe}_2\text{Si}$  solidify or are formed as liquid droplets (Figure 5B). These droplets then react with Si in the gas, forming the  $\text{Fe}_5\text{Si}_3$  rind around the  $\text{Fe}_2\text{Si}$ . After a few seconds the fulgurite cools and the gas condenses as a glass, entraining the silicides within the glassy matrix. This may also suggest that, as the fulgurite cools, the gas may have become more reducing, given that the silicon content of the grain increased in the formation of the reaction rim. This may have been due to separation of oxygen from the environment, perhaps as an expelling of  $\text{CO}_2$ .

This reaction sequence may explain at least some of the silicides found in fulgurites (but likely not all). Iron silicides in fulgurites can form by reaction of gas with a condensed phase (most likely

solid iron metal), and the Southwick fulgurite seems to be capturing one grain in the process of this reaction. Notably, gas-solid reactions can be extremely fast, and similar rinds ( $\sim 10\ \mu\text{m}$  in diameter) have been found in lunar impact rocks, suggesting a timescale of seconds, and reaction kinetics—at least for P reacting with Fe—would reasonably form rinds of the size observed in the Southwick fulgurite.



**Figure 5.** A) Lightning strikes and propagates through soil, the lightning vaporizes a portion of the soil leaving a void space and Si gas, B) As this gas cools, iron-metal rich grains, possibly as  $\text{Fe}_2\text{Si}$  solidify or are formed as liquid droplets, these droplets then react with Si in the gas, forming the  $\text{Fe}_5\text{Si}_3$  rind around the  $\text{Fe}_2\text{Si}$ , after a few seconds the fulgurite cools and a majority of the gas condenses as a glass, entraining the silicides within the glassy matrix

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## Competing Interests

The authors declare no competing interests.

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