Geological and Geochemical Analysis of Phosphorus Bearing Minerals and Natural Glasses on Earth and in Meteorites: Implications of the Origin of Life

Tian Feng
University of South Florida

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Geological and Geochemical Analysis of Phosphorus Bearing Minerals and Natural Glasses

on Earth and in Meteorites: Implications of the Origin of Life

by

Tian Feng

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
School of Geoscience
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Keywords: Phosphorus, Fulgurite, Schreibersite, Struvite, Prebiotic minerals

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DEDICATIONS

This dissertation is dedicated to my parents and my wife. Without their complete support I would not have been able to have finished this dissertation.
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you so much for your encouragement and help in my Ph. D. period. I also thank you spent lots of time on listening to my presentations and providing comments which help me to improve my dissertation work.

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ABSTRACT

Phosphorus is a key element in biogenic molecules and the mineral schreibersite is a major reactive phosphorus source for organic compounds on the prebiotic Earth. In this dissertation, a suite of reactions of phosphorus species, which originate from schreibersite minerals on chondrite meteorites and on the early Earth, have been studied to determine the intermediate geochemical pathways between phosphides and common minerals on meteorites and on the early earth.

I first investigated a unique blue fulgurite that was studied to clarify if this blue color was caused by rich phosphorus content, as has been reported for impact glasses that also have a blue coloration. However, the blue color was shown to originate as a pseudochromatic effect, namely Rayleigh scattering from sub-micron spheres embedded in the matrix. Secondly, a solid-state reaction between schreibersite minerals, olivine and calcium silicate minerals has been analyzed, which reveals new thinking about schreibersite oxidation in meteorites. During schreibersite oxidation, phosphate species were the major final product at high temperature (1000 C). However, phosphite, polyphosphates, hypophosphite, and hypophosphate also occurred when temperatures increased (500 C -800 C). Theoretically, I assume that phosphate species could
further transform into pyrophosphate as a major product if reaction temperatures were extremely high. Moreover, the rate of this schreibersite oxidation process can be defined, which may determine the thermal record and metamorphic history of chondrite meteorite parent bodies. Finally, I investigated the thermal degradation products of the mineral struvite \((\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O})\), under conditions expected in meteorites and on the early Earth. Magnesium pyrophosphate and magnesium triphosphate are the final products for the thermal decomposition of struvite. Moreover, magnesium pyrophosphate transforms into orthophosphate and polyphosphate salts with calcium minerals in meteorites, which demonstrates that struvite may be lost from the geologic record, but could still have been important in the development of life.

The results in this dissertation show that reactive phosphorus species in meteorites and in natural glasses have close ties with prebiotic conditions on the early Earth. Some novel relationships between reduced phosphorus sources and minerals in meteorites and on the early Earth have been demonstrated, which provide assumptions to reveal the origin of phosphorus in life, and to understand the environment of the early Earth.
CHAPTER ONE
INTRODUCTIONS

Phosphorus (P) is a minor element on the earth and phosphate is a key biogenic molecule that plays a significant role in the biochemistry of living organisms (Pasek and Kee 2011; Pasek 2019). There are about 7000 P atoms relative to one million silicon atoms in the cosmos (Anders and Grevesse 1989). P was first discovered by German chemist Hennig Brand in 1669 (Emsley 2000). In the hot, early solar system, phosphorus would have occurred mainly in gaseous form at high temperatures (over 1,000 K) (Pasek 2006) and this phosphorus gas transforms into iron phosphide alloy by a reaction with iron or nickel present in the solids as the temperature decreased. On the Hadean Earth, this iron phosphide alloy could have transformed into the ions phosphite and phosphate by a reaction with water through corrosion (Pasek and Lauretta, 2005).

Orthophosphate minerals are considered to be the major P species on the Earth and the solar system. However, reduced P compounds also exist in earth now. Table 1.1 & Figure 1.1 give the details of various forms of phosphorus compounds (with former oxidation equal or less than 5) e.g. -3, +1, +3, +4, +5 type P compounds (Pasek et al. 2007).

Contrary to the present Earth, reduced P compounds (especially phosphites), were considered to be more prevalent due to the highly reduced conditions in the first billion years of the Earth (Pasek 2008). Such reduced P compounds are also known to have occurred in
fulgurites, which are a special glass that is formed by lightning striking rocks, sand, or soil

**Table 1.1.** Structures of major P species on the Earth and in the solar system.

<table>
<thead>
<tr>
<th>Phosphorus Species</th>
<th>Phosphorus Valence</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus simple substances</td>
<td>0</td>
<td><img src="image" alt="Structure of P or P or P" /></td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>+5</td>
<td><img src="image" alt="Orthophosphate Structure" /></td>
</tr>
<tr>
<td>Phosphite</td>
<td>+3</td>
<td><img src="image" alt="Phosphite Structure" /></td>
</tr>
<tr>
<td>Hypophosphite</td>
<td>+1</td>
<td><img src="image" alt="Hypophosphite Structure" /></td>
</tr>
<tr>
<td>Phosphine</td>
<td>-3</td>
<td><img src="image" alt="Phosphine Structure" /></td>
</tr>
</tbody>
</table>
**Figure 1.1.** Pourbaix diagram for H-O-P system at 298K, $10^{-6}$ M. Dash line represents hydrogen limit of water solution. Gibbs free energy data of each P species were collected from HSC Eh-pH database (Outotec Oy, version 9.3.0.9) (Pasek 2008)
(Pasek and Block 2009). These inorganic phosphite compounds can be transformed into organophosphorus compounds, and so they provide a pathway that offers a possibility that the origin of life in Earth depended on these chemical compounds. (Pasek and Lauretta 2005; Pasek et al. 2007; Gull et al. 2015)

Similarly with reduced P minerals, oxidized P minerals (phosphate minerals) are highly plausible on the early Earth. Hazen (2013) provided a list of phosphate minerals that were predicted to occur within the Hadean Eon (4 billion years, 4 Ga) (Table 1.2). Moreover, Burcar et al. (2016) expanded on this list by demonstrating that the mineral hydroxylapatite can transform into struvite (an ammonium water bearing magnesium phosphate mineral, $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$) through mild conditions. The process is very fast (less than 24 hours) and happens due to a reaction between ammonium- and MgSO$_4$-bearing fluid. This provided the impetus to investigate whether chondrites could possibly have had similar reaction environments (Pizzarello and Williams 2012) and, therefore, hinting for the plausibility of the mineral struvite on the early Earth system as well as within chondrite meteorites.

As mentioned above, the iron-nickel phosphide mineral schreibersite can transform into phosphite and phosphate ions on the early Earth. This happens when this mineral corrodes in water at low temperature ($<100^\circ$ C). However, it is also possible that schreibersite transforms into calcium phosphate minerals at higher temperatures and under dry (solid state) conditions. Such reactions can be plausible within meteorites parent bodies.
Table 1. Preliminary species list for predicted Hadean Eon (>4.03 Ga) phosphate minerals, chemical formulas, and modes of occurrence (Hazen 2013).

*Modes of Occurrence: AK = alkali igneous; CM = contact metamorphism; GR = granitoid igneous; HY = hydrothermal alteration; MA = mafic igneous; MT = meteorite; RM = regional metamorphism; SD = clastic sedimentary environment; SP = serpentinization.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Occurrence*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beusite</td>
<td>Mn$^{2+}$Fe$^{2+}$2(PO$_4$)$_2$</td>
<td>MT</td>
</tr>
<tr>
<td>Childrenite</td>
<td>Fe$^{2+}$AlPO$_4$(OH)$_2$·H$_2$O</td>
<td>HY</td>
</tr>
<tr>
<td>Chlorapatite</td>
<td>Ca$_5$(PO$_4$)$_3$Cl</td>
<td>CM,MA,MT,ZR</td>
</tr>
<tr>
<td>Farringtonite</td>
<td>Mg$_5$(PO$_4$)$_2$</td>
<td>MT</td>
</tr>
<tr>
<td>Fluorapatite</td>
<td>Ca$_3$(PO$_4$)$_2$F</td>
<td>AK,CM,GR,HY,MA,RM,SD</td>
</tr>
<tr>
<td>Galileiite</td>
<td>NaFe$^{2+}$$_2$(PO$_4$)$_3$</td>
<td>MT</td>
</tr>
<tr>
<td>Graftonite</td>
<td>(Fe$^{2+}$, Mn$^{2+}$, Ca$^{2+}$)$_5$(PO$_4$)$_2$</td>
<td>MT</td>
</tr>
<tr>
<td>Hydroxylapatite</td>
<td>Ca$_5$(PO$_4$)$_3$OH</td>
<td>HY,SP</td>
</tr>
<tr>
<td>Johnsomervilleite</td>
<td>Na$<em>{10}$Ca$<em>6$Mg$</em>{18}$Fe$^{2+}$$</em>{25}$(PO$<em>4$)$</em>{36}$</td>
<td>MT</td>
</tr>
<tr>
<td>Merrillite</td>
<td>Ca$_9$NaMg(PO$_4$)$_7$</td>
<td>MT</td>
</tr>
<tr>
<td>Monazite-Ce</td>
<td>CePO$_4$</td>
<td>AK,GR,MA,SD</td>
</tr>
<tr>
<td>Sarcopside</td>
<td>Fe$^{3+}$$_3$(PO$_4$)$_2$</td>
<td>MT</td>
</tr>
<tr>
<td>Stanfieldite</td>
<td>Ca$_3$Mg$_5$(PO$_4$)$_6$</td>
<td>MT</td>
</tr>
<tr>
<td>Triplite</td>
<td>(Mn$^{2+}$, Fe$^{3+}$)$_2$PO$_4$(F, OH)</td>
<td>HY</td>
</tr>
<tr>
<td>Wagnerite</td>
<td>Mg$_3$PO$_4$F</td>
<td>RM</td>
</tr>
<tr>
<td>Wavellite</td>
<td>Al$_3$(PO$_4$)$_2$(OH)$_3$·5H$_2$O</td>
<td>HY</td>
</tr>
<tr>
<td>Whitlockite</td>
<td>Ca$_8$Mg(PO$_4$)$_6$(PO$_3$OH)</td>
<td>MT</td>
</tr>
</tbody>
</table>

I hereby propose a route to test the above-mentioned hypotheses. Firstly, we propose to study the presence of phosphorus in special glasses called fulgurites. Secondly, I present a mechanistic route to find out whether the struvite minerals could have been plausible on the early
Earth and within meteorites. Furthermore, it is also necessary to determine how struvite transforms into other minerals, if it is indeed plausible on the early Earth and in meteorites. Third and last of all, I also analyze the reactions of iron nickel phosphide minerals with silicate minerals such as olivine and pyroxene at high temperature (> 500°C) within the meteorite bodies to determine the solid-state oxidation reactions of schreibersite that may occur in chondrite meteorites.

1.1. Overview of Meteorites

Meteorites are rocks that fall to the earth from space. A small object in the vicinity of the earth in outer space is called a meteoroid. When the small object falls into atmosphere and become visible, we call the glowing object a meteor. Last when the small object falls to the earth surface and is collected we call it a meteorite (Pasek, 2017a).

Meteorites can be classified in three major types: 1) stony type meteorites, 2) stony-iron type meteorites and 3) iron type meteorites (Dodd 1981; Pasek 2017; Mehta et al. 2018) (Figure 1.2). Iron type meteorites can be further divided into three major types: (1) hexahedrites, which are mainly composed of kamacite (an iron-nickel alloy, α-(Fe,Ni)) (Henderson 1965; Scott and Wassonm 1975), (2) octahedrites, which are primarily composed of kamacite and taenite (an
iron-nickel alloy, $\gamma$-(Ni,Fe)) (Buchwald 1975) and (3) ataxites, which are basically comprised of taenite (Buchwald 1975). Ataxites have most amount of nickel percentage in iron meteorites group, which contains over 18% Ni (Buchwald 1975), whereas octahedrites have 5% -18% nickel (Shirley and Fairbridge 1997) and hexahedrites have the lowest amount of nickel percentage, which only contain ~5.8% (Wasson 1985).

Stony-iron type meteorites are hybrid meteorites that bear roughly equal amounts of silicates and metals. Two major classes can be cataloged in stony-iron type meteorites, including: (1) pallasites, which are core-mantle boundary rocks are mainly composed of olivine and iron-nickel matrixes (kamacite and taenite) (Buseck 1977) and (2) mesosiderites, which are similarly with impact breccias and are chiefly formed by pyroxene, plagioclase and iron-nickel matrixes (Grady 2000, Davis 2005).

Stony type meteorites are the most abundant kind of meteorites and comprise of about 95% of all meteorites in the world’s meteorite collection (Rochette et al. 2003). Two major sub-types of these meteorites include: chondrites and achondrites (Weisberg et al, 2006), which are defined by the presence of chondrules (spherical amalgamations of silicate minerals) or their absence. (Mehta 2018). Chondrites are the majority of stony meteorites, with 86.2% of meteorites being chondrite meteorites (Bischoff and Geiger 1995). These can be separated into enstatite group (E-type chondrites), an ordinary group (O-type chondrites), and a carbonaceous group (C-type chondrites). (Weisberg et al, 2006). Table 1.3 shows the details of chondrites meteorites family.
Figure 1.2. Major divisions of meteorites.
Table 1.3. Tables of different group meteorites in chondrites meteorites (Weisberg et al, 2006).

<table>
<thead>
<tr>
<th>Group</th>
<th>Name From</th>
<th>Chondrule Abundances (vol %)</th>
<th>Metal Abundances (vol %)</th>
<th>Major Minerals</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>Ivuna Meteorite (Tanzania)</td>
<td>≤1</td>
<td>0</td>
<td>Phyllosilicate, Magnetite, Sulfide</td>
<td>Endress and Bischoff, 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Endross et al. 1996</td>
</tr>
<tr>
<td>CM</td>
<td>Mighei Meteorite (Ukrainie)</td>
<td>20</td>
<td>0.1</td>
<td>Phyllosilicate, Tochilinite, Olivine</td>
<td>Vdovynkin, 1973</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tomsko, 1990</td>
</tr>
<tr>
<td>CO</td>
<td>Ornans Meteorite (France)</td>
<td>48</td>
<td>1-5</td>
<td>Olivine, Garnet, Pyroxene, Nepheline</td>
<td>Keller and Buseck, 1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Russell et al. 1999b</td>
</tr>
<tr>
<td>CV</td>
<td>Vigarano Meteorite (Italy)</td>
<td>45</td>
<td>0-5</td>
<td>Olivine</td>
<td>McSween, 1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Greenwood et al. 2010</td>
</tr>
<tr>
<td>CK</td>
<td>Karooeda Meteorite (Australia)</td>
<td>45</td>
<td>0-5</td>
<td>Olivine</td>
<td>Kallemeyn, 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Greenwood et al. 2010</td>
</tr>
<tr>
<td>CR</td>
<td>Renazzo Meteorite (Italy)</td>
<td>50-60</td>
<td>5-8</td>
<td>Phyllosilicate, Olivine, Pyroxene, Metal</td>
<td>Weisberg et al. 1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weisberg and prinz.2000</td>
</tr>
<tr>
<td>CH</td>
<td>High Iron</td>
<td>70</td>
<td>20</td>
<td>Pyroxene, Metal, Olivine</td>
<td>Bischof et al. 1993</td>
</tr>
<tr>
<td>CB</td>
<td>Bencubbin Meteorite (Australia)</td>
<td>20-40</td>
<td>60-80</td>
<td>Pyroxene, Metal</td>
<td>Weisberg et al. 2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Krot et al. 2005</td>
</tr>
</tbody>
</table>

1.2. Fulgurites catalogs

A fulgurite is a glass that is formed when an electric discharge flows through materials such as rock, soil, and sand (Pasek and Pasek 2018). The word fulgurite is derived from a Latin word *fulgur*, which means “lighting”. The electric discharge is prevailingly in nature lightning (Essene and Fisher 1986; Pasek et al. 2012). Sometimes, a man-made power line also can be an electric discharge source that produces a fulgurite (Martin Crespo et al. 2009, Feng et al. 2019).
As a fulgurite forms, a high energy electric discharge (peak currents as much as 200 kA) quickly (about 100⁻¹ s) goes through sand, soil and clay. This tremendous electric current rapidly causes melting of the target materials and forms a tubular glassy mixture, which represent the trace of how the current traveled through the target.

Figure 1.3 shows that fulgurites can be cataloged as a type of natural glass (O’keefe 1984; McCloy 2019). Furthermore, fulgurites can be further partitioned based on differing spark sources and different target minerals (Pasek and Pasek 2018) (Figure 1.4). Pasek et al. (2012) also classified fulgurites by morphology and divided the fulgurites into four categories. Type I consists of sand fulgurites with thin glass walls; Type II contains the clay fulgurites with thick, melt-rich walls; Type III is the caliche fulgurites with thick, glass-poor walls; lastly, Type IV includes the rock fulgurites with glass walls surrounded by unmelted rock.

As a natural glass, a fulgurite is more likely to have played a significant role in origin of life, especially with relevance to the reduction of phosphorus on the early Earth. (Pasek and Block 2009; Hess et al. 2021). Copious amounts of reduced state phosphorus compounds, such as phosphide and phosphite, could possibly have been formed by lightning strikes on the early Earth (Hess et al. 2021). Hence, it is possible that these reduced phosphorus compounds formed by the lightning strike were some of the major sources of prebiotic phosphorus, which may have led to the origin of biological phosphorylated biomolecules.
Figure 1.3. Major divisions of natural glasses catalog (McCloy 2019).
In this dissertation, I present the study of an artificial fulgurite from Marquette, Michigan, USA. Different from other general fulgurite glass, this special fulgurite has a unique blue color. Some previous researchers have studied various minerals and rocks with blue coloration, like chalcedony (Pelto 1956), moonstone (Fritsch and Rossman 1988), zircon (Zeug et al. 2018; Sun et al, 2021) and impact glass (Koeberl 1988; Zolensky and Koeberl 1991). In this dissertation, I present various analytical techniques to determine the cause of the blue coloration of this fulgurite.

1.3. Past research on schreibersite

Schreibersite is an iron-nickel phosphide mineral \((\text{Fe, Ni})_3\text{P}\) found on meteorites. Schreibersite is regarded as a role on the early Earth system, where it is considered to be a plausible major source of phosphorus in prebiotic chemistry (Pasek and Lauretta 2005; La Cruz
et al. 2016; Pasek 2017b). Schreibersite readily corrodes in water and releases a variety of inorganic and highly soluble phosphorus compounds, e.g., hypophosphate, phosphite, phosphate and pyrophosphate (Pasek and Lauretta 2005; Bryant and Kee 2006; Pasek et al. 2007). Moreover, it is probably that under mild heating conditions, schreibersite can react with nucleosides, such as adenosine and uridine, to produce their respective nucleotides (Gull et al. 2015).

Schreibersite is the most common phosphide mineral (Prim et al. 2014). However, the mineral is rarely found on the Earth, and its reservoirs on the Earth are so far only limited to the Disko Island, Greenland (Pedersen 1981), Dead Sea, northern Negev Desert and Transjordan Plateau at Middle East (Britvin et al., 2015, 2017) and fulgurites (Essene and Fisher 1986; Pasek et al. 2012; Prim et al. 2014; Hess et al. 2021).

With respect to schreibersite, there are two studied routes for schreibersite transformed on meteorites or on the early earth. On the early Earth, schreibersite corroded in water and released phosphite and phosphate species (Pasek and Lauretta 2005) at lower temperatures (< 300°C) whereas at high temperatures (> 1000°C) within meteorite parent bodies, schreibersite sublimates above 1000°C, and at 800°C it oxidizes, converting from schreibersite to graftonite (Fe₃(PO₄)₂) (Lauretta and Schmidt 2009). Nevertheless, it is highly feasible that phosphorus element in schreibersite not only sublimates in the meteorites but may also have a solid-solid reaction with olivine and diopside at temperatures closer to 700°C. I performed research to establish the thermal history of meteorite parent bodies.
As mentioned above, schreibersite has been proposed as a significant form of prebiotic P source to form molecules in first 1 Ga year of Earth. (Pasek and Lauretta 2005; Gull et al. 2015; Pasek 2017b; Pallmann et al. 2018). Phosphorus is a crucial element which is a limiting nutrient in many ecosystems (Herschy et al. 2018; Pasek 2019), but in general phosphate minerals on the Earth, like apatite and whitlockite, are inert and do not react with organics to promote phosphorylation under realistic prebiotic conditions. However, schreibersite can readily react with organics such as glycerol to form membrane forming molecule glycerol phosphate (Pasek et al. 2013) and nucleosides such as uridine and adenosine phosphates, respectively (Gull et al. 2015). This supports the idea that schreibersite has played an important role in the phosphorylation process on the early Earth. (Gull 2014; Pasek et al. 2017b).

1.4. Struvite mineral in origin of life

Struvite (MgNH$_4$PO$_4$ × 6H$_2$O) is an ammonium phosphate mineral (IMA-CNMNC: 08.CH.40, Nickel and Nichols 1978). It is considered to be a prebiotic mineral (Handschiuh and Orgel 1973). It is likely that favorable geological conditions on the early Earth could precipitate out this mineral (Gedulin and Arrhenius 1994; Hazen 2013; Pasek 2017b). Thus struvite can be classified as a prebiotic mineral. However, struvite suffers from the „unavailability of the direct geochemical evidences” that could confirm its presence on the early Earth (Hazen 2013; Gull and Pasek 2013). Hence, it is speculated that struvite may have been unstable on the early Earth
certain geochemical reactions could possibly convert it into various other forms of minerals that could be more stable. But the exact mechanism is still unknown.

Burcar et al. (2016) discussed the possibility of a rapid (<24h) geochemical transformation of hydroxylapatite (Ca₅(PO₄)₃OH) into struvite on the early Earth. This reaction would have occurred in the presence of higher concentrations of ammonia and magnesium sulfate (MgSO₄) in solution. These same reaction conditions may have also been present on chondritic meteorite parent bodies, as chondrites bear abundant calcium phosphate minerals, such as merrillite (Ca₀NaMg(PO₄)₇), and apatite. Likewise, ammonia and MgSO₄-bearing fluids was likely present in carbonaceous meteorites. (Fredriksson and Kerridge 1988; Pizzarello and Williams; 2012, Zolensky et al. 2018). So, it is possible that struvite is plausible on both early Earth and meteorites.

Furthermore, it is known that struvite is not stable under hot, dry air, so I set out to trace out the degradation product resulting from its heating. Some researchers (Cohen and Ribbe 1966; Babic-Ivancic et al. 2006; Bhuiyan et al. 2008; Novotny 2011) suggest that magnesium acid phosphate (MgHPO₄) is the final product of the thermal decomposition of struvite at high temperatures (>200 °C). However, there is no direct evidence of the occurrence of these acid phosphate or ammonium phosphate minerals in the geological record (>1 Ga) (Hazen 2013). Hence, the presence of struvite or the above-mentioned acid or ammonium phosphate minerals on the early Earth is still unknown. Therefore, it is necessary to trace out the geochemical routes that could clarify the fate of the prebiotic mineral struvite and its plausible product minerals.
CHAPTER TWO

THE ORIGIN OF BLUE COLORATION IN A FULGURITE FROM MARQUETTE, MICHIGAN

Note to Reader:

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2.1. Introduction

Coloration within rocks and minerals may be due to inherent elemental causes (idiochromatic), from trace elements (typically rare earth or transition metals) present as impurities (allochromatic), or by non-chemical causes (pseudochromatic). Similarly, synthetic glasses may be colored using major components, trace additives, or physical effects (e.g. Stookey 1949; Stroud 1971; Puche-Roig et al. 2008). Studies of the coloration of natural glasses is rather limited in contrast to minerals (see Zolensky and Koeberl 1991; Ma et al. 2007) due to the general paucity of glasses produced by natural phenomena and their short-term persistence as glass is susceptible to devitrification reactions, typically caused by water (e.g. Malow et al. 1984).
While terrestrial glasses are rare, there are several types of natural events that form glasses on Earth (O’Keefe 1984). Natural glasses can form via high temperatures that are caused by friction during seismic events, rapid cooling of lava, or during high energy events such as a meteor impact/cloud-to-ground lightning strike. Some examples of natural glasses are obsidian, pumice, scoria, and tachylite from volcanic sources. Generally, pseudotachylites are formed by brittle or brittle-ductile deformation of rock during a seismic event (Philpotts 1964), sometimes an impact. Tektites are formed by the aerodynamic cooling of molten material ejected by impact (Carron and Lowman 1961).

Fulgurites occur on crustal areas of the Earth and are formed by electric discharge, typically when lightning strikes sand, soil, or rock during cloud-to-ground lightning (Yavuz and Can 1999; Spoonholz 2004). With forty-five lightning strikes occurring each second on Earth (Christian et al. 2003) and more than 90% of those strikes occurring over crustal land mass (Altaratz et al. 2003; Williams et al. 2004; Lay et al. 2007), and with about 25% of the lightning occurs as cloud-to-ground lightning, as many as 10 fulgurites may be formed on Earth every second (Pasek and Block 2009). As fulgurites can form over any area, fulgurites should be as chemically diverse as the sand, soil, and rock in which they form. A fulgurite’s morphology (structure) traces the primary path of the electric discharge as the rock, soil, or sand is melted and vaporized through the central plasma channel. The chemical composition of the fulgurite is dependent on the parent material as the energy heats and often melts the minerals present.
Natural fulgurites are formed when cloud-to-ground lightning is the source of the discharge, whereas artificial fulgurites are formed when a high voltage or high current from the breakdown of electric circuits is the source of the discharge (Lowry 1975; Kumaziki et al. 1997; Bidin et al. 2018; Elmi et al. 2018; Pasek and Pasek 2018). The blue fulgurite used in this study from Marquette, Michigan, USA (Figure 2.1) is a fulgurite formed in 2014 when lightning struck a tree, causing it to fall over against two high voltage power lines, with the current then travelling through the tree into sandy-clayey soil along what was apparently a tree root for three hours (Brzys 2014). This fulgurite bears characteristics of both natural and artificial sources as per the classification scheme of Pasek and Pasek (2018). The current forming the Marquette fulgurite was prolonged, which resulted in a long length, large thickness, and blocky, glassy matrix.

The Marquette fulgurite is similar in appearance to blue zhamanshinite, which is an impact melt glass named after an exposed impact crater in Kazakhstan. The blue glass is found with a variety of other impact glasses consisting of other colors, as well as tektite-like glasses that are termed irghizites (Koeberl 1986). The 900,000 (± 100,000)-year old crater has a diameter of 13 kilometers with a bottom width of 6.5 kilometers (Masaitis 1999). The crater is geologically complex with a center of loess and lake sediment. The rim is composed of metamorphic crystalline rocks which include both volcanic and sedimentary series cut by ultrabasic veins (Koeberl, 1986). Furthermore, this crater may be the source of the Australasian tektites, which have an extensive strewn field (Koeberl 1988a; Glass 1990). Generally, the
natural glass found in the crater area is referred to as zhamanshinite. While the existence of the blue glass was first noted by Florenskij and Dabizha in 1980, it was not until Koeberl (1986) chemically examined the glass that the glass was distinguished from other impact glasses. By doing so, Koeberl (1988b) provided major and trace chemical data for the blue zhamanshinites. Zolensky and Koeberl (1991) further examined the morphology and major chemical composition of the blue zhamanshinites, described immiscible glass inclusions, and discussed the role of phosphate inclusions as the cause of the Rayleigh scattering that results in the blue coloring of the glass. This scattering is akin to scattering that results in atmospheric coloration (Bucholtz 1995).

Figure 2. 1. Fulgurite in Marquette, Michigan (Brzys 2014), with general overview (a) and in situ (b&c) pictures.
Figure 2.1 (continued). Fulgurite in Marquette, Michigan (Brzys 2014), with general overview (a) and in situ (b&c) pictures.
Figure 2.1 (continued). Fulgurite in Marquette, Michigan (Brzys 2014), with general overview (a) and in situ (b&c) pictures.

Previous researchers have presented classification schemes for specific tektites and impact glasses found at the Zhamansin crater and for fulgurites. Koeberl (1986) classified glasses into irghizites and into Si-rich (70-80 wt. % SiO$_2$) or Si-poor (less than 55 wt. % SiO$_2$) impact glasses (Koeberl 1988b). Pasek et al. (2012) classified fulgurites by morphology and divided the fulgurites into four categories. Type I consists of the sand fulgurites with thin glass walls; Type II contains the clay fulgurites with thick, melt-rich walls; Type III encompasses the caliche
fulgurites with thick, glass-poor walls; and lastly, and Type IV includes the rock fulgurites with glass walls surrounded by unmelted rock. This fulgurite classification was expanded by Pasek and Pasek (2018) to fulgurites forming from unnatural discharge sources, and from those forming in manmade materials. We apply this prior work to this (thus far) unique blue fulgurite.

We employ Raman spectroscopy, X-Ray Fluorescence (XRF) analysis, Electron Microprobe Analysis (EMPA), and Transmission Electron Microscopy (TEM) to determine the major and minor chemical composition of the Marquette fulgurite and to examine the blue fulgurite’s microscopic morphology. We use the morphology and chemical composition results to classify the fulgurite according to prior fulgurite classification schemes, and to compare the fulgurite with the data from Zolensky and Koeberl’s (1991) earlier analysis of the blue zhamanshinite. We hypothesize that the origin of the blue coloration in this fulgurite is pseudochromatic, due to spherical inclusions (smaller than the wavelength of blue light) in the host glass that create conditions conducive to the scattering of light, yielding a strong blue color. The similarities and differences between the blue fulgurite and blue zhamanshinites may assist in determining some of the Pressure-Temperature-time (P-T-t) features of both discharge and impact cratering events.

2.2. Methods and Materials

Samples of blue fulgurite glass and a sample of the parent soil (from the finder via eBay, located at Marquette, Michigan) were analyzed (Figure 2.2). The fulgurite was found near the south side of Lake Superior (46°29'46.5"N, 87°32'28.4"W) The bedrock geology is characterized
by Archean metavolcanics, specifically greenstone metabasalt, though the fulgurite formed within the A/E/B horizons of soil. A thick section was prepared for analysis. The thick section was mounted on a glass slide using epoxy and polished as per standard methods. Sample morphology was characterized by use of Neiko calipers (Pasek and Pasek 2018)

(a)

**Figure 2.2.** Bulk sample of blue fulgurite, showing cross-sectional (a & c) and lateral views (b)
Figure 2. 2(continued). Bulk sample of blue fulgurite, showing cross-sectional (a & c) and lateral views (b)
Raman point microanalysis of the fulgurite was used to identify minerals in thick section, using an Enwave Opt. Inc. (Model No. EZI-785-A2). The Raman microscope is a Leica DM300 microscope equipped with three objective lenses (×4/0.1 NA, ×10/0.25 NA and ×40/0.65 NA). The spectra were processed using Crystal Sleuth freeware (Laetsch and Downs 2006) and compared to relevant spectra from the RRUFF database (Lafuente et al. 2015).

Samples of the glass and the parent soil were analyzed by X-Ray Fluorescence (XRF) at Hamilton College (NY) on a Bruker AXS S8 Tiger Wavelength Dispersive X-Ray Fluorescence (WDXRF). These samples were also analyzed using Electron Probe Micro-Analysis (EMPA) to determine the major elements of the fulgurite. Electron Probe Micro-Analysis was performed on a JEOL 8900R Super Probe (Florida International University) after samples were carbon coated, and samples were standardized with comparison to EMS-1 Obsidian (Price and Pichler 2006). In this experiment, we remotely probed the fulgurite across a cross section to measure the weight percentages of the major elements in the sample, averaging these points to determine “typical” composition.

Structures on the submicron scale were investigated using a Tecnai G2 F20 TWIN 200 kV / FEG Transmission Electron Microscope (TEM) with a Gatan UltraScan 4000 (4k x4k) CCD camera at University of Florida. Bright Field Transmission Electron Micrograph analysis (BFTEM) and a High Angle Annular Dark Field Scanning Transmission Electron Micrograph analysis (HAADF-STEM) specifically were chosen to determine the shape of several nano-scale
structures. In addition, Energy Dispersive X-Ray Spectrometry (EDS) was utilized to map major elements inside the inner glass (EDAX GENESIS XM2).

2.3. Results

The blue fulgurite was formed as a massive cylindrical shape with multiple tubular chambers. A majority of the blue glass-bearing tubes (Figure 2.2) are massive (75% glass width) with little internal void (0-20%) consistent with an artificial electric discharge source (Pasek and Pasek 2018). In contrast, the less intensely-blue hued samples have larger void proportions (27%), implying these may have been formed during the initial lightning strike. The fulgurite has a hardness of about 4.5 on the Mohs Hardness Scale. The sample does not display cleavage or magnetic attraction. Under fluorescent light, the sample changes color from blue to purple. Furthermore, a thin section changes color to green as it is illuminated from behind with plane polarized light. The soil that was collected by the finders “adjacent” to the fulgurite was a sample of sandy-clay sediment.

The average composition of the fulgurite glass is provided as Table 2.1 & 2.2, based on microprobe and XRF data. Comparison of this data to other fulgurites and zhamanshinites in the literature is provided as a ternary diagram (Figure 2.3). A compositional comparison to the soil suggests the fulgurite and adjacent soil are not compositionally related or suggests significant fractionation occurred during the heating event.
Per Figure 2.3, while this fulgurite is similar to the blue zhamanshinites in color and similar to type II fulgurites in morphology, this fulgurite is chemically distinct from either group (Figure 3), as it is more Fe-, Mg-, and Ca-rich, though other elements (Na, K, Al, Si) are not dissimilar, with the variation explained as dilution caused by increasing CaO and MgO.

Table 2.1. Major element abundances (in wt%) in the blue fulgurite and associated soil sample. Compared with Zolensky & Koeberl (1991). Note: “BDL” stands for Below Detection Limits and represents areas that were below the detection limits of instruments used in this study.

<table>
<thead>
<tr>
<th>Element</th>
<th>EPMA Blue fulgurite</th>
<th>XRF Blue fulgurite</th>
<th>XRF Soil</th>
<th>Zolensky, Koeberl, 1991 Blue Zhamanshinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>62.98</td>
<td>62.70</td>
<td>75.14</td>
<td>74.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.65</td>
<td>7.32</td>
<td>6.43</td>
<td>11.02</td>
</tr>
<tr>
<td>FeO*</td>
<td>2.7</td>
<td>3.41</td>
<td>1.42</td>
<td>4.47</td>
</tr>
<tr>
<td>CaO</td>
<td>16.06</td>
<td>15.89</td>
<td>3.29</td>
<td>4.08</td>
</tr>
<tr>
<td>MgO</td>
<td>9.90</td>
<td>7.36</td>
<td>1.37</td>
<td>1.33</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.36</td>
<td>1.41</td>
<td>2.00</td>
<td>2.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.21</td>
<td>1.32</td>
<td>1.00</td>
<td>1.52</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.15</td>
<td>0.35</td>
<td>0.19</td>
<td>0.58</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.09</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.03</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.15</td>
<td>0.13</td>
<td>0.08</td>
<td>0.80</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>102.3</strong></td>
<td><strong>99.98</strong></td>
<td><strong>90.97</strong></td>
<td><strong>100.6</strong></td>
</tr>
</tbody>
</table>
Raman point analysis of the fulgurite samples generally showed the major material to be highly amorphous, and with little to no Raman scattering peaks. However, a large white mineral grain was found in the sample which was determined through Raman analysis to be cristobalite ($\text{SiO}_2$). Furthermore, blackened material was also found on the sample, which is most likely charred wood. (Figure 2.4).

**Figure 2. 3.** Ternary Diagram, which displays the blue fulgurite and other Type I, II, III, and IV fulgurites from Pasek et al., 2012. Sheffer 2007, Crespo et al., 2009, Elmi et al., 201

**Figure 2. 4.** Laser Raman spectroscopy figures of the host minerals of blue glass, with a) cristobalite (RRuff denotes Raman spectrum of a cristobalite standard) and b) charred root that has been partially graphitized (RRuff denotes Raman spectrum of a graphite standard).
Table 2.2. Trace element abundance (in ppm) of blue fulgurite and soil sample. Compared with Koeberl (1988); Taylor and McLennan (1979); Martin Crespo et al. (2009). Note: “BDL” is below the detected limits of the instruments used.

<table>
<thead>
<tr>
<th>Minor element</th>
<th>Blue fulgurite glass</th>
<th>Blue fulgurite soil</th>
<th>Zh 31/6A</th>
<th>Zh31/6 B</th>
<th>BZ 8601</th>
<th>Australite tektites</th>
<th>Fulgurite of Torre de Moncorvo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>BDL</td>
<td>BDL</td>
<td>11.2</td>
<td>9.0</td>
<td>10.3</td>
<td>13</td>
<td>3.33</td>
</tr>
<tr>
<td>V</td>
<td>54</td>
<td>22</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>83</td>
<td>8.83</td>
</tr>
<tr>
<td>Cr</td>
<td>BDL</td>
<td>BDL</td>
<td>167</td>
<td>111</td>
<td>170</td>
<td>145</td>
<td>17.17</td>
</tr>
<tr>
<td>Co</td>
<td>BDL</td>
<td>BDL</td>
<td>24</td>
<td>14</td>
<td>14.5</td>
<td>25</td>
<td>BDL</td>
</tr>
<tr>
<td>Ni</td>
<td>18</td>
<td>7</td>
<td>&lt;300</td>
<td>&lt;200</td>
<td>&lt;200</td>
<td>&lt;105</td>
<td>3.63</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
<td>14</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>6.5</td>
<td>19.10</td>
</tr>
<tr>
<td>Zn</td>
<td>26</td>
<td>44</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>57.53</td>
</tr>
<tr>
<td>Ga</td>
<td>7</td>
<td>9</td>
<td>20</td>
<td>18</td>
<td>15</td>
<td>BDL</td>
<td>18.23</td>
</tr>
<tr>
<td>As</td>
<td>BDL</td>
<td>BDL</td>
<td>2.5</td>
<td>3.2</td>
<td>5.3</td>
<td>BDL</td>
<td>6.38</td>
</tr>
<tr>
<td>Se</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.4</td>
</tr>
<tr>
<td>Br</td>
<td>BDL</td>
<td>BDL</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>BDL</td>
<td>0.3</td>
</tr>
<tr>
<td>Rb</td>
<td>36</td>
<td>46</td>
<td>74</td>
<td>89</td>
<td>98</td>
<td>BDL</td>
<td>302.17</td>
</tr>
<tr>
<td>Sr</td>
<td>156</td>
<td>176</td>
<td>180</td>
<td>220</td>
<td>150</td>
<td>BDL</td>
<td>80.97</td>
</tr>
<tr>
<td>Y</td>
<td>13</td>
<td>6</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>31</td>
<td>12.97</td>
</tr>
<tr>
<td>Zr</td>
<td>138</td>
<td>133</td>
<td>450</td>
<td>600</td>
<td>210</td>
<td>264</td>
<td>60.72</td>
</tr>
<tr>
<td>Nb</td>
<td>4.7</td>
<td>2.2</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>18.7</td>
<td>10.75</td>
</tr>
<tr>
<td>Mo</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.3</td>
<td>0.13</td>
</tr>
<tr>
<td>Sn</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>1.3</td>
<td>33.83</td>
</tr>
<tr>
<td>Sb</td>
<td>BDL</td>
<td>BDL</td>
<td>1</td>
<td>1</td>
<td>1.18</td>
<td>BDL</td>
<td>3.87</td>
</tr>
<tr>
<td>I</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
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TEM analysis of the fulgurite reveal the presence of abundant nanospheres (~100 nm in diameter, Figures 2.5 and 2.6). EDS mapping of spheres at this scale showed that the major element inside the spheres was Si (Figure 2.7) and were in general much lighter in elemental composition than the glass groundmass.

**Figure 2.5.** Bright Field Transmission Electron Microscopy (BFTEM) image of the fulgurite sample. In BFTEM, lighter contrasts correspond to lighter Z elements.

**Figure 2.6.** High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) image of the fulgurite. With DFTEM, darker contrasts correspond to lighter Z elements.
Figure 2. TEM images of (a) spherules within the fulgurite, and (b) corresponding EDS elemental map, with blue corresponding to Si, green to Mg, and red to Ca.
2.4. Discussion

As per the Pasek et al. (2012) classification scheme, this fulgurite is a Type II fulgurite based on its morphology. We consider now the origin of the blue coloration of this fulgurite. Blue coloration within fulgurites has not been reported previously to date (this is the only known example). Most Type I (sand) fulgurites are white to beige, reflecting the coloration of the original sand. Type II fulgurites are more diverse in color, with typical samples ranging from brown to gray-black to bottle-green. Given the uniqueness of this coloration, we consider the possibility that the fulgurite may have formed through an unusual heating event or environment. We then consider the origin of the blue coloration as due to chemical interactions and how this fulgurite and others may serve as impact material analogs.

2.4.1. Origin of the Fulgurite

The fulgurite as described by the finders would be characterized as a natural and artificial fulgurite, describing the source of the discharge. The presence of cristobalite supports a longer formation timescale than typical fulgurites formed solely by lightning, as the conversion of quartz to cristobalite requires elevated temperatures that persist for minutes to hours (Pasek and Pasek 2018). Although Elmi et al. (2017) report cristobalite within a fulgurite from Italy, the formation temperature of the Italy fulgurite appears to have been moderated by the combustion of lichen, which may have allowed for elevated temperatures to have persisted for long enough to convert quartz to cristobalite. Beyond this one occurrence of cristobalite within a natural fulgurite, cristobalite is surprisingly absent from the mineralogy of natural fulgurites. The
longer persistence of high temperatures during formation of this fulgurite may have allowed for
the separation of the matrix into two immiscible components. This may indicate why no wholly
natural fulgurites have been reported with a strong blue hue.

When we compare the mineralogical composition of the blue fulgurite to that of the Type
II fulgurites (Pasek et al., 2012) we see that this fulgurite is not chemically similar. The presence
of cristobalite and graphite in the fulgurite instead of lechatelierite—amorphous SiO$_2$—indicates
this fulgurite was not formed in the same manner as a typical Type II fulgurite. The formation of
cristobalite limits the temperature reached to less than roughly 2,000 K, the melting point of SiO$_2$
(Breneman and Halloran 2014). This indicates slower heating as opposed to the rapid heating at
high temperatures typical of Type II fulgurites (Pasek and Pasek 2018). The presence of
multiple chambers where tree roots would be expected also supports the conclusion that the
lightning struck the tree and not the ground, as does the lack of melted conducting wire (also an
indicator of origin per Pasek and Pasek 2018).

The fulgurite is otherwise not compositionally distinct from other Type II fulgurites, though it is slightly poorer in SiO$_2$, and richer in CaO and MgO than most Type II fulgurites
(Figure 2.3). This is likely due to the fulgurite forming within the weathered and leached soil
horizons on top of Archean metavolcanics (specifically Greenstone metabasalt). The fulgurite
formed in soil from which alkalis are leached into surface groundwater, and alkali earths migrate
downwards in the soil column, leaving an SiO$_2$-enriched residue that can mix with the Ca/Mg
rich soil layer below, hence its deviation from a typical basaltic composition. Morphologically
the fulgurite is consistent with a Type II fulgurite, though some of the more massive pieces match well with artificial fulgurites as per the scheme in Pasek and Pasek (2018). Pasek and Pasek (2018) do note that determining the origin of a type II fulgurite based on morphology is less robust than finding melted conductor wire and/or cristobalite.

2.4.2. Cause of the Blue Coloration

We evaluate the cause of the blue glass, considering whether the blue coloration is due to the presence of specific compounds that modify the color of the glass (e.g., copper), or to other physical features. The bulk composition of the fulgurite is similar to other fulgurites, which eliminates the possibility of idiochromaticity being the cause for the unique color. In addition, the amount of typical abundances of key trace elements does not suggest any allochromatic effects when contrasted to other glasses without blue hue. For example, the Torre de Moncorvo fulgurite (Crespo et al. 2009) had >20 ppm Cu, similar to the Marquette fulgurite, but did not have a blue hue. Additionally, while Ni and Co could provide a blue coloration, tektites have as much or more of both elements (Taylor and Mclennan 1979) but also lack a blue hue.

We propose the blue coloration in this fulgurite is due to pseudochromatic effects, namely Rayleigh scattering by nanoscale spherules within the glassy matrix, as demonstrated by the TEM images (Figures 2.5-2.7). Thus, the blue coloration within the Marquette fulgurite is likely akin to the blue coloration of blue Zhamanshinites as described by Zolensky and Koeberl (1991): nanospheres formed from separation of immiscible components within a melt. The blue zhamanshinites also had spherules with a similar size (~100 nm). Unlike the blue zhamanshinite samples, the spherical inclusions within the Marquette fulgurite are not rich in
phosphorus but instead are silica-rich with a lighter average atomic number. While these impurities could impart some color to the fulgurite, none account for the blue color. It is more probable these inclusions create the physical conditions conducive to Rayleigh scattering of light and give the fulgurite its blue color.

2.4.3. Spherules in impact glasses and in fulgurites: similarities between causal phenomena

Nanoscale and microscale spherules embedded in glass are known in the impact literature and include carbonate-silicate (Graup 1999), sulfide-silicate (Grieve et al. 1981), metal-silicate (Brett 1967) and silicate-silicate immiscible melts (Pratesi et al. 2002). In the cases of carbonate-silicate, metal-silicate, and sulfide-silicate the spherules are often large (microns to sub-millimeters), likely due to the significant immiscibility of the two melts, which differ fundamentally by major element chemistry. In contrast, the silicate-silicate immiscible melts typically have much smaller spherules (~100 nm) that are capable of scattering light and affecting a blue hue. These smaller spherules appear to have origins consistent with longer, lower pressure heating timescales based on the presence of cristobalite, for instance in Libyan desert glass (Pratesi et al. 2002) and the blue zhamanshinites (Zolensky and Koberl 1991; Gornostaeva et al. 2017). This presents a conundrum: why might these glasses have taken longer to form smaller spherules? A possible answer may lie in the fact that these two melts do not differ nearly as much compositionally as the carbonate-, sulfide-, and metal-silicate melts, hence the separation of silicates from compositionally different silicates takes longer than separation of carbonates and other disparate materials from silicates.
The fact that the Marquette fulgurite bears immiscible melt spherules highlights yet another similarity between rocks affected by electric discharge and those affected by impact. With the recent claims of shocked quartz present in fulgurites (e.g., Carter et al. 2010a and b; Ende et al. 2012; Gieré et al. 2015; Chen et al. 2017), fulgurites are only the second natural material that has been demonstrated to bear shocked mineral phases. This arises as a consequence of the rapid deposition of energy into the target rock/soil during the lightning strike (e.g., Collins et al. 2012; Gieré et al. 2015), which parallels the rapid energy deposition of an impact.

The typical energy deposition of a lightning strike is similar to that of an impact, hence the similarities between the two materials produced by these phenomena might be expected to be analogous. An impacting rock that has not decelerated adequately through ablation (e.g., Mehta et al. 2018) strikes the Earth with an energy density of at least several megajoules per kg (MJ/kg), and similarly the energy density of a lightning strike is also high enough to completely vaporize quartz (>15 MJ/kg, Pasek and Hurst 2016). While the scale of a lightning strike is much smaller than that of a terrestrial impact, a zone of shocked material is plausible adjacent to the melt.

Materials affected by lightning and impacts also share some compositional and mineralogic similarities. For instance, baddeleyite is produced in some lighting material (Pasek et al. 2012) as a decomposition product of zircon, and it is present in impact glasses as well (El Goresy 1965). In addition, reduction of iron has been proposed as an intrinsic compositional change that comes about from both impacts and lightning (Sheffer 2007), and extremely reduced
minerals are well-known from fulgurites (Essene and Fisher 1986; Pasek et al. 2012) and impact glasses (Brett 1967).

Lightning may also cause molten glass to splash out from its strike zone, forming aerodynamic beads of glass termed exogenic fulgurites (Pasek et al. 2012). Such structures may parallel tektites (a typical impact glass), though on a much smaller, less wide-spread scale.

Fulgurites, hence, might serve as a good analog rock to impact rocks. Given that lightning strikes are ubiquitous (see Pasek and Block 2009) and can potentially occur across many varieties of soil, study of fulgurites may reveal petrologic and mineralogic characteristics that could be used for impact studies. Given the scale of the phenomena is much smaller and more widespread than impacts, some care must be taken in this approach, but fulgurites may serve as a useful proxy for impact-induced mineralogic and petrologic changes.

2.5. Conclusions

The intense blue coloration of the Marquette, Michigan fulgurite has only one natural analog: the blue zhamanshinites. The coloration is likely due to the presence of nanoscale spherules that scatter light. However, composition of the spherules does not appear to be important in the scattering of light, as the spherules within the zhamanshinite are more P-rich than the Si-rich fulgurite spherules. Instead, the size and ubiquity of the spheres in the matrix is likely critical to providing a blue hue to glass (Kawamura et al. 2017).

Although this investigation may seem to be narrow in focus, the investigation of the Marquette, Michigan fulgurite may provide some important clues on the Zhamanshin cratering
event (and thereby cratering as a whole). Specifically, the requirement for a longer duration heating event for the formation of a blue hue (3 hours) may suggest that the blue glass at Zhamanshin crater formed with the persistence of high-temperature heat for minutes to hours. Such a claim may be consistent with the small spherules (especially relative to other impact melt spherules, see section 2.3 above), given the similarity in composition between spherules and matrix glass. Shorter timescales appear to be unable to generate the conditions necessary for the development of spherules in fulgurites and, thereby, the immiscible melt and blue coloration, given that natural fulgurites thus far have not demonstrated consistent blue coloration. However, more examples would need to be collected of blue glasses to demonstrate the longer heating timescales. This work falls within a broader theme of investigating parallels between lightning-formed materials and impact materials, such as elemental reduction (Essene and Fisher 1986; Pasek 2008; Pasek and Block 2009) and the potential for forming shocked quartz by lightning (Carter et al. 2010a and b; Ende et al. 2012; Giere et al. 2015; Chen et al. 2017).
CHAPTER THREE

THERMAL OXIDATION OF SCHREIBERSITE IN METEORITES

3.1. Introduction

As discussed in chapter one, phosphorus is a key minor element that is important to the development of life on the Earth. However, in general phosphate minerals on the early Earth react poorly with organic compounds to facilitate phosphorylation under realistic prebiotic conditions. Pasek et al. (2013) and Gull et al. (2015) suggested that schreibersite can easily react with organics such as glycerol to form glycerol phosphate. Hence, iron-nickel-phosphide alloys can be considered as a major source of phosphorus in prebiotic chemistry on the early Earth.

Lauretta and Schmidt (2009) determined that phosphorus element from schreibersite on meteorite parent bodies sublimes into vapor at high temperatures (> 1000° C), while at 800° C, schreibersite oxides into graftonite (Fe₃(PO₄)₂). However, it is possible that during the heating of schreibersite on meteorites, schreibersite oxidizes to form non-iron lithophilic (silicate rock-loving) phosphate minerals. This reaction process is a solid-solid reaction on meteorite bodies, which occurs between a calcium silicate mineral (likely diopside CaMgSi₂O₆), schreibersite, and olivine at high temperature (> 500° C). The reaction is shown as below:
\[2\text{Fe}_3\text{P} + 3\text{CaMgSi}_2\text{O}_6 + 3\text{Mg}_2\text{Si}_4\text{O}_4 + 2.5\text{O}_2 = \text{Ca}_3(\text{PO}_4)_2 + 6\text{Fe} + 9\text{MgSi}_3\text{O}_6\]  (17)

The phosphorus content in the Earth’s crust is about \(10^{19}\) kg, and 3 ppm to 400 ppm of these phosphorus species were at one time schreibersite (Pasek 2017). Carbonaceous meteorites are phosphate dominant and contain minimal phosphide minerals, which only bear 1% P in schreibersite. Ordinary chondrites have about 10% phosphide minerals in total P. Enstatite chondrites and iron meteorites are phosphide rich, about 100% of their P species are metal phosphides (Pasek and Laruretta 2008; Pasek 2017). Considering that carbonaceous meteorites and ordinary meteorites are rich in olivine and calcium silicate minerals, a solid-state reaction between olivine, calcium silicate and iron-nickel phosphides is highly plausible on chondrite parent bodies.

The rate of the thermal oxidation of schreibersite is not clear. In this project, my aim is to determine this rate. Huss et al. (2006) demonstrated that metamorphic temperature is related with petrographic type. Hence, it is possible that the thermal record and metamorphic history of meteorite parent bodies can be clarified, if we can demonstrate the phosphide oxidation rate on chondrites.

3.2. Materials and Methods

3.2.1. Materials

Magnesium olivine sample mineral rock (\(\text{Mg}_2\text{Si}_4\text{O}_6\)) and diopside sample mineral rock (\(\text{CaMgSi}_2\text{O}_6\)) were bought from Ward’s Science Website, and iron phosphide (\(\text{Fe}_3\text{P}\)) was
purchased from *Alfa Aesar*. Ferric oxide powder (Fe$_2$O$_3$) and iron oxide powder (Fe$_3$O$_4$) were bought from *Alfa Chemicals* to make mineral redox buffers to control oxygen fugacity for the experiment, which is likely a function of logarithm oxygen fugacity ($\log f_{O_2}$) and the reaction temperature (Pasek 2015; Pasek 2017) (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1.** Oxygen fugacity dependence on mineral buffers as a function of temperature. MH is magnetite–hematite, WM is wustite–magnetite, and IW is iron–wüsite. (Pasek 2015; Pasek 2017b). The oxygen fugacity of lunar rock is also included (Sato et al. 1973).

To make sure the experiment’s oxygen fugacity was constrained primarily by mineral redox buffers; argon gas was utilized to fill in the furnace glass tube to flush out all atmospheric gas before the experiment started. This industrial grade argon gas (99.997% CGA-580) was
3.2.2. Methods

Two ceramic-based crucibles (one large, one small) were utilized to do this experiment. Mixed olivine, diopside and schreibersite powders were added into the small crucible. The molar ratios of these mixing olivine, diopside and schreibersite powders were 10:10:1. These powders were first pressed into a pellet and then put inside the small crucible. The large crucible was covered by a mineral redox buffer. Hematite-Magnetite (HM) mineral redox buffer was used in this experiment. The molar ratios of mineral composition of the buffer were 1:1.

The setup of two crucibles is shown as below (Figure 3.2). The small crucible was bottom up covered in the large crucible, so that it can provide a space to scrub oxygen gas from the mineral redox buffer in the large crucible into the small crucible. Furthermore, this small crucible can provide a space that avoid contaminate by mineral redox buffer.

![Figure 3.2](image)

**Figure 3.2.** Sample figure of experiment crucible placement method. The inner crucible holds the sample pellet (green), which is surrounded in the outer crucible by the redox buffer (pink).

In the experiment, the small pellet crucible and large HM buffer crucible were stacked
together, and put inside a 1.75-inch diameter × 40-inch length glass tube to heat. Heating temperatures and heating time for this experiment were 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C, for 1 or 5 days each.

A Thermo Scientific Lindberg Blue M HTF55000 Series Hinged Tube Furnace was used to heat the sample. The furnace was controlled by Thermo Scientific Lindberg Blue M CC58114A control consoles (120V/11A/1330W), which can ramp up to 1200 °C in 20 min (Figure 3.3).

Figure 3.3. Images of tube furnace for experiment work.

All the products were analyzed by 31P nuclear magnetic resonance (NMR), scanning
electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), and powder X-ray diffraction (XRD) after heating.

A Bruker D8 ADVANCE Powder X-Ray Diffractometer from the Department of Chemistry, University of South Florida was utilized to identify the formation of any new phosphorus products from the experiments. This X-Ray Diffractometer has a LYNXEYE high-speed 1-D detector and DAVINCI TWIN-TWIN optics. Bruker EVA (LUATION) software was used to analyze and image XRD data.

Furthermore, all sample products were used by scanning electron microprobe analysis in the College of Art, Science & Education at Florida International University to show the sample crystal image. This scanning electron microprobe analysis was performed by JEOL-IT-500hr Field Emission 2018. In addition, an Energy Dispersive X-Ray Spectrometry, performed by Bruker -Quantax- SDD-EDS, was utilized to demonstrate the elemental percentage in our sample product. Sample images were made by Esprit software 2018.

For further investigation of the phosphorus species during the reactions, the samples were studied by $^{31}$P-NMR analysis. As described in chapter three, $^{31}$P-NMR was run on a Unity INOVA spectrometer with a variable temperature controller. The INOVA 400 runs $^{31}$P-NMR at 161.84 MHz, and 6000 normal scans were run with a 1 second delay between acquisitions. The spectral width was 200 ppm and running temperature was at 25 °C.
3.3. Results

X-Ray Diffractometry showed that due to high temperature heating, the sample products were different than samples before heating (Figure 3.4). At 1000°C, only olivine and diopside peaks were dominant, and schreibersite peaks were reduced compared with room temperature samples.

Table 3.1 shows the average composition of sample product at different heating temperatures by EDS analysis. Simultaneously, scanning electron microscopy determined that at room temperature, schreibersites were easily found in the sample products. However, at 600°C and 1000°C reaction temperature, schreibersite disappeared in the sample mixtures. Furthermore, at elevated temperatures (1000°C), the major product minerals in the sample products were olivine, diopside, iron and calcium phosphate (Figure 3.5).

![Figure 3.4](image)

**Figure 3.4.** Powder X-Ray Diffraction patterns for schreibersite-olivine-diopside oxidation (molar ratio 1: 10:10) sample product at a) room temperature. Olivine (expressed by black color
O) and diopside (expressed by orange color D) are dominate in both two patterns.

![Figure 3. 4 (continued). Powder X-Ray Diffraction patterns for schreibersite-olivine-diopside oxidation (molar ratio 1: 10:10) sample product at a) room temperature. Olivine (expressed by black color O) and diopside (expressed by orange color D) are dominate in both two patterns. However, schreibersite (expressed by pink color S) disappear at 1000 °C and an unknown mineral (expressed by red color U) is present instead.](image)

$^{31}$P-NMR was used to determine the type of P species at different reaction temperatures. At the low reaction temperatures (500 °C and 600 °C), hypophosphate species (P$_2$O$_6^{4-}$), hypophosphite species (H$_2$PO$_2^-$), phosphite species (HPO$_3^{2-}$) and orthophosphate species (PO$_4^{3-}$) are present. Furthermore, polyphosphate species, like pyrophosphate species (P$_2$O$_7^{4+}$) and triphosphate species (P$_3$O$_{10}^{5+}$) are also produced. As temperature elevate to 700 °C, hypophosphate species, hypophosphite species and polyphosphate species all disappeared, and only phosphite and phosphate species are present. Moreover, pyrophosphate reappears again
Table 3.1. Major element abundances (in wt%) in the sample product at different reaction temperatures. Note: “BDL” is below the detected limits of the instruments used.

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<td>0.12</td>
<td>0.12</td>
<td>0.02</td>
<td>0.02</td>
<td>0.12</td>
<td>0.12</td>
<td>0.08</td>
<td>0.16</td>
<td>0.10</td>
</tr>
<tr>
<td>Na</td>
<td>0.19</td>
<td>0.05</td>
<td>0.23</td>
<td>0.15</td>
<td>0.19</td>
<td>0.21</td>
<td>0.17</td>
<td>0.06</td>
<td>0.07</td>
<td>0.39</td>
<td>0.15</td>
</tr>
<tr>
<td>O</td>
<td>34.61</td>
<td>35.56</td>
<td>33.49</td>
<td>35.17</td>
<td>27.64</td>
<td>24.83</td>
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<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
**Figure 3.** Scanning Electron Microscopy images for schreibesite (SCH)-olivine (OL)-diopside (DI) oxidation (molar ratio1:10:10) sample product at a) room temperature, b) 600°C and c) 1000°C. Olivine and diopside were abundant appear in all images. Unknown P species minerals (expressed by P) occurred at 600°C reaction temperature. Moreover, iron (expressed by Fe) and calcium phosphate (expressed by CaP) emerged when temperatures were elevated to 1000°C.
Figure 3. 5 (continued). Scanning Electron Microscopy images for schreibesite (SCH)-olivine (OL)-diopside (DI) oxidation (molar ratio1:10:10) sample product at a) room temperature, b) 600°C and c) 1000°C. Olivine and diopside were abundant appear in all images. Unknown P species minerals (expressed by P) occurred at 600°C reaction temperature. Moreover, iron (expressed by Fe) and calcium phosphate (expressed by CaP) emerged when temperatures were elevated to 1000°C.
Figure 3.5 (continued). Scanning Electron Microscopy images for schreibesite (SCH)-olivine (OL)-diopside (DI) oxidation (molar ratio 1:10:10) sample product at a) room temperature, b) 600°C and c) 1000°C. Olivine and diopside were abundant appear in all images. Unknown P species minerals (expressed by P) occurred at 600°C reaction temperature. Moreover, iron (expressed by Fe) and calcium phosphate (expressed by CaP) emerged when temperatures were elevated to 1000°C.

When temperatures were increased to 800°C. While temperature continually increased, phosphite and pyrophosphate decreased to zero and only phosphate persists at extremely high temperatures (1000°C) (Figure 3.6).
Figure 3.6. $^1$H-decoupled $^{31}$P- NMR spectra for schreibeisite-olivine-diopside oxidation (molar ratio 1: 10:10) sample product at a) 500 C, b) 600 C. (spectra acquired at 161.8 MHz and pH 9). Peaks are identified as (1) orthophosphate, (2) phosphite, (3) pyrophosphate (4) triphosphate (5) hypophosphate and (6) hypophosphite. The reaction time for all experiments was 1 day and under argon.
Figure 3. 6 (continued). $^1$H-decoupled $^{31}$P- NMR spectra for schreibehsite-olivine-diopside oxidation (molar ratio 1: 10:10) sample product at, c) 700 C, d) 800 C (spectra acquired at 161.8 MHz and pH 9). Peaks are identified as (1) orthophosphate, (2) phosphite, (3) pyrophosphate (4) triphosphate (5) hypophosphate and (6) hypophosphite. The reaction time for all experiments was 1 day and under argo
Figure 3. 6 (continued). $^1$H-decoupled $^{31}$P- NMR spectra for schreibeisite-olivine-diopside oxidation (molar ratio 1:10:10) sample product at e) 900 C, f) 1000 C. (spectra acquired at 161.8 MHz and pH 9). Peaks are identified as (1) orthophosphate. The reaction time for all experiments was 1 day and under argon.
3.4. Discussion

XRD analyses, SEM-EDS analysis and $^{31}$P-NMR analyses reveal the pathway of schreibersite’s transformation with olivine and calcium silicate minerals on parent meteorite bodies at high temperatures. Previous researchers reveal that schreibersite corroded into P species on highly aqueously altered carbonaceous chondrites at low temperatures (< 300 °C) (Pasek and Lauretta, 2005) or sublimed into gas phase at high temperature (> 1000 °C) (Lauretta and Schmidt, 2009). In contrast to the schreibersite sublimation process, I instead propose a solid-state reaction where schreibersite is oxidized into phosphate minerals by calcium silicate (likely diospide, CaMgSi$_2$O$_6$), and olivine.

Furthermore, Figure 3.7 provides the relationship between major element weight percentage (Fe and P) in the products at different temperatures. As temperature increased, iron phosphide alloys rapidly decomposed. Figure 3.7 same reveals that as schreibersite decomposed on meteorites, some of them sublimed. However, the other parts of these phosphides transformed into phosphate minerals and were preserved on meteorite parent bodies. All these results contrast with Lauretta and Schmidt (2009), in which it was reported that schreibersite sublimed at elevated temperature (1000° C).
Figure 3.7. Scatter plot graphs about iron (Fe), phosphorus (P) and silicon (Si). Experimental data (points) is compared to a simple linear fit (red line). All data of graphs are selected from Table 3.1.
$^{31}$P-NMR analyses determined the trace amount of schreiberite oxidation with silicate minerals. Table 3.2 shows yields (%) calculation of this schreiberite oxidation at different reaction temperatures. Figure 3.8 provides the P species percentage changing at different temperatures. The P species changing by schreiberite oxidation is surprising. Rare P species, like hypophosphate, hypophosphite and polyphosphates have a high degree of diversity of all phosphorus species in sample products at low reaction temperatures (500 °C and 600 °C). These uncommon P compounds transform into phosphite species as the temperature elevates. The percentage of phosphite is greater than phosphate at 700 °C and 800 °C reaction temperatures (Table 3.2 and Figure 3.8). When temperatures are over 800 °C, phosphite transforms into orthophosphate. In addition, some orthophosphates react into pyrophosphate. The phosphorus species in schreiberite oxidation process with metamorphic minerals is shown below (Figure 3.9).

**Table 3.2.** $^{31}$P-NMR based yields (%) calculation of the schreiberite oxidation process with olivine and diopside at different temperatures.

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
<th>900 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate</td>
<td>35.97%</td>
<td>62.89%</td>
<td>34.72%</td>
<td>39.53%</td>
<td>97.09%</td>
<td>100%</td>
</tr>
<tr>
<td>Phosphite</td>
<td>16.19%</td>
<td>16.98%</td>
<td>65.28%</td>
<td>58.50%</td>
<td>1.94%</td>
<td>0</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>16.55%</td>
<td>9.43%</td>
<td>0</td>
<td>1.97%</td>
<td>0.97%</td>
<td>0</td>
</tr>
<tr>
<td>Triphosphate</td>
<td>11.87%</td>
<td>4.40%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>hypophosphate</td>
<td>11.87%</td>
<td>4.40%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>hypophosphite</td>
<td>7.55%</td>
<td>1.89%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3.8. 100 % stacked column figure of different P species $^{31}$P-NMR based yields (%) of the schreibersite oxidation process with olivine and diopside at different temperatures level.

Figure 3.9. The changing of different phosphorus species in schreibersite oxidation process at temperature elevation.
The reduced oxidation state phosphorus compounds (especially phosphite) play a significant role in origin of life (Pasek 2008). Phosphite is known to occur in fulgurites (Pasek and Block 2009; Hess et al. 2021), in rivers and lakes (Pasek et al. 2014), in serpentinite minerals (Pasek et al. 2020) and in impact glasses (Pasek et al. 2021, in review). The transformation among schreibersite, olivine and calcium silicate minerals on meteorite bodies demonstrates that it is plausible that solid-state reactions are active on meteorite parent bodies. Furthermore, these iron phosphide oxidations with silicate minerals occurred in one day, which is in agreement with Rambaldi and Wasson (1981). Rambaldi and Wasson proposed that schreibersite oxidized rapidly with Mg and Ca silicate minerals. Additionally, contrasted with Lauretta and Schmidt (2009), schreibersite did not oxidize directly into phosphate. Instead schreibersite transformed into phosphite and phosphate with a series of complex processes with temperature increased, which is associated with some other rare phosphorus species during the reaction. At the highest temperatures, phosphite compounds oxidized into phosphate species. Simultaneously, some of the phosphate polymerized into pyrophosphate, as it did in the struvite decomposition process in chapter three. Such research reveals that it is probable that there is a new third pathway for schreibersite oxidation on meteorites and the early Earth.

3.5. Conclusions

In this work, I investigated the thermal schreibersite oxidation process on chondrite meteorites. Schreibersite may corrode in water at mild temperatures (Pasek and Lauretta, 2005;
Gull et al. 2015), or phosphorus from schreibersite sublimes into volatiles at elevated temperature (Lauretta and Schmidt, 2009). We believe that there possibly is a third pathway, that schreibersite transforms into phosphate minerals by reacting with olivine and calcium silicate minerals on chondrite meteorites. Furthermore, the rate of this schreibersite oxidation process is suitably slow, thus it may provide some clues to evaluate the relationship between temperature and time in chondrite metamorphism.
CHAPTER FOUR
THE EVOLUTION OF STRUVITE ON PLANETARY ENVIRONMENTS

Note to Reader:

This chapter has been published: Feng, T., Gull, M., Omran, A., Abbott-Lyon, H., Pasek, M. A. (2021). The evolution of ephemeral phosphate minerals on planetary environments.

4.1. Introduction

Phosphorus (P) is a minor element on the Earth and is a key biogenic molecule that plays significant roles in the biochemistry of living organisms. These roles include cell metabolism, structure, and information storage (Pasek and Kee 2011; Gull 2014; Pasek 2019a). The cosmic abundance of P is about 0.007 atoms per silicon atom (Anders and Grevesse 1989) and the Earth is comprised of about $10^{22}$ kg phosphorus (~0.0017) with respect to total mass (Smith 1981; Nash 1984; McDonough and Sun 1995). In the solar nebula, the most prominent gaseous phosphorus compound are P, PO, PO₂ (Pasek 2019b), which at moderately high temperatures (700 - 1,100K) would have reacted with iron or nickel within dust grains to form metal phosphides (Fegley and Lewis 1980; La Cruz et al. 2016; Pasek 2019b). At comparatively lower temperatures (300-700K), these metal phosphides are oxidized and transformed into phosphate
minerals such as minerals within the apatite group \( \text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl}) \) and the mineral merrillite \( \text{Ca}_9(\text{Mg}, \text{Fe})(\text{Na}, \text{H})(\text{PO}_4)_7 \) (Zanda et al. 1994; Huss et al. 2006; Kimura et al. 2008; Pasek 2015; Jones et al. 2016). This occurs via reaction with common mafic minerals such as diopside \( \text{CaMgSi}_2\text{O}_6 \) and ferrosilite \( \text{FeSiO}_3 \), which would presumably be present in a typical meteorite, or on the early earth as a constituent of basalt. A simplified reaction (1) for this oxidation is shown below (Agosto et al. 1980):

\[
2\text{Fe}_3\text{P} + 3\text{CaMgSi}_2\text{O}_6 + 5\text{FeSiO}_3 = \text{Ca}_3(\text{PO}_4)_2 + 11\text{Fe} + 3\text{MgSiO}_3 + 8\text{SiO}_2
\]

Phosphorus minerals within many chondritic meteorites are dominated by these calcium phosphates including merrillite and the apatite mineral group (Van Schmus 1969). Iron meteorites and pallasites have other phosphate minerals, primarily due to phosphide oxidation with counterbalancing cations \( \text{Na}^+, \text{Fe}^{2+}, \text{Mg}^{2+} \), though most of the phosphorus is within phosphide minerals. These other minor phosphate minerals include sarcopside \( \text{Fe,Mn}_3(\text{PO}_4)_2 \), graftonite \( \text{Fe, Mn}_3(\text{PO}_4)_2 \), farringtonite \( \text{Mg}_3(\text{PO}_4)_2 \), stanfieldite \( \text{Ca}_4(\text{Mg,Fe})_5(\text{PO}_4)_6 \), brianite \( \text{Na}_2\text{MgCa}(\text{PO}_4)_2 \) and panethite \( \text{Na}_2\text{Mg}_2(\text{PO}_4)_2 \) (Fuchs 1969).

Hazen et al. (2008) introduced the concept of mineral evolution, which can be used to estimate the evolution of a planetary system, as well as the prebiotic mineral inventory of an early Earth-like planet (Hazen 2013). According to this model, phosphorus minerals on the prebiotic/Hadean Earth include the apatite mineral group, as well as rare Earth element
phosphates (e.g., monazite). Absent from this original list are any mineral that is not reported in Archean rocks, including ammonium and magnesium phosphate minerals. Such minerals may be at best ephemeral: forming under certain conditions on the early Earth, but readily degrading during diagenesis. We test this hypothesis below.

Recently it has been demonstrated that calcium phosphate minerals are readily altered by NH$_3^-$ and MgSO$_4$-bearing fluids (Burcar et al. 2016). In these experiments, urea served as a source of ammonium and helped facilitate the transformation of apatite into struvite. The overall reaction (2) is given below and strongly favors products (reaction K $\sim 10^{108}$):

$$2H^+ + 3(NH_2)_2CO + 60H_2O + 9Mg^{2+} + 10SO_4^{2-} + 2Ca_3(PO_4)_3OH =$$

$$6MgNH_4PO_4 \cdot 6H_2O \quad \text{(Struvite)} + \quad 10CaSO_4 \cdot 2H_2O \quad \text{(Gypsum)} + 3MgCO_3 \quad \text{(Magnesite)}$$

In solutions with less ammonium, the mineral newberryite (MgHPO$_4 \cdot 3H_2O$) is instead the major product of this alteration (Burcar et al. 2019). Alternatively, newberryite may form preferentially if the redox conditions of the fluid are not permissive to NH$_4^+$/NH$_3$ (Burcar et al. 2019). We do not examine more oxidizing conditions in this work, as extraterrestrial conditions are presumably sufficiently reducing that ammonia is stable (Pignatelli et al. 2017), and though the chemistry of N on the early earth is an open question (Stüeken et al. 2016), we assume likewise for the Hadean earth that ammonia would have been present at least in local environments.
Struvite (MgNH₄PO₄·6H₂O) is a prebiotic mineral (Lohrmann and Orgel 1971) that has been suggested to form a key reactive phosphate compound known as trimetaphosphate (P₃O₉³⁻) (Osterberg and Orgel 1972) that readily phosphorylates organics such as sugars under certain conditions (discussed further below). Furthermore, struvite is more soluble than the precursor apatite minerals, and it is hence likely that favorable conditions on the early Earth could facilitate phosphorylation via this mineral (Gedulin and Arrhenius 1994; Hazen 2013; Pasek et al. 2017). The work done by Burcar et al. (2016) could be relevant to the reactions that were likely active on the early, prebiotic Earth.

In addition to terrestrial systems, the chemical composition of many meteorites includes fluids that bear ammonia (Pizzarello and Williams 2012) and dissolved MgSO₄ (Fredriksson and Kerridge 1988). It is highly plausible that fluid alteration of meteorite parent bodies could result in the conversion of apatite into ammonium-bearing minerals such as struvite. However, there is no evidence of struvite or newberyite in the ancient geologic record and, intriguingly to date; it has never been detected in meteorites (Rubin, 1997; Hazen 2013; Gull and Pasek 2013). Within the altered carbonaceous chondrites, this lack of identification may be due to the general difficulty in finding phosphate minerals within these meteorites via microscopy (e.g., Nagy and Andersen 1964; Buchwald 1984; Brearley and Chizmadia 2005). Phosphate within carbonaceous chondrites and aqueously altered ordinary chondrites is dispersed either as nanoscale minerals too small for investigation by microscopy or that phosphorus may substitute at the atomic level for other elements within minerals (such as P for Si).
The plausible conditions leading to the formation of struvite is explored and motivates a study of the chemical pathway struvite (and other ammonium-bearing phosphate minerals) could possibly follow during thermal alteration/metamorphism. Studying such potential chemical routes would not only help in understanding the fate of struvite or other ammonium-bearing phosphate minerals in rocky planets and planetesimals but could also help identify whether such minerals ever appeared on meteorites. Additionally, such an investigation could determine their stability over geologic time in meteorite parent bodies. Furthermore, understanding these transformations could provide evidence of these minerals in the past in meteorites.

The transformations of struvite have been studied previously. It has been demonstrated that high temperatures and dry air conditions transform struvite into dittmarite (MgNH₄PO₄·H₂O) and/or newberyite (MgHPO₄·3H₂O), and subsequently into dimagnesium phosphate (MgHPO₄) (Cohen and Ribbe, 1966; Babic-Ivancic et al. 2006; Bhuiyan et al. 2008; Tansel et al. 2018; Bayuseno and Schmah 2020). The suite of reactions is given below (Reactions (4), (5) and (6)):

\[
\begin{align*}
\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} & \xrightarrow{\text{Loss of Water}} \text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O} \quad (4) \\
\text{Struvite} & \quad \text{Dittmarite} \\
\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O} & \xrightarrow{\text{Decomposition}} \text{MgHPO}_4 \\
\text{Dittmarite} & \quad \text{Dimagnesium Phosphate} \\
\end{align*}
\]

With a net process:
Hence, the thermal decomposition of struvite as well as newberyite under anaerobic conditions could help identify the ultimate products and plausible mechanism of mineral degradation. For instance, the heating of ammonium and acid phosphates is known to produce polyphosphates, through dehydration and condensation of phosphate tetrahedra. These polyphosphates include linear polyphosphates with the formula $P_nO_{3n+1}^{-(n+2)}$ (Van Wazer 1958; Cotton and Wilkinson, 1988; Albi and Serrano, 2016; Bhuiyan, 2019) as well as cyclic species. Polyphosphates, especially triphosphates and cyclic trimetaphosphate, have been employed extensively in the prebiotic synthesis of organophosphates (Ponnamperuma et al. 1963; Chung et al. 1971; Osterberg and Orgel 1972; Yamagata et al. 1991; Kolb and Orgel 1996; Zubay and Mui 2001; Cheng et al. 2002; Pasek et al. 2017). In the context of mineral evolution, such compounds could represent a tool for investigating the former presence of acid and ammonium phosphate minerals, as these ions could be chemical ‘fossils’ representing the loss of these minerals by heating as many are slow to hydrolyze. Polyphosphates form from heating acid phosphates to high temperatures, and thus their formation would not be unique to the heating of struvite. Nevertheless, polyphosphates could provide a useful constraint on the prebiotic inventory of the early earth (Arrhenius et al. 1997). However, such a case may only be valid if the polyphosphates—the simplest of which is the dimer, pyrophosphate—are also stable over long geologic timescales.

As a typical linear polyphosphate, pyrophosphate plays a significant role in
phosphorylation chemistry (Neuman et al. 1970; Gull 2014; Gopinath et al. 2015). However, even though previous research has investigated the way pyrophosphate was synthesized (Keefe and Miller 1996), there is no indication that pyrophosphate minerals are plausible on the early Earth (Hazen 2013), and they are certainly absent from the geologic record (Pasek et al. 2017).

We investigate here the stabilities of Mg- and NH$_4$-phosphates in heating under anaerobic and low-pressure conditions. We do this in the context of the general idea of mineral evolution proposed by Hazen et al.(2008). Mineral evolution is quite useful for understanding how minerals have changed with an evolving earth and with the evolution of life. In particular, the identification of the minerals of the Hadean earth provides needed guidance for the prebiotic chemistry reactions that are both plausible and that involve minerals that were like present at the time of the origin of life. For instance, reactions that employ Cu$^{2+}$ or U$^{6+}$ are unlikely to be prebiotically relevant, due to the highly oxidizing conditions needed for their formation. However, some minerals may be ephemeral—easily formed yet easily lost from the geologic record—hence their presence on a prebiotic earth may not be unreasonable. We evaluate this below.

We also investigate whether polyphosphates are also readily lost through heating, including heating in the absence of water. A common critique (Keefe and Miller 1996) of polyphosphates in prebiotic chemistry is that polyphosphate minerals are exceedingly rare in the geologic inventory of minerals (Pasek et al. 2017). We propose that this rarity is also due to ephermality: polyphosphates can be formed but do not persist under metamorphic processing.
In the present work we investigated polyphosphate stability at 0.5 atm under argon or were performed at low pressure (0.01 atm), allowing investigation of some of the chemical changes at lower pressure. The geochemical stabilities of polyphosphates not been studied extensively.

We briefly evaluate the potential for ammoniated phosphates to form preferentially in contrast to NH₄-bearing silicates. NH₄-bearing silicates such as clays are generally assumed to be a major mineralogic reservoir of ammonia in rocks (Stüeken 2016), but NH₄-bearing phosphates may be a reasonable reservoir. A full investigation of N-mineralogy and abundance is beyond the scope of this paper, but this section will endeavor to justify the presence of NH₄-bearing phosphates. In the case of simple NH₄⁺ competition, Mg-phosphates such as newberyite react with ammonium to form struvite, whereas silicates such as potassium feldspar react to form buddingtonite (an ammonium feldspar). Although clays may be more likely to trap ammonia (Stüken et al. 2016), thermodynamic data for NH₄-bearing clays is not available and hence buddingtonite is used as a proxy (Watkins 1981) with data for struvite from Faure (1997). The reaction:

\[ H^+ + KAlSi_3O_8 + MgNH_4PO_4*6H_2O = MgHPO_4*3H_2O + NH_4AlSi_3O_8 + K^+ + 3H_2O \]

(7)

provides the basis for the dominance diagram between struvite and buddingtonite, which is calculated using this thermodynamic data (Figure 4.1), but has not been demonstrated in laboratory or natural settings. Struvite is preferred in solutions with high pH and high K⁺. At the conditions of the ocean (pH ~ 8 and K⁺ 0.01 M) struvite and buddingtonite are roughly
equivalently important to $\text{NH}_4^+$ capture, and at higher pH (in fluids with serpentinizing rock such as in chondrite interiors) struvite is dominant.

![Diagram of pH and struvite stability](image)

**Figure 4.1.** The dominance diagram for the reaction of struvite with potassium feldspar to give newberyite and buddingtonite.

In Burcar et al. (2016) the formation of struvite from apatite occurs through the reaction of apatite with Mg sulfate and urea, which serves as an ammonia source (reaction 2). Such a reaction is highly exergonic and proceeds effectively to completion as a function of urea molarity. More generally, the reaction of ammonia, CO$_2$, Mg sulfate, and apatite to give struvite is:

$$4\text{H}_2\text{O} + 2\text{CO}_2 + 3\text{NH}_4^+ + \text{Ca}_5(\text{PO}_4)_3\text{OH} + 3\text{MgSO}_4*7\text{H}_2\text{O}$$

$$= 3\text{MgNH}_4\text{PO}_4*6\text{H}_2\text{O} + 3\text{CaSO}_4*2\text{H}_2\text{O} + 2\text{CaCO}_3 + 3\text{H}^+$$

(8)

This reaction favors struvite formation at high $\text{NH}_4^+$ and CO$_2$, and high pH (Figure 4.2). For the early Earth with a higher CO$_2$ partial pressure (Toner and Catling 2020), struvite is hence accessible from apatite at neutral to alkaline conditions at 1 mM ammonium concentrations. On chondritic meteorite parent bodies where pressures are likely lower, an activated ammonium
source such as urea may be required to promote the reaction.

**Figure 4.2.** The dominance diagram for the reaction of apatite to give struvite at varying CO$_2$, pH, and ammonium molarities. The lines correspond to $10^{-4}$ atm CO$_2$ (blue), $10^{-2}$ atm CO$_2$ (orange), and 1 atm CO$_2$ (gray).

The above scenario is contingent on sources of ammonia on either an early earth or on meteorite parent bodies. The degree to which nitrogen was present in the early earth system is an open discussion (Atreya et al. 1980; Summers 1999; Som et al. 2016; Stüeken et al. 2016), where the average ammonium global concentration is capped by the total nitrogen budget of the earth at around ~0.01 M (if all atmospheric nitrogen is reduced to NH$_3$, as per Gull and Pasek (2013)). Local enrichments are plausible, for instance through cyano group hydrolysis (Lago et al. 2020), and hence higher ammonium concentrations are feasible in early environments.

On chondritic parent bodies, the amount of ammonium varies substantially between individual meteorites. Ammonium is most abundant in the CR2 chondrite GRA 95229, where it is present at 19 µmol/g (Pizzarello and Holmes 2009). The water content of CR meteorites varies from a few percent to up to 10% by mass (Weisberg et al. 1993). Correspondingly, ammonium concentrations in excess of 1 M are feasible.
The strongest lines of evidence for ammonium in meteoritic materials comes from studies of the largest asteroid Ceres. Ammonium-bearing phyllosilicates are suggested to be widespread across Ceres’ surface based on VIR data from the Dawn Mission (De Sanctis et al. 2015; Ehlmann et al. 2018), with a source that may either be organic or ices. Given that the location of many carbonaceous chondrite parent bodies is likely proximal to Ceres, such a result highlights the presence of ammonia as a mineralogic component in the solar system and in meteorites, though ammoniated minerals have not been reported as a meteoritic constituent.

To this end, ammoniated phosphates are feasibly produced both on the early earth and on meteorite parent bodies. This work explores whether such minerals could remain in the rock record of the early earth, or if they could be present on meteorite parent bodies, most of which have experienced some degree of thermal metamorphism.

4.2. Materials & Methods

4.2.1. Materials

Ammonium phosphate ((NH$_4$)$_2$HPO$_4$, dibasic, 98%), sodium phosphate (Na$_2$HPO$_4$, dibasic, 98%), calcium sulfate dihydrate (CaSO$_4$·2H$_2$O, 98%), sodium hydroxide (NaOH, 98.5%), deuterated water (D$_2$O, 99.8 atom % D) and calcium carbonate (CaCO$_3$, 98%) were purchased from Acros Organics, while magnesium chloride anhydrous (MgCl$_2$, 99%) and magnesium pyrophosphate (Mg$_2$P$_2$O$_7$, 99%) were from Alfa Aesar, and ammonium chloride (NH$_4$Cl, 99.5%) was from Fisher Chemicals. Ethylenediaminetetraacetic acid powder (H$_4$EDTA, 99.5%) was from Sigma-Aldrich.

Deionized water (DI H$_2$O) used in the experimental studies was purified in house using a
Barnstead (Dubuque, IA) Nanopure Diamond Analytical combined reverse osmosis-deionization system, providing water with a resistivity of 18 MΩ. Industrial grade argon gas (99.997%, CGA-500) was purchased from Airgas.

Struvite was prepared by the method as previously reported by Gull and Pasek (2013) whereas newberyite was synthesized by the method described by Frost et al.(2012). In each reaction, the mineral was separated as a white precipitate via filtration, dried, and stored in a sealed container. The structures of the minerals were confirmed using Raman spectroscopy (Laetsch and Downs 2006) and Powder X- Ray diffractometry (Figures 4.3 & 4.4, where both techniques are finger-printing techniques for mineral identification). The median grain size of this synthetic material was 50 μm.

The syntheses are given below (9 and 10):

\[
\text{MgCl}_2 + (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{Cl} + 6\text{H}_2\text{O} \rightarrow 3\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \quad \text{(Struvite)} \quad \downarrow + 2\text{NH}_4\text{Cl} \\
\text{(9)}
\]

\[
\text{MgCl}_2 + \text{Na}_2\text{HPO}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \quad \text{(Newberyite)} \quad \downarrow + 2\text{NaCl} \\
\text{(10)}
\]

where the down arrow implies a precipitate.
Figure 4. Raman Spectra for a) struvite and b) newberyite with comparison to the spectroscopic standards from the RRUFF database (RRUFF ID: R050511, RRUFF ID: R050513).
Figure 4.4. Powder X-Ray Diffraction patterns for a) struvite and b) newberyite with comparison to the diffractometry standards from RRUFF database (RRUFF ID:R050511, RRUFF ID:R050513).
4.2.2. Methods

A ceramic-based crucible furnace was used for studying the thermal decomposition reaction of the minerals. In the first series of reactions, 2.00 g of powdered struvite was placed within the crucible. In order to generate anoxic conditions and to establish a pressure of 0.1 MPa (1 atm), the furnace tube was flushed with argon gas three times to make sure the reaction conditions inside the glass furnace tube were minimally oxic. For vacuum experiments, the furnace was placed under vacuum prior to sealing that achieved pressures inside the furnace of <0.01 atm. Struvite samples were heated at 70 °C, 100 °C, 130 °C, 170 °C, 200 °C, and 500 °C for 6 hours in both argon and vacuum. Similar conditions were repeated for the second series of reactions in which powdered newberyite mineral was used as a starting material.

About 1.11 g (0.005 mol) of magnesium pyrophosphate (Mg₂P₂O₇) and a calcium mineral (calcite, CaCO₃, 3.00 g, 0.03 mol; or gypsum, CaSO₄·2H₂O, 5.16 g, 0.03 mol) in dried powdered forms, were mixed using a mortar and pestle. The subsequent powdered mixture was introduced into the ceramic tube furnace purged with argon gas or heated under vacuum. The reactions were carried out at 200 °C for 6 hours to test for the possibility of further degradation of pyrophosphate. The mole ratios of calcite or gypsum to magnesium pyrophosphate in the experiment were 6:1 respectively. Similar reaction conditions were used for experiments where the mole ratios of calcite or gypsum to magnesium pyrophosphate in the experiment were 12:1.

The samples were heated inside a 1.75-inch diameter × 40-inch length glass tube within a ceramic crucible. A Thermo Scientific Lindberg Blue M HTF55000 Series Hinged Tube Furnace was used to heat the sample. The furnace was controlled by Thermo Scientific Lindberg Blue M
CC58114A control consoles (120V/11A/1330W), which can ramp to 1200 °C in 20 min (Figure 3.3).

All the products were analyzed by $^{31}$P Nuclear Magnetic Resonance (NMR), Thermogravimetric Analysis (TGA), Laser Raman Spectroscopy and Powder X-Ray Diffraction (XRD) after heating.

An Enwave Opt. Inc. (Model No. EZI-785-A2) Laser Raman Spectroscopy was utilized to determine the sample product after heating. The Raman microscope was a Leica DM 300 microscope equipped with three objective lenses ($\times 4/0.1$ NA $\times 10/0.25$ NA and $\times 40/0.65$ NA). Every mineral sample analysis had five replicates, with each integration time varying between 30 s to 60 s by using a 785 nm Laser (300 mW) (Pasek and Pasek 2018). To determine the sample product, Crystal Sleuth software was utilized (Laetsch and Downs 2006) and was compared with the data provided in RRUFF database (Lafuente et al. 2015).

A BTX-402 benchtop XRD was utilized to study the formation of any new products from the sample decomposition experiments. A calibrated ion chamber, Ludlum Model 9-3 Radiation Ion Chamber, was obtained for the measurements which measured radiation level counting range of 0 to 2000 $\mu$Sv/Hr.

For further investigation of the generation of pyrophosphate minerals during the reactions, the samples were studied by $^{31}$P-NMR analysis. The $^{31}$P-NMR parameters were similar as reported previously (Gull and Pasek 2013; Gull et al. 2015; La Cruz et al. 2016; Herschy et al. 2018). For $^{31}$P-NMR analysis, the sample was air dried at room temperature under a fume hood
in a watch glass (the drying process was also investigated but did not show polyphosphate formation in this procedure using sodium phosphate). The dried reaction mixture was mixed with D₂O and EDTA to dissolve the powders completely (visually inspected). ³¹P-NMR was run on a Unity INOVA spectrometer with a variable temperature controller. The INOVA 400 runs ³¹P-NMR at 161.84 MHz, and 450 normal scans were run with a 1 second delay between acquisitions. The spectral width was 200 ppm and running temperature was at 25 °C.

Struvite and newberyite decomposition studies were further investigated by Thermogravimetric Analysis (TGA). The equipment used was a Shimadzu TGA-50 series with maximum temperature of 950 °C and a 20 mg counterbalance. Samples were run in aluminum pans under argon with a flow rate of 30 ml/min and the heating rate was 10 °C per minute.

4.3. Results

4.3.1. Struvite decomposition result

Raman Spectroscopy showed that on raising the temperature, struvite and newberyite both rapidly (less than six hours at 200 °C) volatilized and decomposed, yielding either new mineral phases (Figure 4.5) or an amorphous material from which the Raman scattering ceased and from which XRD revealed no definitive patterns.
Figure 4.5. Raman spectra for a) struvite and b) newberyite heated under argon at: 1) room temperature, 2) 70 °C, 3) 100 °C, 4) 130 °C, 5) 170 °C, 6) 200 °C. Each reaction was run for 6
h.

Struvite (Figure 4.6a) and newberyite (Figure 4.6b) TGA data revealed that struvite and newberyite both decomposed rapidly due to heating. The total remaining mass after heating the struvite sample during TGA was about 45.60%, and these results were consistent with the previously reported results of the total remaining mass after sample heating, i.e., 50.41% from Novotny (2011) and 48.98% from Frost et al. (2004). By using TGA data the final mineral composition after struvite heating could be calculated via equation (i):

\[ A = \frac{M_p}{M_0} \times 100 \% \quad \text{or} \quad M_p = A \times M_0 \quad (i) \]

where A is the total remaining mass percentage after sample heating, \( M_p \) is the molar mass of the product sample (g/mol), and \( M_0 \) is the molar mass of the reactant sample (g/mol).

Figure 4.6. TGA and DTG graphs for struvite decomposition from room temperature to 500 C under argon.
Figure 4.6 (continued). TGA and DTG graphs for newberyite decomposition from room temperature to 500 C under argon.

In the reaction studies, A = 45.60 %, the $M_0$ of struvite (245 g/mol), corresponds to a sample product molar mass $M_p = A \times M_0 = 45.60\% \times 245$ g/mol = 111.72 g/mol. This mass was found to be consistent with struvite transforming into magnesium pyrophosphate (molar mass Mg$_2$P$_2$O$_7$, 222 g/mol, half mass is 111 g/mol) with the reaction formula shown as below:

$$2\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{Decomposition}} \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 \uparrow + 7\text{H}_2\text{O} \uparrow$$

(11)

where the up arrows imply loss as vapor. This result contrasts with Bhuiyan et al.(2008), in
which it was reported that the final product of the thermal decomposition of struvite was magnesium acid phosphate, due to the lower temperatures used by Bhuiyan et al. (2008).

Newberyite had similar decomposition products as that of struvite. The reaction is shown as below:

\[ 2\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \xrightarrow{\text{Decomposition}} \text{Mg}_2\text{P}_2\text{O}_7 + 4\text{H}_2\text{O} \uparrow \]  

(12)

Figure. 4.6 shows the time derivative TGA graph for struvite and newberyite decomposition. For struvite, the degradation process started at around 70 °C, from 70 °C - 150 °C it decomposed rapidly; after 150 °C, the decomposition rate declined, as struvite had already volatilized much of its ammonia, and the rest of the reaction was the slower loss of water. Newberyite likewise exhibited rapid decomposition, though its decomposition was separated into at least two events, as is visible by the derivative of the TGA (the DTG).

The kinetics of struvite decomposition from the TGA were calculated using the rate of mass loss estimated from the TGA (e.g., the DTG). From these values, rate constants of reactions \( k \) were determined. The simplest approach is a fit to the Arrhenius equation (following the procedure of Bhuiyan et al. (2008) for \( \text{dm/dt} \) as a function of \( \text{dm/dT} \) and \( \text{dT/dt} \) from 70 °C -150 °C (Figure 4.7) as given below (equation (ii)):

\[ k = A e^{-\frac{E_a}{RT}} \]  

(ii)
where $R$ is the gas constant ($R=8.314 \text{ J/(mol} \cdot \text{K})$), $T$ is the temperature in Kelvin, $E_a$ is the activation energy in Joules, and $A$ is the pre-exponential factor (s$^{-1}$). The Arrhenius equation is an empirical formula best used to describe isothermal, first-order reactions and it can be expressed logarithmically to solve for the activation energy of a reaction as shown in Eq. (iii) and(iv):

\[
\ln k = \ln A - \frac{E_a}{RT} \quad \text{(iii)}
\]
\[
\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \quad \text{(iv)}
\]

**Figure 4.7.** Degradation rate graphs for struvite from 70 C -150 C. Experimental data (points) is
compared to a simple Arrhenius fit (black line) and an Arrhenius-style fit with a temperature dependent pre-exponential (red line)

Figure 4.7 provides the relationship between the natural logarithm of the rate constant and the reciprocal reaction temperature of struvite degradation from 70 °C to 150 °C. From this relationship, it is clear that the reaction is not perfectly first-order. This would be expected as rates of these reactions are dependent on grain size and gas flow rates, which are often TGA-specific. Additionally, TGA experiments inherently rely upon dynamic temperature changes rather than isothermal conditions. However, the Arrhenius fit provides an initial estimate of the stability of these phases as a function of temperature by providing an estimate of the activation energy. The activation energy for struvite decomposition (done in triplicate) from 70 °C to 150 °C was equal to 49.2 kJ/mol (via (iv)). Alternatively, several researchers have proposed that an Arrhenius-style fit with a temperature-dependent pre-exponential (equation (v)) can be utilized to fit thermally-stimulated solid-state reactions (Cai et al. 2008, 2009).

\[ k = A_0 T^n e^{-\frac{E_a}{RT}} \]  

(v)

This Arrhenius-style fit (Fig. 3.8) with a temperature-dependent pre-exponential does significantly better at capturing the curvature of the data presented. However, this fit should be taken as mostly an empirical model with limited significance being ascribed to the parameters \( A_0 \) and \( E_a \), as these do not have the same meaning as those presented in equations (iii) and (iv) with respect to free energy calculations.

These results contrast to Bhuiyan et al.(2008), who reported a 4.6 kJ/mol activation energy for struvite decomposition (at 20 °C per min) and a 6.8 kJ/mol activation energy when
struvite decomposes at 5 °C /min, and when heated under N₂. However, due to differences in heating rate, grain size, and gas flow rates between this work and Bhuiyan et al. (2008), and the variation in calculating the fit (equation v), this difference should be expected. The salient finding here is that the rate of degradation is sufficiently fast under low temperatures that struvite—if present—should decay rapidly when heated.

³¹P-NMR was utilized to determine if the products contained pyrophosphate. The ³¹P-NMR of both struvite and newberyite samples that were heated to 200 °C revealed a majority of the P was phosphate, though pyrophosphate and triphosphate were also present (Figure 4.8). At elevated temperatures (500 °C), the major product in both struvite and newberyite’s thermal decomposition seemed to be magnesium pyrophosphate with appreciable triphosphate. Struvite appeared to generate more pyrophosphate than newberyite. The products yield of the decomposition reactions of each mineral is shown as Table 4.1, as calculated by NMR peak integration.

Figure 4. 8. ¹H-Decoupled ³¹P-NMR spectra for struvite and newberyite decomposition under Argon (spectrum acquired at 161.8 MHz and pH 9). The reaction time for all experiments was
6 hours. a). Struvite sample decomposed after heating after 200 C. Peaks are identified as (1) orthophosphate, (2) pyrophosphate and (3) triphosphate.

Figure 4. 8 (continued). $^1$H-Decoupled $^{31}$P-NMR spectra for struvite and newberyite decomposition under Argon (spectrum acquired at 161.8 MHz and pH 9). The reaction time for all experiments was 6 hours. b). Struvite sample decomposed after heating after 500 °C. c).
Newberyite sample after heating after 200 °C. Peaks are identified as (1) orthophosphate, (2) pyrophosphate and (3) triphosphate.

Figure 4. 8 (continued). $^1$H-Decoupled $^{31}$P-NMR spectra for struvite and newberyite decomposition under Argon (spectrum acquired at 161.8 MHz and pH 9). The reaction time for all experiments was 6 hours. d). Newberyite sample decomposed after heating after 500 °C. Peaks are identified as (1) orthophosphate, (2) pyrophosphate and (3) triphosphate.

Table 4. $^{31}$P-NMR based yields (%) calculation of the thermal decomposition products of struvite and newberyite minerals 200 °C and 500 °C under Argon and vacuum. The yields were calculated by peak integration method as done previously (Gull and Pasek 2013, Pasek et al. 2013).

<table>
<thead>
<tr>
<th>Decomposition Environment Conditions</th>
<th>Argon</th>
<th>Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>200 °C</td>
<td>500 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite Newberyite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>98.5%</td>
<td>94.0%</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>0.3%</td>
<td>4.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite Newberyite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>67.1%</td>
<td>92.6%</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>22.1%</td>
<td>5.6%</td>
</tr>
</tbody>
</table>
4.3.2. Pyrophosphate Decomposition results

$^{31}$P-NMR analysis showed that magnesium pyrophosphate salts were partially transformed into orthophosphate salts after reacting with calcite or gypsum (Figure 4.9). In most cases, a non-zero amount of polyphosphate were also produced, including peaks corresponding to both triphosphate and trimetaphosphate, as well as larger polyphosphates with peaks that did not overlap with either of these tri-P species, implicating longer polyphosphate production (Table 4.2).

![Figure 4.9](image-url)

**Figure 4.9.** $^1$H-decoupled $^{31}$P-NMR spectra for a) magnesium pyrophosphate and calcite, in molar ratio of 1:6, heated after 200 °C. The phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under Argon.
Figure 4.9 (continued). $^1$H-decoupled $^{31}$P-NMR spectra for b) magnesium pyrophosphate and calcite, in molar ratios of 1:12, heated after 200°C, (spectra acquired at 161.8 MHz and pH 13), and c) magnesium pyrophosphate and gypsum, in molar ratio 1:6, heated after 200°C. (spectra acquired at 161.8 MHz and pH 9). The phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under Argon.
Figure 4.9 (continued). $^1$H-decoupled $^{31}$P- NMR spectra for d) magnesium pyrophosphate and gypsum, in molar ratio 1:12, heated after 200 °C. (spectra acquired at 161.8 MHz and pH 9). The phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under Argon.

Table 4.2. $^{31}$P-NMR based yields (%) calculation of magnesium pyrophosphate and calcium minerals (Calcite and Gypsum) retransformation process at 200 °C under Argon and vacuum, the mole ratios of calcium minerals to magnesium pyrophosphate in the experiment were 6:1 and 12:1.

<table>
<thead>
<tr>
<th>Reaction Environment Conditions</th>
<th>Argon</th>
<th>Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Minerals</td>
<td>Calcite</td>
<td>Gypsum</td>
</tr>
<tr>
<td>Molar ratios with Mg$_2$P$_2$O$_7$</td>
<td>6:1</td>
<td>12:1</td>
</tr>
<tr>
<td>Phosphate</td>
<td>28.5%</td>
<td>29.8%</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>60.6%</td>
<td>58.5%</td>
</tr>
<tr>
<td>Triphosphate</td>
<td>10.9%</td>
<td>11.7%</td>
</tr>
</tbody>
</table>
4.3.3. Low Pressure Results

Struvite decomposes at lower temperatures under low pressure than under 0.5 atm N$_2$ (Figure 4.10, Table 4.1). This is likely due to the volatilization of NH$_3$ from the mineral. In addition, the mineral generates polyphosphates much more readily under low pressure, with higher yields as water is also more easily volatilized during the phosphate condensation (Figure 4.11).

![Raman spectra for struvite heated under vacuum at: 1) 100 C, 2) 130 C, 3) 170 C, 4) 200 C. Each reaction was run for 6 h.](image)

**Figure 4.10.** Raman spectra for struvite heated under vacuum at: 1) 100 C, 2) 130 C, 3) 170 C, 4) 200 C. Each reaction was run for 6 h.
Figure 4. $^1$H-Decoupled $^{31}$P-NMR spectra for struvite decomposition under vacuum (spectrum acquired at 161.8 MHz and pH 9). The reaction time for all experiments was 6 hours. a). Struvite sample at room temperature. b). Struvite decomposition after heating after 170 °C. c). Struvite sample decomposed after heating after 200 °C. d). Struvite sample decomposed after heating after 500 °C. Peaks are identified as (1) orthophosphate, (2) pyrophosphate and (3) triphosphate.
Figure 4.11 (continued). $^1$H-Decoupled $^{31}$P-NMR spectra for struvite decomposition under vacuum (spectrum acquired at 161.8 MHz and pH 9). The reaction time for all experiments was 6 hours. a). Struvite sample at room temperature. b). Struvite decomposition after heating after 170 C. c). Struvite sample decomposed after heating after 200 C. d). Struvite sample decomposed after heating after 500 C. Peaks are identified as (1) orthophosphate, (2) pyrophosphate and (3) triphosphate.
However, under low pressure the reactions of pyrophosphate with other calcium minerals does not fully favor dimer breakdown. In the case of gypsum, the breakdown of pyrophosphate occurs more readily under low pressure than under N₂ (Table 4.2). However, the reaction of calcite with pyrophosphate favors a disproportionation reaction, wherein equal amounts of triphosphate and orthophosphate are generated from pyrophosphate (Figure 4.12).

![Figure 4.12](image)  
**Figure 4.12.** $^1$H-decoupled $^{31}$P- NMR spectra for a) magnesium pyrophosphate and calcite, in molar ratio of 1:6, heated after 200 °C. Same like Fig 5, the phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under vacuum.
Figure 4.12 (continued). $^1$H-decoupled $^{31}$P- NMR spectra for b) magnesium pyrophosphate and calcite, in molar ratios of 1:12, heated after 200 °C, (spectra acquired at 161.8 MHz and pH 13), and c) magnesium pyrophosphate and gypsum, in molar ratio 1:6, heated after 200 °C. (spectra acquired at 161.8 MHz and pH 9). Same like Fig 5, the phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under vacuum.
Figure 4.12 (continued). $^1$H-decoupled $^{31}$P- NMR spectra for d) magnesium pyrophosphate and gypsum, in molar ratio 1:12, heated after 200 °C. (spectra acquired at 161.8 MHz and pH 9). Same like Fig 5, the phosphate peak (1) and pyrophosphate peak (2) are dominant. However, small peaks of polyphosphate (3) can also be clearly seen. The reaction time for all experiments was 6 hours and under vacuum.

4.4. Discussion

The thermal degradation reactions of struvite and newberyite were studied to understand whether these minerals may be present over geologic time periods and hence whether they would be recognized as “prebiotic” in the mineral evolution paradigm. “Mineral evolution” is a powerful paradigm with the potential to greatly constrain potential prebiotic reactions, but ephemeral minerals—those readily formed and readily destroyed—may be absent from the geologic record, which serves as a ground-trothing tool for constraining this evolution (Hazen 2013). A case in point are phosphate minerals such as struvite. We find that these minerals are unstable upon heating above 70 °C, whereupon they transform to new minerals.
The reaction rates demonstrate this occurs rapidly on geologic timescales. Minerals and salts such as dittmarite (MgNH₄PO₄·H₂O), dimagnesium phosphate (MgHPO₄), and magnesium pyrophosphate (Mg₂P₂O₇), are produced as a consequence of heating struvite. However, instead of being a mineralogic “fossil” resulting from struvite heating, magnesium pyrophosphate itself readily reacts with calcium minerals such as gypsum and calcite, retransforming into more stable calcium orthophosphate minerals. These decomposition reactions appear to be accelerated under low pressure, suggesting that in environments of low pressure (such as small asteroids with diameters <~20 km), these minerals would be unlikely to persist at the timescales they could persist on the earth.

Furthermore, the ³¹P-NMR, TGA, Raman spectra and XRD analyses reveal the pathway of struvite’s transformation. The TGA analyses revealed that with the rise in temperature (from room temperature to 70 °C), struvite first converts into magnesium anhydrous ammonium phosphate (MgNH₄PO₄). Then, it decomposes by deamination into an anhydrous magnesium acid phosphate (MgHPO₄). Ultimately, it changes into magnesium pyrophosphate (Mg₂P₂O₇) and magnesium triphosphate (Mg₂.₅P₃O₁₀), as the temperature continues to increase from 70 °C to 210 °C and higher. These results parallel findings of previous researchers (Abdelrazig and Sharp 1988; Babić-Ivančić et al. 2006; Bayuseno et al. 2018; Bayuseno and Schmahl 2020), who report similar mineralogic changes. Newberyite similarly dehydrates to MgHPO₄ and then to Mg₂P₂O₇. It is apparent from this pathway that the loss of water precedes the loss of ammonia for struvite. Broadly, this process follows expected mineral stability fields.
(Michałowski and Pietrzyk 2006) (Figure 4.13). Generally, the ammonium-magnesium phosphates are stable over a larger $P_{H2O}$ and $P_{NH3}$ region than are the hydrated magnesium phosphates. This may implicate ammonium phosphates as being a sink for ammonia in dry environments that do not reach high temperatures.

**Figure 4.13.** Dominance diagram for the system MgO-P$_2$O$_5$-NH$_3$-H$_2$O. This system incorporates thermodynamics from Faure (1997) for most species, with the addition of data for Mg$_3$P$_2$O$_7$ from Nanbu (1988). The dominance regions were calculated at 298 K and 1 atm total pressure, compared to the partial pressures of NH$_3$ and H$_2$O.

The phosphate ion within both magnesium phosphate minerals eventually condenses to form pyrophosphate, the phosphate dimer, during heating. Although such an ion would be ideal as a “fossil” identifying the presence of metamorphosed Mg-phosphates, the ion is inherently
unstable and reacts to form orthophosphate. This occurs through three processes, including hydration:

\[ \text{H}_2\text{O} + \text{Mg}_2\text{P}_2\text{O}_7 = 2\text{MgHPO}_4 \]  
(13)

reaction with carbonate or gypsum:

\[ 3\text{CaCO}_3 + \text{Mg}_2\text{P}_2\text{O}_7 = \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_2 + 2\text{MgCO}_3 \]  
(14)

\[ 3\text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Mg}_2\text{P}_2\text{O}_7 = \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + 2\text{MgSO}_4 + 5\text{H}_2\text{O} \]  
(15)

And disproportionation:

\[ 4\text{Mg}_2\text{P}_2\text{O}_7 = \text{Mg}_5(\text{P}_3\text{O}_{10})_2 + \text{Mg}_3(\text{PO}_4)_2 \]  
(16)

The experiments with \( \text{CaCO}_3 \) and \( \text{CaSO}_4\cdot2\text{H}_2\text{O} \) demonstrate that several of these reactions leading to pyrophosphate breakdown are likely active. Most of the phosphorus within the pyrophosphate heating experiments that reacts forms orthophosphate, implicating reactions (13), (14) and (15), with hydration likely being a lesser pathway, as dry argon was purged over the experiments. The majority of the pyrophosphate did not react over the six-hour reaction timescale. A lesser but still significant pathways was the disproportionation reaction (16). Reaction (14) appears to be the principal reaction pathway under low pressure between struvite and \( \text{CaCO}_3 \). In the disproportionation reaction, the roughly energy-neutral (Pasek 2019) formation of triphosphate and monophosphate from two diphosphates occurred and is clearly indicated in the \( ^{31}\text{P}-\text{NMR} \) spectra. However, even though reaction(13), (14) and (15) can be shown clearly by \( ^{31}\text{P}-\text{NMR} \) spectra, it is often ignored by previous researchers, given that struvite and magnesium pyrophosphate are rare on meteorites parent bodies in reality, and common
crystal analysis methods like Laser Raman spectroscopy and Powder X-Ray diffractometry, only investigate all sample produced compound patterns. These data mislead researchers to ignore the evidence for tiny percentages of magnesium pyrophosphate emerging and disappearing during the struvite and newberyite degradation process (Figure 4.14 and Figure 4.15). ³¹P-NMR analysis can perfect avoidance of this issue because ³¹P-NMR can only provide the trend of anion P species, and thus can outline the whole process of struvite and newberyite degradation in meteorites and early Earth, without interference from other phosphorus-bearing substances. Furthermore, larger polyphosphates are also likely present but are harder to identify via ³¹P-NMR (and by other analytical tools such as Mass Spectrometry).

The rapid breakdown of Mg₂P₂O₇ demonstrates why, even if the transformation of calcium phosphates to Mg- and NH₄- phosphates occurs, such a process would be difficult to recognize in the geologic record. The direct metamorphic products of Mg- and NH₄-phosphates are inherently unstable and convert to the Ca-phosphates readily. It is likely that some favorable geological conditions on the early Earth could precipitate struvite (Gedulin & Arrhenius 1994; Burcar et al. 2016) and such a reaction would also be facilitated in meteorites through low-temperature and high-ammonia activity alteration. Such minerals may be the source of phosphorus within the most highly aqueously altered carbonaceous chondrites, where an actual mineral phase of phosphate has yet to be identified (Pasek and Lauretta 2005). Struvite’s formation is relatively facile under dry, NH₃- and SO₄- rich environments, and both ions were likely present within carbonaceous chondrites (Fredriksson and Kerridge 1988, Pizzarello and
Williams 2012). Hence, it is possible that struvite as well as newberyite could have occurred on the early Earth, even though the plausibility of such reactions still lacks distinctive geochemical evidence (Gull and Pasek 2013).

**Figure 4. 14.** XRD pattern of (6×, 12×) calcite and Mg₃P₂O₇ when heated to 200 °C for six hours shows only calcite and the starting Mg₃P₂O₇

**Figure 4. 15.** XRD pattern of (6×, 12×) gypsum and Mg₃P₂O₇ when heated to 200 °C for six hours shows only hemihydrate (CaSO₄·0.5H₂O)
4.5. Conclusion

In this work, we have focused to resolve the likelihood that struvite and newberyite were present on the early Earth and in meteorites. Struvite holds a special place in the realm of prebiotic phosphorylation chemistry, owing to its good reactivity towards biomolecules under mild heating conditions, which produces a plethora of phosphorylated biomolecules such as those that are essential for life (Handschuh and Orgel 1974; Rivadeneyra et al. 1983; Gull and Pasek; Gull et al. 2014; Burcar et al. 2016). It is also readily formed from corrosion of calcium phosphate minerals, possibly hinting at its presence as distributed grains within chondrites. Identification of these minerals in aqueously altered meteorites at the micro- or nanoscale would be a confirmation of the premise of this work.

We hence propose that the lack of identification of struvite/newberyite within both meteoritic and early earth environments is due to the ephemerality of these minerals: heating above 200 °C in an oxygen poor environment for even short periods of time results in their destruction. The minerals are even less stable under low pressure, implying that in a low-pressure environment (such as within an asteroid interior), these minerals would readily decompose. The early Earth likely had a period that would have enabled the formation of struvite, but since terrestrial Archean rocks are all metamorphosed and Hadean rocks virtually non-existent (especially rocks that have experienced a low temperature metamorphic history), any trace of struvite on the prebiotic Earth would have been lost. Future work in this field should include an
investigation of the stability of polyphosphates under higher (metamorphic pressure) and their ability to persist as trace constituents in substituting for other ions, thus leading to their preservation.

In contrast to these environments, in a location where ammoniated minerals are broadly stable the ammonium phosphates may also be present. Such a location may be the asteroid Ceres, whose surface bears ammoniated phyllosilicates. In such an environment, struvite may be an important phosphate mineral, where its formation from primordial phosphates and phosphides would have occurred but not been erased by metamorphic heating. Future sampling missions may reveal the presence of this mineral, which could be a substantial store of ammonia on asteroids. The presence or absence of these ephemeral minerals in the solar system is a knowledge gap that, if filled, reveals the potential for a reservoir of P and possibly N in mineralogical form. Given the relationship of asteroids to the bombardment history of the inner solar system, constraints on composition are relevant to constraints on delivery and the inventory of key elements at or prior to the origination of life on the earth.
CHAPTER FIVE
DISSERTATION CONCLUSIONS

In this dissertation, I present several ideas about the relationship that the speciation and mineralogy of phosphorus in natural glasses and on meteorites. Phosphorus plays a key role in the biochemistry of living organisms. However, reactive phosphorus is rare on Earth as most terrestrial phosphorous inorganic minerals, like apatite and whitlockite, are difficult to utilize as P sources to form organic phosphorus compound from reaction with organic solvents and water (Orgel 2004; Gull, 2014). How then does prebiotic phosphorylation happen on the early Earth?

Pasek and Lauretta (2005) presented schreibersite, an iron-nickel phosphide mineral, as a source of P leading to organic phosphorus compounds on the early earth. Schreibersite is abundant within some fulgurites (Hess et al. 2021) and even more on meteorites (Pasek 2017). Schreibersite reacts to facilitate the formation of organic phosphorus compounds, such as glycerol-P and choline-P, in solvents that include organic solvents and water (Pasek et al. 2013; Gull et al. 2015; La Cruz et al. 2016). However, parts of schreibersites oxidation in fulgurites and on meteorites are not clear. In this dissertation, several significant points are addressed to fill the gaps about these issues.

Chapter two presents the results of unique blue coloration of an artificial fulgurite. Schreibersite and phosphite are plausible inside of fulgurites (Pasek and Block, 2009; Hess et al.
2021), and some impact glasses, which also have blue coloration, are rich in phosphorus (Koeberl 1988; Zolensky and Koeberl 1991). Hence, my research into this blue fulgurite sought to determine if this blue color was dependent on P-rich materials (such as schreibersite or phosphite) within it. However, Raman spectroscopy, X-Ray Fluorescence (XRF) analysis, Electron Microprobe Analysis (EMPA), and Transmission Electron Microscopy (TEM) show that phosphorus is rare. Furthermore, both the glass overall and spherules, which are ubiquitous inside the blue glass, are the same in all major elemental percentages. Therefore, I propose that the blue coloration in this fulgurite is due to pseudochromatic effects, namely Rayleigh scattering by nanoscale spherules within the glassy matrix. This result falls within a broader theme of investigating parallels between lightning-formed materials and impact materials, and the potential for forming shocked quartz by lightning.

Chapter three studies the thermal oxidation of schreibersite with silicate minerals on chondrite meteorite parent bodies. Like chapter three demonstrated, phosphorus minerals can transform to other phosphate minerals on chondrites. However, the detailed transformation pathway of schreibersite into orthophosphate was missing. Hence, my findings demonstrate that schreibersite is transformed into phosphate while reacting with olivine and calcium silicate minerals like diopside at elevated temperature (1000 °C) on chondrites, and the rate of this schreibersite oxidation process is suitably slow. Furthermore, in contrast with Lauretta and Schmidt (2009), phosphate species were not the only product during the schreibersite oxidation process. Phosphite, polyphosphates, hypophosphite, and hypophosphate were all formed when
temperatures were on the low end and at medium reaction temperatures (700 °C -800 °C), Phosphite species were more abundant than phosphate compounds during the schreibersite oxidation. Moreover, some of the orthophosphate polymerized into pyrophosphate, which supported a hypothesis that schreibersite might be transformed into polyphosphates if high reaction temperatures are present. Such results may provide some tools to evaluate the relationship between temperature and time in chondrite metamorphism.

Chapter four discusses if struvite was plausible on the early Earth. Schreibersite is oxidized into inorganic phosphate minerals, such as apatite and merrillite at comparatively lower temperatures (300-700K) (Zanda et al. 1994 Jones et al. 2016, Pasek 2019a). Furthermore, apatite minerals are readily altered into struvite by NH$_4^+$ and MgSO$_4$-bearing fluids (Burcar et al. 2016). Struvite is a prebiotic mineral (Lohrmann and Orgel 1971) but lacks evidence in the ancient geologic record (Rubin, 1997, Hazen 2013, Gull and Pasek 2013). Hence, my research sought to reveal the thermal degradation process of struvite on the early Earth and in meteorites. Magnesium pyrophosphate is the final product as a consequence of heating struvite. Furthermore, magnesium pyrophosphate itself readily reacts with calcium minerals such as gypsum and calcite and disproportionates into orthophosphate and triphosphates. This result determines that some favorable geological conditions on the early Earth could precipitate struvite and such a reaction would also be facilitated in meteorites through low-temperature and high-ammonia activity alteration, even though the plausibility of such reactions still lacks distinctive geochemical evidence (Hazen 2013, Gull and Pasek 2013).
For future work, I want to demonstrate the relationship between natural glass and the origin of life. Hess et al. (2021) claimed that iron phosphide and phosphite species are abundant in fulgurites. This opinion provides a pathway to combine natural glass and organic phosphorous compounds in an early Earth scenario. Hence, it is interesting to study other compounds similar to iron phosphide in fulgurites. I would like to research iron silicide minerals and iron nitride minerals, and use organic substrates to determine the relationship between natural glass and the origin of life. Such research may reveal what role fulgurites played in the development of life on the early Earth.
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