Novel biochemical evolution of the early Earth: space debris and the genesis of prebiotic molecules during entry

Introduction

While “life” has fascinated the human mind for generations, its origins remain a mystery. One puzzling aspect of life’s origins is how prebiotic molecules—a necessary ingredient for life that is thought to have been abundant in the waters of early Earth—were made. Extraterrestrial objects (comets, meteorites, and other space debris) have long been proposed as one possible source for prebiotic molecules. While various experiments and observations have been undertaken to understand the entry and energetic impacts of such debris (a diverse sampling of recent work includes: (Jenniskens et al. 2004; Vondrak et al. 2008; Kuwahara and Sugita 2015; Marty et al. 2016)), to date there is no universal agreement on the role of space debris in evolving the early Earth’s composition.

Space debris enters the Earth’s atmosphere at speeds between ~10 to 70 km/sec (Baggaley 2000), during which collisions with atmospheric atoms and molecules are hyperthermal (Vondrak et al. 2008). The reaction mechanisms of hyperthermal collisions are unlike those of more commonly studied reactions as it occurs far above the necessary activation energy for the reaction (Jankunas et al. 2012; Yang et al. 2012); for the most part, hyperthermal reactions remain novel and underexplored synthesis mechanism due to their relatively unusual high energy. The question therefore arises, if space debris entering our atmosphere is involved in hyperthermal collisions, what chemical reactions occur as it falls? More importantly, **what role could hyperthermal reactions of space debris entering the atmosphere have played on a global scale in creating or evolving the prebiotic composition of Earth?** The proposed research answers these broad questions by (1) experimentally investigating synthesis routes of prebiotic molecules via hyperthermal impact of an early Earth atmosphere with space debris like surfaces, and (2) incorporating these findings into an interactive probability based computer model that extrapolates this data to the global scale of early Earth conditions and across its first billion years.

Background

Space debris provides a realistic mechanism for evolving the early Earth’s composition towards its modern state. A longstanding idea is that volatile elements and molecules, such as C, N, and H_2O, arrived via comets or chondrites after Earth’s initial accretion (O’Brien et al. 2014), and that prebiotic molecules were abundant enough by 3.8 to 3.5 billion years ago for life to form (Whittet 1997). Theories of space debris’ role in Earth’s chemistry fall into three categories: **import,** which consider space debris as a mechanism to transport outside materials to Earth; **impact,** which consider the reactions and implications of space debris impacting the surface of Earth; and **reactivity,** which consider the reactive conditions posed by the atmosphere and space debris. Most work focuses on import’s role in fostering prebiotic molecules (Packan et al. 1998; Jenniskens 2001). Due to experimental challenges, a smaller body of work investigates impact and reactivity. Objects entering the Earth’s atmosphere typically do so at high kinetic energies: 10 to 75 km/sec (Baggaley 2000). Human-made experimental apparatuses, such as light-gas gun impact setups (Burchell et al. 2014; Okochi et al. 2015), often have maximum impact speeds of ca. 8 km/sec (Fat'yanov and Asimow 2014); however, this work has provided insight into the survivability of molecules during impact. Another approach uses high-energy laser light to simulate impacts within gas mixtures to approximate impacts and their resulting reactions (McKay and Borucki 1997). Observations and simulations constitute the bulk of research insight into the reactive decent and impact. Such studies include simulations of the compression and expansion of molecular compositions similar to space debris ices (Goldman and Tamblyn 2013) and observations of emissions from suspected reaction products (Jenniskens et al. 2004). This experimental, observational and computational research has indicated a variety of synergistic and competing reaction mechanisms that could have played a role in evolving the molecular composition of the early Earth.

Recently, the surprising observation of diatomic oxygen (O_2, a molecule thought to be scarce in the universe) near a comet (Bieler et al. 2015) prompted the astronomy community to reconsider the breadth of chemical mechanisms that could produce such a result. Among them, Yao and Giapis proved that hyperthermal ions (molecules or atoms with 10 – 500 eV), such as H_2O^+ traveling at speeds of 10 to 70 km/sec, could dynamically generate new molecules such as O_2 after colliding with a solid surface (Yao et al. 2017). The reactive role of hyperthermal collisions in their work draws attention the need to consider the reactive possibilities of hyperthermal collisions in a geologic setting, as well as the unexplored potential that important prebiotic molecules or radicals could be synthesized during collisions.

Research questions

Apart from the preliminary and intriguing results of Yao and Giapis (Yao and Giapis 2017a, 2017b; Yao et al. 2017), the reactions of hyperthermal collisions in reasonably occurring natural environments are unexplored experimentally. The objective of this research is to investigate the possible role of hyperthermal collisions between early Earth atmospheric compositions and space debris like surfaces in evolving the molecular composition of Earth. Special attention is given to the intriguing possibility that this mechanism may be a key contributor to evolving the early Earth's composition by directly creating prebiotic molecules or by generating radicals likely to form prebiotic molecules. Specific questions include:

1. What reaction mechanisms driven by hyperthermal collisions can occur under the conditions of the early Earth?

Hypethermal reactions are marked by high kinetic energies, which can reactively both break and form bonds to generate new molecules, eject radicals which react with other materials later, and eject material from the surface via sputtering. This first question will observe reactions that result under characteristics of the Early earth's atmosphere and the debris entering. While specifying the Earth's ancient environments is challenging and estimates are often uncertain, compositions of both the early Earth's atmosphere and space debris can be bounded within a somewhat limited range. As an example, the potential contributions of the ancient accretion rate of carbonaceous matter can be bounded by modern rates as an extreme low (3e5 kg/year) (Baggaley 2000), but was likely higher; estimates of 5e7 kg/year have been proposed (Whittet 1997). The surface area of these particles can be bounded by the small modern particle sizes as well as extremely large space debris. Using the extreme examples as an upward bound, carbonaceous material with an equivalent surface area to our Earth could have been exposed during entry into Earth's atmosphere as often as every 5 million years (assuming 5e7 kg/year carbon influx, 50 um diameter particles, spherical particles, and C density equivalent to graphite). These are exposed to hypethermal collisions until the space debris slows to a speed below 10 km/sec or impacts into Earth, and all surfaces (not just C) have the potential of playing a reactive role.

While estimates of Earth's early atmosphere vary, we use Kuwahara and Sugita's (2015) model of early Earth atmosphere from post accretion impacts to inform possible compositions for the experimental work. Commonly mentioned compositions for an early Earth atmosphere are summarized in Table 1.

Table 1. Possible components of the early Earth's atmosphere (Kuwahara and Sugita 2015).

Atmospheric components	Approximate abundance	Research priority
H_2O	high	high
CO_2	high	high
CH_4	high (possibly low)	high
H_2	medium	medium
H_2S	medium	medium
CO	medium	low
SO_2	medium - low	medium
N_2	low	medium
NH_3	extra low	low

Table 2. Analogous surfaces to those found in space debris

Analogous debris surfaces	Example composition	Research stage
Metals	Fe, Fe-Ni alloys	1
Carbon	Amorphous C, graphite	1
Metal oxide	FeO, MgO, CaO	3
Silicates	Mg_2SiO_4, SiO_2	3
Ice	H_2O	3

Modern space debris is thought to be approximately representative of the space debris of early Earth, and for this project can be simplified into meteors (metallic, stony, and carbonaceous) and comets (Lodders 2000). Meteors can contain a variety of compositions. However, the most common contain primarily silicates and metals, with a small abundance of oxides, carbon, sulfides, carbides, and nitrides. Comet compositions were characterized by the recent European Space Agency mission to visit comet 67P, which discovered molecular complex ices (Goesmann et al. 2015). The majority of comet ice (81%) is water, which contains simple molecules (3%) such as CO and CH_4 and larger prebiotic molecules (16%) such as CH_3CONH_2 (Goesmann et al. 2015). Table 2 summarizes simplified surface compositions representative of meteors and comets that will be investigated in this study.

Carbon, hydrogen, oxygen and nitrogen are the most common elements in living organisms. The probability of forming molecules containing these elements from the list above is high. Traditional thinking anticipates that most molecules disassociate into fragments and radicals that bounce off the surface, with a smaller population reacting with the surface via an Eley-Rideal mechanism or adsorbing onto the surface. As a caveat to traditional thinking, hyperthermal collisions have in some cases been observed to contain high yields of non-disassociated particles (St. John and Whetten 1992), and the dominate reaction pathway may depend on subtle aspects of the collision which cannot be realized without experimentation. Eley-Rideal reactions involve the direct synthesis of a gas phase product from a direct reaction between a surface product and a colliding molecule, without adsorption of the input molecule (Yao and Giapis 2016). Fast rates and high energy of both Eley-Rideal reactions and disassociation often results in charged particles being ejected at high speeds. These fast charged particles have significant drive to react with the atmosphere they are scattered into. For instance, CO_2 collisions with an ice surface could feasibly produce HCO radicals, a possible precursor to methanol, especially if the atmosphere was also rich in H_2. This same radical is also likely to form after the collision of methane (CH_4) with a silicate, and the immediate environment is likely to have available H radicals. The approximate total yield of scattered radicals should be similar across substrates and should depend primarily on the molecules' capacity to respond to the impact by dissipating energy nondestructively.

2. What influence does the temperature play in the reactivity of hyperthermal collisions?

As space debris enters the Earth's atmosphere, its initial temperature is usually close to absolute zero, and as it falls it warms up, possibly even to the material's vaporization temperature. At elevated temperatures, there is additional energy that may influence hyperthermal reactions both indirectly (e.g., changes in the surface structure of the space debris) and directly (e.g., changing the energy contributions of the surface to the total reaction). At cryogenic temperatures, reactions should be almost entirely driven by the kinetic energy of the colliding molecule. Understanding the role of temperature in these reactions may provide valuable insight into the necessary conditions and probability that hyperthermal reactions resulting in prebiotic molecules might occur.

3. What reactions and conditions could have influenced the prebiotic composition of the early Earth?

To understand the likelihood that observed reactions led to prebiotic molecules, we must extrapolate our experimental findings to the scale of the Earth, in both size and time (the 1 billion or so years in which prebiotic molecules appeared and supported the origin of life). Newly-identified synthesis routes will be placed in the context of early Earth's possible conditions and in dialogue with existing and competing reaction mechanisms. The stability of generated prebiotic molecules and reactivity of generated radicals will be considered under the timeframe that it takes these molecules to reach the Earth's surface or become destroyed. Furthermore, Earth science research itself has a temporal component, where tomorrow's research will continue refining our understanding of Earth's history. To best serve future generations, the results should be easily accessible or the calculations involved should be easy to update. These considerations will be addressed via a computational model of the Earth's molecular evolution.

Research approach

These research questions will be addressed through experimental analogs of expected space debris surfaces and early atmosphere compositions. In the experiments, a fixed space debris surface will be bombarded by early atmosphere molecules and atoms accelerated to equivalent speeds of space debris entry using a molecular beamline. A mass spectrometer will observe and quantify the resulting products, from which the reactions can be understood and described. These results will be summarized into a probabilistically based software model, which extends these reactions to the billion-year scale of early Earth's evolution. The research is divided into 3 phases. The initial phase will begin work on the currently operating ion beamline in the Giapis lab. The second phase will modify the beamline to address challenging but more geologically-relevant compositions. The last phase will address the influence of temperature and investigate more complex compositions close to geologic systems. Work on the model will begin immediately and progress in parallel to the experiments.

Stage 1: Exploratory compositions compatible with current instruments

Initial experimental work targets compositions and experiments currently possible in the Giapis lab ion beam setup. In its current setup, the Giapis lab's ultra-high vacuum ion beam and scattering system presents many important capabilities. A plasma reactor with flexible gas input allows the synthesis of a variety of plasmas. Positive ions, such as such as H_2O^+, CO_2^+, CH_4^+, can then be extracted from the plasma chamber, isotopically purified and directed onto a 3 mm spot size on a sample plate. The beam can be tuned to produce impinging ions at the sample plate between 1 to 210 eV. A detector port lies at 90 degrees from the incident beam and is equipped with a quadrupole mass spectrometer, an adjustable bias channeltron, and an electrostatic energy analyzer, enabling the quantification of both positive and negative ions at specific exit energies. The sample plate can freely rotate. An Ar gas sputtering gun for sample cleaning and an inlet to allow dosing of gasses onto the sample's surface are also present.

Preliminary experiments will provide a first approximation into reactions achievable during hyperthermal collisions. Electrically conducting substrate samples of amorphous carbon, graphite, iron, and iron-nickel alloys will be obtained or synthesized. High and medium priority gases from Table 1 will be ionized and directed towards the substrates to observe ion yields as they react with surface species, disassociate, undergo electronic or vibrational excitation, implant into the subsurface, or sputter the surface. The resulting gas phase products will be characterized via mass spectrometry with a single channel electron multiplier and electrostatic analyzer. The resulting data indicates the abundance of produced molecules, as well as the resulting speed (energy) of the produced molecules.

This initial research will give some insight into how the ion's energy and composition, angle of impact, and the surface's composition influence the resulting products.

Stage 2: Instrument modification

The scattering apparatus will be modified to produce neutral hyperthermal molecules, enable investigations of non-electrically-conductive substrates, and control the surface's temperature.

Ion beam neutralization: While ionizing particles serves to accelerate them to hyperthermal velocities, the reactions of interest are collisions between neutral molecules colliding with a neutral surface, not charged ones. To neutralize an ion beam, a supply of electrons is provided to the ion beam after its purification. A parallel electron source within or near the sample chamber as described in *Ion beam neutralization* (Humphries, Jr. 1990) will be designed and installed. Even without 100% neutralization efficiency, the ability to compare and contrast fully ionized and partially neutralized beams will enable quantification and investigation into neutral collisions.

Electron gun for surface neutralization: A commercial electron gun will be installed to neutralize the sample plate and prevent charge buildup. This modification enables the research to proceed without complete neutralization of the ion beam and to no longer be limited to conductive substrates or exceptionally thin substrates that could be ablated during the hyperthermal collisions.

The development heating a cooling capabilities: Space debris traveling within Earth's atmosphere experiences a wide temperature range, from cryogenic space to temperatures at which metals vaporize. To understand the role of decreased and elevated temperature, the capacity to control temperature must be added. Preliminary designs for a new sample holder have been developed and include a resistive heating element and removable thermal contact to a liquid nitrogen cryostat. Further work on these designs will be conducted to interface the sample holder with a preexisting commercial cryostat owned by the Giapis lab. The necessary modifications and fabrications will then be performed. The size and temperature requirements are nearly identical to high temperature and cryogenic probes for NMR systems, which the author has experience designing and fabricating.

Stage 3: Insulating surfaces, neutral collisions and temperature

With the enhanced capabilities of the modified experimental apparatus, the final experimental work will investigate electrically insulating surfaces (listed as stage 3 materials in table 2) and neutral collisions. Initial work in this stage will start with room temperature experiments. In this work we anticipate the detection of products that are larger than the initial input molecule, especially after collisions with diatomic molecules (i.e. H_2, CO, N_2), as well as radicals. Identification of such reactions will help prioritize later work and point toward reactions that could occur in the atmosphere in the presence of observed radicals.

Next, each of the surfaces of interest (table 2) will be brought to cryogenic temperatures and bombarded with each of the high and medium priority molecules listed in table 1. The cryogenic surfaces present an opportunity to understand the hyperthermal contribution to the reactions and its mechanism. Comparative experiments between ions (i.e. H_2O^+) and neutrals (i.e. H_2O) will be conducted. During this stage, ice will also be synthesized on the cryogenic surface, and the products of all molecules on this surface (high to low from table 1) will be investigated as both neutrals and ions. This body of experiments should also help identify what type of reaction (Eley-Rideal or otherwise) is occurring with collision. Understanding these reactions across the many variables proposed above should enable broad trends to be identified and general predictions beyond the specific conditions investigated.

Stable surfaces (such as the silicates, but not the ice) will be heated to investigate the effect of increased temperature on the resulting products. Early experiments will investigate reactions at the maximum achievable surface temperature, with later experiments at intermediate temperatures. In addition to the possible changes of surface structure and the total available energy, an increased temperature will discourage surface adsorbates of the colliding molecule. Although the energetic landscape of the surface will be more complex, elevated temperatures may give insight into the role of a clean surface without interfering adsorbates, a likely setting geologically due to the ablation of space debris as it enters the atmosphere.

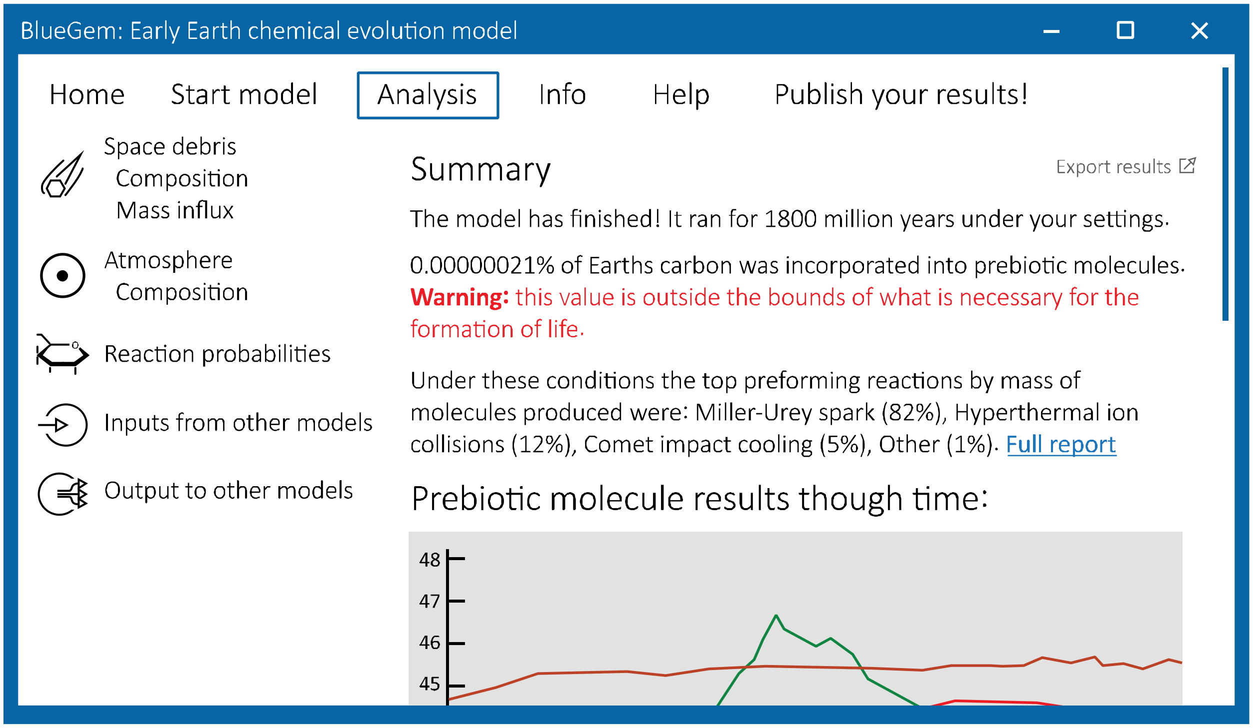
Given the nature of the suspected Eley-Rideal reactions, a change in the orientation of surface structure and collision angle may significantly influence the yield and may enable additional or different products to be formed. On ice, Fe-Ni alloy, and olivine (Mg_2SiO_4) an investigation of the scattering angle will be undertaken. Although the apparatus cannot detect products from all possible scattering angles, a simplistic investigation of a few different angles may be sufficient in understanding the approximate importance of scattering angle, and whether this topic should be one of future study.

The model: Extending to the spatial and temporal scale of Earth

The experimental work is expected to discover new reactions possible in the early Earth. However, their implications depend on whether they occur frequently or generate substantial mass. To extrapolate the experimental results to the scale of the early Earth, in both mass and across the timespan of early Earth, a probabilistic model with an instructional graphical user interface will be developed.

The model will initially use coarse probabilistic calculations of reactions and disequilibrium processes, but will be structured as a collaborative platform that can include and contrast additional approaches, such as Miller-Urey synthesis of prebiotic molecules (Cleaves et al. 2008), destruction of synthesized molecules by UV light (Cleaves and Miller 1998), and different proposed compositions for Earth’s atmosphere (Tian 2005). Each known or theorized reaction will be itemized and assigned probabilities of occurring when necessary conditions are met; these will be kept in an easy to edit database. The chemical model will draw on global parameters that will initially be set by the user, and once started will then evolve with the chemical and molecular composition of Earth within a given timeframe. Within the timeframe a series of intermediate time steps would be calculated. For each time step, the model would first set up budgets of available components, and then distribute those components into reaction products or unused products in the following time steps budget. During the distribution step, events such as a comet entering Earth's atmosphere, are also accounted for probabilistically.

Further investment in the model's scientific rigor, usability, and graphic interface will provide engaging and sharable science that can serve as a platform for collaboration and outreach. For researchers, hands on manipulation will help users understand the importance of individual reactions, quickly calculate and test new ideas, and refine predictions of the early Earth's molecular evolution. For outreach, an instructional graphics interface will enable students to learn interactively about the chemical evolution of the Earth and provide an opportunity for users to contribute their findings to the online database in a citizen science approach. A mockup of the graphic interface illustrating its approachable appearance and collaborative aspects is presented in Figure 1.



Summary

The model has finished! It ran for 1800 million years under your settings.

0.00000021% of Earths carbon was incorporated into prebiotic molecules. **Warning:** this value is outside the bounds of what is necessary for the formation of life.

Under these conditions the top preforming reactions by mass of molecules produced were: Miller-Urey spark (82%), Hyperthermal ion collisions (12%), Comet impact cooling (5%), Other (1%). Full report

Prebiotic molecule results though time:

Figure 1. Conceptual mockup for the prebiotic chemistry model, illustrating an intuitive graphic user interface, the collaborative intent of the software to interact with other models, and the opportunity for model users to contribute their discoveries to the scientific community.

Early drafts of the model will be developed in Excel to encourage collaborative input and enable easy database management among colleagues. The later interactive versions are anticipated to be programed into C# or C++, enabling the model to be distributed as both an executable with simple graphic interface and as a highly annotated piece of share-alike code, enabling additional computationally minded researchers to incorporate it into their own calculations.

Expected Project Significance

By experimentally investigating the role of hyperthermal collisions, a known reaction pathway that has been minimally explored in Earth systems, this research will enable a more complete understanding of early Earth's molecular evolution. The proposed chemical model will link some of the competing ideas about early Earth into an interactive teaching, learning, and research environment. This research contributes to ongoing debates and theories of Earth's prebiotic composition, its origin, and the origins of life.

Work on hyperthermal collisions has broader synergies with research in bioscience, cosmochemistry, and surface deposition. Ion beams have been proposed to finely control surface functionalization by organic molecules and place large molecules on surfaces for further study. Cosmochemistry may benefit from the reaction mechanisms discovered in this work, as some extraterrestrial environments share similar fundamental properties and conditions as Earth. Finally, the increasingly complex thin film depositional and etching techniques in materials science may benefit from additional insight of the reactive role and mechanisms of relatively lower energy ions on complex surfaces.

Proposed Professional Development Activities and Broader Impacts

Developing research skills: The interdisciplinary nature of the proposed research provides a breadth of exposure to new skills, techniques, and research methods, which will be invaluable in launching my research career. It also presents multiple avenues for establishing collaborators. The model will provide incentive to further sharpen my skills as a programmer, a practical skillset for modern scientists.

Development of expertise in mobile-friendly teaching: Cellphones—advanced computers with built in cameras, geographical and spatial positioning abilities, Bluetooth connectivity to scientific instruments, and the capacity to connect users to the largest collection of human knowledge and data ever assembled—are a significantly underutilized and often stigmatized teaching resource. Unfortunately, teaching with cellphones is difficult. This technology is relatively new, was absent from my own education, can be a complete nuisance, and lacks device-appropriate online educational materials. I propose to develop online, phone-friendly teaching materials for undergraduate classrooms, and to perfect my personal teaching style which will one day include cellphones as seamlessly among lectures as pen and paper activities and discussions. Online material intended for use on mobile phones will be developed on three topics on the Scale in Earth systems that I have found is challenging to convey in the classroom:

a) Chemistry from 1 amu to 1 Earth,
b) Our first billion: The evolution of the early Earth,
c) From rare to there! Catalytic sites and reactions on Earth's many surfaces.

Modules are intended for undergraduate level courses, and will contain lecture videos, slides and notes for the instructors, and small break out videos and modules for students to interact on their mobile phones during specific points of the lecture.

Developing as an instructor by co-teaching at Caltech: To develop my skills teaching graduate level courses, I will co-teach a course on surface science reactions and run a workshop aimed at improving the research experience and quality of PhD students. First, co-teaching a new course on surface science reaction hosted by a chemical engineering department will help stretch me as a scientist (I'm a mineralogist/geochemist), while providing me with additional depth in the subject material. Second, I intend to run a workshop on *Visual thinking for sharing science,* which aims to provide young researchers with action based tools and approaches for generating ideas and progressing research. The workshop aims to encourage creativity and teach practical aspects of creating visuals, aesthetics, and how graphics can enrich science. After fine tuning the workshop, it is my intent to summarize it in a free online text, anticipating that such a product will be an attractive component of my faculty application.

Developing as an adviser though diversity in STEM outreach: As a minority in STEM who is also well connected with other minorities in STEM, I have realized the value and importance of high quality mentoring in creating an ideal research setting. If I am to one day lead a research lab, I believe it is imperative that I have a depth of experiences and resulting skill in mentoring and advising. I believe exposing other minorities to the value of diverse ideas in the research setting will also prove an enriching experience for those I advise. I intend to develop several small research opportunities related to the early Earth model to involve 2-6 underrepresented minority (URM) undergraduate students from Los Angeles area community colleges.

Justification for Caltech

The Giapis lab and Caltech setting presents a unique opportunity to pursue this research, as well as a broad and advantageous environment to support my future goals. Fundamentally, the proposal requires an ion beam line and scattering chamber that can be modified to control temperature. In this regard, the functionality and availability of the Giapis lab beamline presents a serendipitous opportunity. A driving factor to interact with Dr. Giapis is gaining more experience in engineering and constructing “one of a kind” scientific apparatuses for cutting edge science. His broader lab setting also provides experience with additional spectroscopic techniques and problem solving approaches. The opportunity to co-teach with Dr. Giapis will provide upper division teaching experience I currently lack.

At the conclusion of my PhD experience, I realized (but admittedly a bit to late) the value of establishing collaborations, and I am eager to establish projects, research directions, and collaborative teaching colleagues to cultivate over my career. The interdisciplinary setting of Caltech, with blurred boundaries between the geology, biology, and chemistry departments, provides a valuable setting for the interdisciplinary work necessary to theorize possible reactions, develop the model, and understand the implications of our results. Caltech’s setting in Los Angeles also presents multiple avenues to have a broad impact while establishing networks across institutions of potential employment. Specifically for broader impact, the abundant community colleges are actively seeking course material that is easily accessible for their often-changing teaching faculty, and the California State Science Fair is held annually a short drive away at the California Science Center, an event which Giapis lab members are often involved in.