Creating the ingredients for life by smashing molecules into comet ice

Introduction

While "life" has fascinated the human mind for generations, its origins remain a mystery. One puzzling aspect of life's origins is where prebiotic molecules—a necessary ingredient that is thought to have been abundant in the oceans where life was first created—came from. Comets have long been proposed as one possible source for prebiotic molecules. This, however, raises the question of how prebiotic molecules got onto the comets. This question has recently returned to the focal point of scientific discussion with the wealth of observations obtained by the European Space Agency's Rosetta spacecraft. Rosetta and its lander added new chemical insights as it analyzed the composition of the coma and surface ice of 67P/Churyumov-Gerasimenko. In addition to various prebiotic molecules abundant in the comet's ice (Goesmann et al. 2015), the spacecraft also observed hyperthermal ions (charged atoms or molecules with 1-500 eV) originating from the comet (Gombosi et al. 2015; Nilsson et al. 2015). Hyperthermal ions present a variety of unexplored chemical mechanisms to form prebiotic molecules and their precursors in cometary environments. The proposed research will investigate the synthesis of prebiotic molecules via hyperthermal ion bombardment on comet-like surfaces, and then summarize these and competing findings into a conceptual comet model.

Background

Chemical reactions on a comet's surface have long been thought to be controlled primarily by radiolysis and photolysis. Radiolysis involves the ionization of ice and molecules by fast electrons or photons and is an important mechanism in places like Saturn's rings (Johnson et al. 2006) or Jupiter's moons (Carlson 1999). Photolysis involves the breaking of chemical bonds by ultraviolet light (photodissociation) and is recognized to play a significant role in comet chemistry (Bieler et al. 2015; Bodewits et al. 2016; Yao et al. 2017).

The new-found presence of hyperthermal ions, however, provides an additional mechanism for shaping a comet's chemical speciation. Ions are generated around a comet when comet ice is ejected from the comet's surface comet and into the surrounding regions of space. The ejected material is then thought to be ionized by photoionization and/or electron-impact ionization (Galand et al. 2016), which can then be accelerated by the solar wind (Nilsson et al. 2015). As reported from Rosetta, the majority of present ions are water (H_2O), and most water ions occur with energies between 120 to 300 eV, although they can reach energies greater than 1 keV (Nilsson et al. 2015). Hyperthermal ions, the focus of this proposal, are those with energies between 1 to 500 eV and encompass the majority of water ions around comets. These ions' impact on surfaces provides significant kinetic energies that can drive chemical reactions, but not so large that collisional cascade and ejection of surface material dominates. Strong fluxes of accelerated water ions are thought to be consistently present near the comet and on its surface as the comet passes close to the sun (Nilsson et al. 2015).

Preliminary work on this topic by Yao and Giapis indicates that this flux may play a role in comet chemical evolution. For instance, work performed on the Caltech ion beam contributed an explanation for the high levels of diatomic oxygen (O_2) detected by Rosetta (Bieler et al. 2015), a surprise as diatomic oxygen is thought to be scarce in the universe. Water ions (H_2O^+) with hyperthermal energies between 10 to 200 eV were impinged upon metal surfaces, and resulting gas phase products were observed (Yao and Giapis 2017a, 2017b; Yao et al. 2017). The work showed that the ions' impact allows for dynamic reactions that can produce O_2^- and HO_2^- in addition to expected disassociated radicals like atomic O, H, and molecular OH (Yao et al. 2017). Their work suggests that hyperthermal bombardment, radiolysis, and photolysis may all work together to produce the observed molecular composition of comets.

The composition of comet 67P has been highly characterized by the Rosetta mission, presenting a limited set of molecular ions and surface compositions to investigate the role of reactions driven by hyperthermal bombardment on 67P and similar comets. Table 1 lists the most abundant molecules found in 67P ice, Table 2 lists the most common ions found in the coma, and Table 3 lists classes of surfaces plausible on comets; together these form the set of reactions the proposed work will investigate.

Table 1. Highly abundant molecules in the ice of 67P (Goesmann et al. 2015)

Name	Formula	Mass percent
Water	H_2O	80.92
Methanamide (formamide)	$HCONH_2$	3.73
Isocyanomethane (methyl isocyanate)	CH_3NCO	3.13
Ethanamide (acetamide)	CH_3CONH_2	2.2
Methylamine	CH_3NH_2	1.19
Carbon monoxide	CO	1.09
Methanenitrile (hydrogen cyanide)	HCN	1.06
Propanone (acetone)	CH_3COCH_3	1.02
Ethanal (acetaldehyde)	CH_3CHO	1.01
2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO	0.98
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$	0.79
Ethylamine	$C_2H_5NH_2$	0.72
Methane	CH_4	0.7

Table 2. Ions present in comas, from Rosetta data and models (Fuselier et al. 2016; Heritier et al. 2017)

Ions	Approximate abundance	Research stage
NH_4^+, H_3O^+, H_3S^+, H_2O^+	High	Early
O_2^+, NH_3^+, H_2S^+, H_2CO^+	Medium	Middle
$CH_3OH_2^+$, $HCNH^+$, H_3CO^+	High	Later
CO_2^+, CO^+, H^+, HCO_2^+, HCO^+, OH^+, O^+	Low	Possible

Table 3. Surfaces of interest found on comets

Surfaces of interest	Example composition	Research stage
Ice	H_2O	Early
Silicate surfaces	Mg_2SiO_4	Middle
Metal surfaces	Fe-Ni alloys	Middle
Metal oxide surfaces	FeO	Middle
Ice containing additional species (i.e. clathrate hydrates)	$4CH_4 * 23H_2O$	Later

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 ions in comet like environments are unexplored experimentally. The objective of this research is investigating the possible role of hyperthermal ion bombardment on comet like surfaces in evolving the molecular composition of comets. Special attention is given to the intriguing possibility that this mechanism may be a key contributor to creating prebiotic molecular compositions on comets. Specific questions include:

1. **What products are created from hyperthermal ion bombardment in comet like conditions? How do these products vary with the ion's composition and energy and the surface's composition, structure, roughness, and temperature? What specific reaction mechanism is taking place?**

Rosetta found different chemical abundances (such as abundant O_2) on 67P than would be expected from radiolysis or photolysis alone, suggesting that an additional reaction pathway may play a role. The mission also detected hyperthermal ions, and the bombardment of these ions might provide the missing additional reactions needed to explain the observed abundances. The reactions with the surface are expected to follow an Eley-Rideal model, where a gas phase interacts directly with the surface without adsorption to produce a gas phase product. The specific characteristics of the ion and the surface will likely affect what products result.

2. **What role do generated radicals play in the comets molecular composition, especially during warming of the ice?**

Following bombardment, generated radicals likely accumulate in or on the ice, these may influence the reactions of subsequent impinging ions and/or react during the warming of comet ice. As the ice warms it may undergo phase transitions (such as clathrate hydrate decomposition) and sublime into gaseous produces, creating an environment in which charged radicals are likely to interact and react with the surrounding compositions. This provides a plausible route to synthesize larger prebiotic molecules like isocyanomethane, methanamide, and ethanamide from otherwise simple products easily created by ion bombardment disassociation.

3. **At what energies can large molecules be ejected from comet ice and safely return?**

Current comet ice contains lots of “larger” simple molecules containing 6 or more atoms (see table 1). As a significant components of the ice (ca. 12% by mass), it is likely that these molecules are ejected into the coma, with some returning to the comet surface. As they return to the surface, they either land intact (a “soft landing”) or are dissociated into smaller fragments. Soft landings require that the majority of the energy is dissipated nondestructively, such as by activating vibrational and electronic states but not breaking bonds. Studying the energies for soft landings could give insight possible surface enrichment processes.

4. How do these new reactions and previously identified processes contribute to the molecular evolution of a comet?

The new synthesis routes identified need to be placed in context with existing work, such as radiolysis and photolysis. Each reaction mechanism requires unique settings (such as exposure to photons or ions with hyperthermal energies) and timespans (during short passes by the sun or a comet’s entire lifespan). Other models for coma chemistry, such as that developed by Vigren and Galand (Vigren and Galand 2013), have been used to understand the collected data of Rosetta as well as test and justify proposed reactions in the coma (Fuselier et al. 2016; Heritier et al. 2017).

Research approach

These research questions will be addressed through experiments on the Giapis lab’s ultra-high vacuum ion beam and a computational model of comet chemistry.

Ion beamline and scatting apparatus

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^+, O^+, N^+, H^+, 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.

The scattering apparatus will be modified to better replicate the comet like environment by adding a) a cryogenic surface on which to form ice, b) heating capabilities to warm the ice, c) neutralization of bombarded surface, and d) improved vacuum quality.

The development of a cryogenic sample plate with heating capabilities: To enable the synthesis of comet like ices, a cryogenic surface that can condense gases pumped through the gas inlet is needed. Although commercial cryostat options were explored, a suitable UHV cryogenic surface with heating capabilities that fits within the current scattering chamber geometric constraints was not identified. Instead, preliminary designs for a UHV cryostat and improved removable sample plate have been designed. The cryogen delivery tube is intended for liquid nitrogen but can also pass liquid helium. The size and requirements of the cryostat is similar to cryogenic probes for NMR systems, which the author has experience designing and fabricating. This design would need to be further developed, constructed and installed. The removable sample plate design consists of an improved version of the previous sample plate which is easier to replace, and includes resistive heating elements behind the sample surface. An important aspect is high thermal conductivity to the LN reservoir during ice deposition and scatting, but minimal conductivity and controllable fast heating rates during warming.

Electron gun for surface neutralization: A commercial electron gun will be installed to neutralize the sample plate and prevent charge buildup. Without this modification, the research is limited to conductive substrates or exceptionally thin substrates, restrictions which may hinder the duration of scatting experiments since it is plausible that during scatting the cryogenic surface will encourage material deposition.

UHV improvements: Currently, the exposed cryogenic surfaces and ice can condense contaminate gases within the chamber, which could be decreased by improving the quality of the vacuum. Currently the UHV system can routinely reach ca. 1×10^{-8} Torr but has difficulties reaching vacuum pressures. Several "quick fix" non-UHV compatible components installed by previous users have been identified and should enable the scattering chamber to reach 1×10^{-11} to 1×10^{-12} Torr, which should be sufficient for ice purity and help increase the signal to noise ratio of the observations.

Proposed experiments and anticipated results

What products are created from hyperthermal ion bombardment in comet like conditions? What is the role of the ion's composition and energy?

Experimental work will begin by bombarding H_2O^+ on a surface of pure ice, seeking to replicate the similar generation of O_2^- on a metallic surfaces. Using this simple substrate, the work will expand to investigate the "early" research stage ions listed in Table 2. We will observe whether the ion reacts with surface species, disassociates, undergoes electronic or vibrational excitation, implants into the subsurface, or sputters the surface, and how this varies with the ion's energy and composition, angle of impact, and the surface's composition. We anticipate that most ions will disassociate into fragments that bounce off the surface, with a smaller population adsorbing to the surface and some reacting with the surface. The surface reactions are expected to follow an Eley-Rideal model, where a gas phase interacts directly with the surface without adsorption to produce a gas phase product. We expect the approximate yield of scattered radicals to be similar across ions and to be primarily dependent on the composition and possibly the bonds within the ion.

Characterization, via mass spectrometry and single channel electron multiplier, of positively and negatively charged products of these simple impinging ion should enable a prediction of products resulting from other ions with 2 - 4 atoms. The focus on simple surfaces and simple ions will help in determining the underlying reaction mechanisms which are present, which will likely have broader scientific value.

Additional work will expand into the "middle" stage ions as listed in Table 2. These will build towards actual comet compositions (a mixture of all ions discussed) by characterizing each ion-surface combination individually.

Although large prebiotic molecules with 6 or more atoms are not anticipated to be formed directly, later stage work will investigate whether impinging already large ions at lower energies results in the synthesis of even larger products.

Some exploratory work will be performed on the low abundance “possible” research stage ions from table 2. Although these ions are low abundance, these ions are good candidates for forming important radicals for prebiotic synthesis, such as HCO. Detecting such a product on a simple surface would warrant further investigations necessary to determine the reaction mechanism and estimate yields possible in comet like environments.

What is the role of surface composition, structure, roughness, and temperature on resultant products?

Initial work will focus on small changes in the surface, such as the influence of surface temperature or differences in surface composition. As defined in the surfaces of interest (Table 3), other surfaces (silicates, metal oxides, and metals) that are also present on comets will be investigated. The resulting products of the surfaces is likely to be similar for any given ion. However, given the nature of the suspected Eley-Rideal reactions, a change in the orientation of surface adsorbates may significantly influence the yield and may enable additional or different products to be formed.

What specific reaction mechanism is taking place?

The above experiments will also help identify what type of reaction (Eley-Rideal or otherwise) is occurring with bombardment. Understanding these reactions across the many variables proposed above should enable broad trends to be identified and general predictions beyond the specific conditions investigated.

What role do generated radicals play in the comet’s molecular composition, especially during warming of the ice?

Hyperthermal ion bombardment on ices will almost certainly produce charged radicals, which are likely to accumulate on the surface or possibly a small distance within the ice. The role these radicals play may be immediate and observable as products in the scattering chamber, may be slightly delayed, requiring an additional ion to impinge upon the surface and react with a waiting radical, or may be intermittent, only participating in a reaction during warming. To investigate the delayed reactions, a surface, such as ice with N radicals present, will be generated; this surface will a) be bombarded with a hyperthermal ion (such as CO^+) to observe changes in the scattering products or b) will be warmed to observe the products released from the ice.

As ice warms, it is likely that these radicals have enough energy to react with neighboring molecules and form larger prebiotic molecules. To investigate these types of reactions, the sample plate will be designed with warming capabilities that are controlled by the power passed through a heating element on the back side of the sample plate. Some molecules might also form through interactions with radicals on the surface, but these molecules may not be capable detaching and being observed as a scattering product. If these types of molecules are generated, they will likely be only observable when released from the ice via warming.

At what energies can large molecules be ejected from comet ice and safely return?

Initial work would begin using a stable surface (such as FeO or Mg_2SiO_4) at cryogenic temperatures, which will be bombarded with large ions at a specific energy. After a short period of bombardment, the surface will be warmed so that the products are released and can be observed. Intact products observed at this point are almost certainly the result of soft landings. Accessing the released products from different impinging energies will help determine the likelihood of these same molecules safely returning to the comets surface after being ejected. Ideal candidates for this are the molecules composed of 6 or more atoms and listed in Table 1.

How do these new reactions and previously identified processes contribute to the molecular evolution of a comet?

To situate the proposed experiments, a chemical model that uses the required conditions and probabilities for ion bombardment to predict estimated yields will be built. The model will provide a platform to compare existing and novel reaction processes and enable a better understanding of comets' role in producing prebiotic molecules for the formation of life.

The envisioned model itemizes each known or theorized reaction and its known probable outcomes if its necessary conditions are met. The itemized reactions will be kept in an easy to edit database. The chemical model then draws on global variables (conditions), which will initially be set by the user, and once started will then evolve the chemical and molecular composition of the comet within given timeframe (one such global variable). We are hopeful that the model's simple design will encourage incorporation and collaboration with other comet models. For example, a reaction that requires UV light could iteratively ask a geometric model the percentage of the comet that is exposed to light at time "t", and then use this exposure for its calculations; conversely, the geometric model's exposure to sunlight parameter could be reduced to a probability that a surface is exposed to light, and then this probability used in the calculation.

Reaction rates and their influence on a large compositional system can be difficult to grasp intuitively. Hands on manipulation of an easy to use graphic interface that connects the reactions to the modeling environment could help researchers understand the importance of individual reactions, and result in better predictions of comet molecular evolution. A conceptual mockup of the graphic interface is presented in Figure 1, illustrating with one example how the model may help researchers connect the whole process.

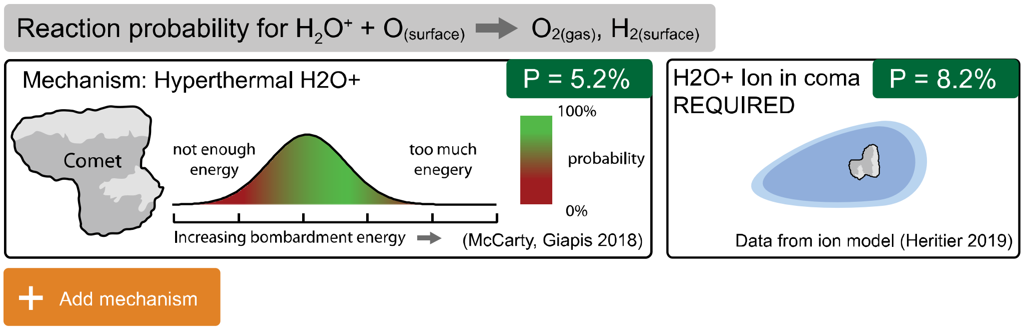

Figure 1. Conceptual mockup of model graphic user interface.

Early drafts of the model will be developed in Excel to encourage collaborative input and enable easy database management. Later 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 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 ion bombardment on comets, this research will enable a more complete understanding of comet chemical processes. The proposed chemical model will link ion bombardment with existing models of radiolysis and photolysis to predict actual chemical speciation as observed on comet 67P. This research contributes to debates about the origins of life by testing whether prebiotic molecules can plausibly be formed via surface reactions.

Work on hyperhermal ions may have synergies with similar work in bioscience 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. The increasingly complex thin film depositional techniques may benefit from additional insight of the reactive role and mechanisms of relatively lower energy ions on complex surfaces.

Proposed Educational Activities and Broader Impacts

College level courses to be taught at Caltech: Classroom teaching will consist of co-teaching a course on abiotic surface science reactions, and running a workshop aimed at improving the research experience and quality of PhD students. First, a new course on surface science reaction will have broad appeal to astrochemists, chemical engineers, material scientists, and geochemists, as it explores the role of inorganic surfaces in chemical reactions. The course will focus on the role of the surface to offset the energy cost of a reaction, exposing students to topics such as Eley-Rideal reactions, the role of catalytic step edges, and techniques to study surface reactions. Second, a workshop on *Visual thinking for sharing science* aims to provide young researchers with action based tools and approaches for generating ideas and progressing research. It is a single day, 8 hour workshop split between a) setting up workflows to develop, create, and refine scientific though graphics, b) time saving and/or quality improving tricks and tips in graphic design programs, and c) a discussion of aesthetics and using graphics to enrich the thinking process. The workshop's practical focus will provide busy PhD students with significant "bang" for their time commitment "buck".

Mobile-friendly teaching resources: Cellphones—advanced computers with built in cameras, geographical and spatial positioning abilities, 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, as they are a relatively new device, can be a complete nuisance, and lack device-appropriate online educational materials. I propose to create online, phone-friendly teaching materials for undergraduate classrooms, as well as material for teachers that helps them understand the value of using cellphones to excite students towards technology. Online material intended for use on mobile phones will be developed on three topics: Eley-Rideal reactions, hyperthermal ions, and comet ice. 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.

Wikipedia editing: It's arguable that more people learn about science through Wikipedia than through any other source, so improving Wikipedia articles and references possibly has a larger influence than producing textbooks and other educational materials. I will actively create or adopt 3-6 Wikipedia pages and improve their content quality. For example, there is currently no "hyperthermal ion" page, and the comet entry has no presentation of the composition of the ice.

Diversity in STEM outreach: As a minority in STEM who is also well connected with other minorities in STEM, I believe that it is not "broad impacts" that will make significant progress towards increasing diversity in STEM, but rather narrow, personalized advice, mentoring and attention. However, creating opportunities for personalized interactions is challenging, as is motivating fellow minorities to entering a field that will likely pay less than other options, is arguably harder to succeed in, includes fewer role models, and contains higher levels of employment uncertainty.

A primary place to create such targeted interactions is in doing research. I have found that diversity in background results in diversity of thought, enabling more creative research whose varied interpretations push conclusions closer towards the truth. Exposing minorities to their value in the research setting is the primary goal of my outreach. I intend to develop several small research opportunities to involve underrepresented minority (URM) undergraduate students from Los Angeles Community College District. Although specific projects will need to be developed, the comet modeling aspect of the research presents multiple opportunities to involve additional diverse minds. The research is intended as a platform to connect with and mentor students, share my own experience, give insight into 4-year and grad school applications, and encourage them to join supportive networks like SACNAS (Advancing Chicanos/Hispanics and Native Americans in Science). I anticipate that four to six students will be involved and mentored in this outreach.

Justification for Caltech

The Giapis lab at Caltech 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 better replicate comet like environments. In this regard the functionality and availability of the Giapis lab beamline presents a serendipitous opportunity. 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. Furthermore, Caltech's relationship with the Jet Propulsion Laboratory—which was centrally involved in the Rosetta mission—presents an additional setting for developing collaborations, discussions, giving presentations, and networking opportunities. Caltech's setting in Los Angeles also presents a scientist with multiple avenues to have a broad impact. For example, the abundant community colleges are actively seeking free 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.

Candidate's career goals

I seek to pursue a research career that focuses on observing and studying chemical reactions on or within inorganic solids. I believe part of my scientific forte involves an aptitude to design and fabricate new scientific instruments, which was a driving factor to interact with Dr. Giapis, an experienced engineer who has overseen and mentored people building numerous "one of a kind" apparatuses. I will also acquire experience with additional spectroscopic and computational techniques, which will provide me with additional problem solving approaches. The opportunity to co-teach with Dr. Giapis will provide upper division teaching experience I currently lack.

I am hopeful that a postdoctoral position at a prestigious institute like Caltech will propel me towards a research career with a significant level of interaction with students, ideally a tenure track professorship. It is my belief that the university setting presents the most opportunity to influence the direction of STEM though teaching and outreach. As the first in my family to pursue graduate studies, and a Hispanic minority in the scientific and engineering community, I have felt and responded to a strong calling to notice, encourage, and support a diverse array of thinkers in the sciences. My own entry into science was only made possible through the openness of some scientists, enthusiastic mentoring, engaging teaching, inspiring examples to model myself after, and likely in my case fair colored skin and an Irish last name. My own experience has convinced me that although physical, societal, economic, or perceived disadvantages present real and challenging hurdles for those who have them, they can all be overcome by pivotal actions and words coming from the right people. It is my passion to further open the sciences, something I believe I can best accomplish as an enthusiastic mentor, an engaging teacher, and a transparent (in the bureaucratic sense) and visible (in the community sense) scientific leader; all of which I believe I could best accomplish as an academic educator in a research environment.