PNAS COMMENTARY

Unraveling the complex inventory of biorelevant organics in the plumes of icy moons

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The very first detection of the exoplanets Poltergeist and Phobetor in the constellation Virgo in 1992 by Wolszczan and Frail (1) manifested the backbone of mankind's belief that we might not be alone in the Universe. Although these rocky exoplanets are constantly exposed to ionizing radiation from the neutron star PSR B1 257+12 that they orbit and hence cannot support organic life as we know it, the very proof of the existence of planets outside our Solar System paved the way for the fundamental prerequisite of prospective life beyond Earth: extrasolar, potentially habitable worlds. Exploiting direct imaging along with astrometry, radial velocity, transit event observation, and microlensing, some 5,500 exoplanets—comprising the first extragalactic exoplanet M51-ULS-1b observed in the Whirlpool Galaxy—in 4,000 plus planetary systems have been confirmed over the last three decades (2, 3). Among them, the exoplanet Kepler-452b and its G-type star are considered the closest analog to the Earth and Sun so far (4). Kepler-452b is contemplated to be rocky with an atmosphere, water, and land located within the habitable zone of a G-type star similar to our Sun and hence represents the prime candidate of hosting extraterrestrial life.

However, the distance of Kepler-452b of 1,402 light years from Earth and the lack of adequate space propulsion technology precludes any visitor from our planet from determining to what extent Kepler-452b is habitable and harbors life. Therefore, an alternative strategy is required. In PNAS, Burke et al. (5) present such a novel development and present the design and performance of a Hypervelocity Ice Grain Impact Mass Spectrometer (HIGIMS). This instrument is designed to search for molecular signatures of life closer to home in our Solar System to eventually answer the question if life exists beyond Earth. Rather than searching for extraterrestrial life explicitly, astrochemists and astrobiologists have begun identifying the fundamental chemical processes and searching for the basic molecular building blocks of life. The complex organics can be arranged into several key classes of biological relevance: amino acids, sugars, nitrogen bases, phosphates, glycerol, and fatty acids along with their polypeptide, nucleotide, adenosine triphosphate, phospholipid, and triglyceride linkages. Those species resemble vital molecular building blocks in contemporary biochemistry connected to genetic information, cellular energy storage, cell membranes, and metabolisms, thus representing the critical prerequisite to life on the molecular level as we know it. This is achieved through the design of laboratory simulation experiments which replicate chemical and physical conditions and initiate chemical reactions in, e.g., hydrocarbon-rich atmospheres of planets and their moons (gas phase) (6, 7) and on icy planetary bodies (condensed phase) (8–10) often through ionizing radiation in the form of charged particles (solar wind, magnetospheres, and galactic cosmic rays) or solar photons. Critical progress in this field of astrochemistry and astrobiology and in untangling the underlying processes to synthesize biologically relevant molecules connected to the *Origins of Life* theme requires novel technology and next-generation experimental setups capable of mimicking the extreme physical and often nonequilibrium conditions under which chemical reactions operate in our Solar System.

Burke et al.'s (5) truly unique instrument experimentally simulates hypervelocity impacts of submicron-sized, organics-doped icy particles from the plumes of Saturn's moon Enceladus and conducts for the first time an accurate in situ mass spectrometric characterization of the content of the ice grains, thus providing unprecedented evidence on the origin of the organics detected. The instrument is of critical need to the astrochemistry, planetary science, and astrobiology communities. Enceladus and Jupiter's moons Europa, Callisto, and Ganymede hide massive global liquid water oceans beneath their icy crusts. As the ice shell of, e.g., Enceladus distorts and cracks emerge, liquid water along with potential organics and microbial lifeforms might be ejected from the subsurface oceans via plumes rising up to 160 km above the surface. This phenomenon was observed spectroscopically by the Keck Observatory in Hawaii and in situ by the Cassini spacecraft travelling through the plume to sample and analyze the composition via impact ionization mass spectrometry of hypervelocity icy grains from orbit (11, 12). The composition of the material in these plumes can then be analyzed to ascertain whether these oceans might harbor alien life or molecular precursors.

However, whereas the Cassini spacecraft unambiguously detected organic compounds from the flumes that could provide ingredients for the formation of amino acids (13, 14), the interpretation of these data has been challenged. The source of the detected organics has been deeply questioned, and no consensus has been reached if these organics originate from the plumes or if they are formed as the result of the hypervelocity impact of the icy grains onto Cassini's ice collector. That dilemma is the direct consequence of a complete lack of fundamental understanding of the potential chemistry as the outcome of the hypervelocity impacts. Therefore, a laboratory validation of the stability and detection of organics

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from hypervelocity impacts of icy grains is clearly required to support—or disprove—that biomarkers such as amino acids can survive an impact at hypervelocity speeds.

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Burke et al. (5) accepted this tremendous challenge and developed a HIGIMS. Rather than disseminating appealing images of planets and their ice moons, the authors diligently followed the principle "Physical Chemistry First" and designed an instrument capable of simulating the effects of hypervelocity impacts of icy grains on the chemical composition of the organics embedded in these ice particles. This requires a critical understanding of physical chemistry and capability of designing new instruments of fundamental relevance to Solar System research as provided here. Exploiting amino acids as benchmarks, the authors provided compelling evidence that at a velocity of 4.2 km s^{-1}, amino acids embedded in micrometer-sized icy grains do survive the impact with results correlating exceptionally well with Cassini data. The authors also afforded persuasive testimony that salts embedded with amino acids in these ice grains significantly reduce the detectability and hence survivability of amino acids, thus making this instrument particularly important to validate data from past, present, and future space missions probing the plumes of icy ocean worlds. Through cutting-edge physical chemistry experiments, this work delivers a fundamental benchmark for the orbital sampling method to successfully detect organic molecules such as amino acids in the plumes of Enceladus and within the framework of the Europa Clipper mission relevant to the search for the Origin of Life.

The authors anticipate that future works will explore the survivability of more chemically complex and fragile biorelevant molecules such as dipeptides (15), lipids (16), glycerol phosphates (17), and nucleotides embedded in ices. Experiments can also be carried out to probe the synthesis of biosignature molecules from simple precursors upon impact. This setup is truly versatile and opens new research directions of testing the survivability of organics embedded in proxies of meteoritic parent bodies upon delivery to early Earth. Synthesized within ices on interstellar grains in molecular clouds and later partially incorporated into the parent bodies of, for instance, the Murchison meteorite, the survival rate of these organics upon impact on proto-Earth is truly unknown, but it is critical to place constraints on the survivability of abiotically synthesized organics in deep space, which demonstrates the potential impact and versatility of the instrument. After all, the understanding of our origin is intertwined with the comprehension of the chemical evolution of the Solar System. Here, chemistry is vital in unraveling the evolution of matter including biorelevant molecules from the microscopic level (elementary chemical reactions) to the macroscopic scale (planets and moons). Since the present composition of each Solar System body reflects the matter from which it was formed and the processes that have changed the chemical nature since its origin, a detailed investigation of the processes altering the chemical composition of the pristine environment is critical to rationalize the contemporary chemical makeup of the Solar System and to decipher the Origin of Life on the molecular level. This requires analytical instruments and techniques as developed by Burke et al. (5) eventually providing new fundamental knowledge of the chemistry of space and specifically on the persuasive detectability of biomarkers such as amino acids in plumes of icy moons that we did not know before.

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