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Technology Considerations Relevant to an Exobiology Surface-Science Approach for Europa

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ABSTRACT

If Europa is to be of primary exobiological interest, namely, as a habitat for extant life, it is obvious that (a) a hydrosphere must prevail beneath the cryosphere for a long time, (b) internal energy sources must be present in a sufficient state of activity, and (c) a reasonable technical means must be available for assessing if indeed life does exist in the hypothesized hydrosphere. This discussion focuses on the last point, namely, technological issues, because the trend of the compounding evidence about Europa indicates that the first two points are likely to be true. First, we present a consideration of time-of-flight mass spectroscopy conducted *in situ* on the cryosphere surface of Europa during a first landed robotic mission. We assert that this is a reasonable technical means not only for exploring the composition of the cryosphere itself, but also for locating any biomolecular indicators of extant life brought to the surface through cryosphere activity. Secondly, this work also addresses practical issues inherent in any kind of instrumental interrogation of a surface whose properties are governed by radiation chemistry. This includes advocating the construction of a Europan surface simulator to familiarize instrumental system developers with the spacecraft- and instrument-scale conditions under which such an interrogation would take place on Europa. Such a simulator is mandatory in certification of the functional utility of a flight instrument. **Key Words: Europa—Instrument methods—*In situ* science—Exobiology—Astrobiology. Astrobiology 1, 467–476.**

INTRODUCTION

Mounting evidence suggests that the Jovian satellite Europa could be a habitat for extant life, as amply summarized in the National Research Council Space Studies Board's (1999) document *A Science Strategy for the Exploration of Europa*, with the references therein providing persuasive arguments. The trend of discovery of knowledge of Europa, particularly that derived from the Galileo space probe as it orbits Jupiter, has tended to reinforce the original hypothesis (Squyres *et al.*, 1983) that substantial amounts of internal liquid water exist on Europa—including the possibility of an ice-capped ocean or hydrosphere. Following the Galileo mission, a Europa

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orbiter and then landed spacecraft will serve as platforms for *in situ* investigations directed toward issues relevant to both planetary science and exobiology.

Deployment of instruments from a landed spacecraft platform on Europa will be a unique experience, even when compared with the Huygens probe now directed to Titan. While laboratory-scale experiments done at cryogenic temperatures will serve to provide an understanding of possible radiation-induced physical chemistry, including that useful for developing a lander's instrumental operating principles, the physical scales of these activities are insufficient for anticipating issues that can arise in the deployment of an instrument system attached to the landed spacecraft platform. For that, a Europa surface simulator of spacecraft- and instrument-scale dimensions is in order.

The Jovian magnetosphere inflicts Europa with a proton flux of $1.9 \times 10^9\ m^{-2}\ s^{-1}$ for $E > 2.5$ MeV (Vogt *et al.*, 1979). Two consequences of this environment were recognized in the National Research Council's report: (a) radiation chemistry will play a significant role at the surface and (b) deployed instruments must be radiation hardened. Thus, the *in situ* instrument challenge is to arrive at an instrument or instrument suite that is robust and yet still capable of doing high-quality science in the service of both planetary science and exobiology. The development of such devices should be of the highest priority. After consideration of all aspects of the issue, it is our assessment that time-of-flight (TOF) mass spectroscopy (MS) is the instrumental technique most suitable for deployment on the surface of Europa. It permits a definitive level of identification for both those smaller molecular species considered to be likely residents of the cryosphere itself and any larger biomolecules brought to the surface from the hypothesized hydrosphere through ice-cap activity, were the hydrosphere populated by extant life. This technique should be less susceptible to a high-radiation environment than optical devices.

The major constituent of the Europan cryosphere, on the basis of spectroscopic measurements, is H_2O (Pilcher *et al.*, 1972; Clark *et al.*, 1986; Calvin *et al.*, 1995). Other molecular species, usually small molecules, can also be inferred. These include sulfur, SO_2, $MgSO_4 \cdot 6\ H_2O$, and $MgSO_4 \cdot 7\ H_2O$ (Lane *et al.*, 1981; Noll *et al.*, 1995; Spencer *et al.*, 1995; McCord *et al.*, 1998). In addition, $Na_2CO_3 \cdot 10H_2O$ and hydrogen peroxide (H_2O_2) appear to be present (McCord *et al.*, 1998; Carlson *et al.*, 1999). The latter is of particular interest because H_2O_2 is the likely result of radiation chemistry induced by high-energy particles from the Jovian magnetosphere that bombard the water–ice surface. This result should not be surprising, given the long experience with the radiation chemistry of water (e.g., Moore and Hudson, 2000, and references therein). The presence of H_2O_2 on Europa imparts exobiological considerations from the standpoint that, first, it is an oxidant capable of reacting with biomolecules (should such species be brought to the surface by ice activity transport) and, second, as an oxidant it could sustain a biosphere if transported downward (Chyba, 2000). Europan brines may contain NaCl, and radiation is known to induce a color center absorption band in NaCl between 400 and 500 nm (Kittel, 1976). Had Galileo's UV spectrometer been capable of measurements <1,000 nm, it would have been possible to detect any frozen-out NaCl crystals where the ice cap is breached from below. The yellow coloration in Voyager and Galileo images is provocative in this regard. All of the species mentioned in the above discussion (and many others) are measurable by MS, including TOF MS.

TOF MS TECHNOLOGY

Recent developments in the commercial sector have resulted in the offer for sale of TOF mass spectrometers that have been reduced from "stand-on-the-floor" console size to a bench-top footprint. This bodes well for *in situ* space applications. It was exactly this process in the history of laboratory Raman spectrometers around 5 years ago that presaged the development of the miniature Raman spectrometer originally intended for the Athena Rover, and now for other landed missions. To be specific, the Kratos KOMPACT matrix-assisted laser desorption ionization (MALDI) system is now the same physical size as the Kaiser Raman spectrometer from which the Athena instrument draws significant heritage.

New advances in technology, including the increase in the digitization rate of the data collection electronics and the trend in miniaturization and simplification of laser systems, are going to reduce dramatically the size of the laser mass spectrometer in the next few years. To collect a meaningful TOF spectrum, the minimum steps of the time measurement at the detector must be, say, at least one order of magnitude smaller than the typical peak width in the mass window of interest. Clearly, for a linear TOF instrument, a longer flight tube results in greater peak widths and a wider separation between mass peaks. This permits a slower data-sampling rate. For many years, the upper limit for high-speed multiplexed flash analog-to-digital (A-to-D) converters was 100 MHz. In order to study interesting biological molecules, this meant you needed flight times on the order of 100 μs. Using typical Wiley–McLaren voltages ($\sim$2–3 kV), that translated to flight tubes of 1–1.5 m in length. In the last few years, significant advances in high-speed VLSI chips (e.g., 0.3 μm etching) mean that it is not terribly difficult to build 1–5-GHz A-to-D converters. This order-of-magnitude increase should allow for a mass spectrometer with a much shorter flight length ($\sim$0.1 m!).

For Europa, it is mandatory that electronic components be configured against radiation effects by hardening and shielding; Of course this is the case for all instruments; therefore the advantage of TOF MS, in this regard, lies in the low susceptibility of the components involved in the TOF mass separation process—namely, the electrode assembly and flight tube. There may be radiation effect issues regarding the multichannel plate detector of the TOF MS, although they should be less severe than in the case of, for example, the CCD detectors used in optical instruments. Metallic shielding can be utilized to reduce these effects. It may be that in order to carry out any kind of surface operation on Europa for extended periods of time (i.e., longer than what is experienced by a Jovian orbiter while in the vicinity of Europa), key parts of the spacecraft and instruments will have to be shielded by the Europan surface material itself. This could be accomplished by a mechanically active spacecraft component previously not required in landed missions on other bodies.

Lasers are utilized in TOF MS for volatilization and ionization. This may involve multiple lasers or a single laser to carry out both of these functions. By "laser" we not only mean devices that contain a single lasing component but also complex devices that can have two or more lasing subcomponents, including semiconductor and optical hybrids. Commercial laser systems are generally large, expensive, and extremely delicate (e.g., the shorter the operating wavelength of the laser, the more sensitive the end-mirror output couple alignment). Recent advances in solid-state semiconductor laser diode technology are about to change this picture entirely. For the first step (the first "L" of L^2MS), which is the desorption of neutrals from a substrate, pulsed mid-IR single-heterostructure lasers such as the injection GaAlAs diode lasers, in small, compact packages, can be made to generate 200 ns pulses up to 50 W with repetition rates up to several kilohertz. A second laser, usually delayed and emitting shorter pulses at UV wavelengths (the second "L" of L^2MS), is required to ionize the desorbed molecules, which then travel down the flight tube to the detector. It is the pulse width of this ionizing laser that determines the resolution of mass separation.

Furthermore, through improvements in the fabrication of quantum-well and strained-layer structures, as well as the use of nonabsorbing mirrors and/or chemical passivation to avoid facet damage, it is feasible to envision the use of direct intracavity harmonic generation in pulsed high-power GaAlAs diode lasers within the next 5 years. This would offer blue and UV laser light suitable for MALDI, laser desorption MS, and laser polarization in a package no larger than a box of matches. The UV ionization laser need not have the power of a desorption laser; indeed, too high a power results in production of a plasma out of the plume induced by the desorption laser. Therefore achieving very-short-duration pulses with this laser is less of a technological challenge. Of course, it will be important to investigate how lasers employed in TOF MS can be shielded against a charged-particle radiation environment or hardened by means of appropriate fabrication methods.

RECONCILIATION OF MEASUREMENTS AT LOW AND HIGH MOLECULAR WEIGHT

Given the potential presence of biomolecules that originate from Europan xenospecies (perhaps revealing themselves in the dark linae observed on Europa's surface) and the technical challenge of actually putting a lander on the surface of Europa, the instrument should have the capability of large biomolecule/biopolymer detection. Recent years have shown the usefulness of MS for such tasks, including the characterization of microorganisms (Fenselau, 1994). In life-science laboratories, a method of choice for measurement of large biomolecules is MALDI-MS, which employs as its basis the TOF technique in either the linear flight tube mode or the reflectron flight tube mode.

The "secret" to MALDI-MS is to place the sample in close proximity to an agent that vaporizes and ionizes under the action of a UV laser pulse and then transfers its charge to the sample molecules also placed in the vapor phase. In the laboratory setting, this means simple mixing of the sample with the MALDI agent. The most significant benefit of this process is that delicate molecular species such as DNA, which fragment under other ionization techniques (thus greatly compounding the task of identification), remain intact and are only singly charged. The importance of this MALDI-MS feature for understanding the nature of biomolecular species cannot be overemphasized.

While strikingly successful for biomolecules with molecular masses as high as 10^6 daltons, MALDI agents such as 2,5-dihydroxybenzoic acid (for peptides, proteins, and polysaccharides), 3-hydroxypicolinic acid (for oligonucleotides and nucleic acids), and 2,4,6-trihydroxyacetophenone (for oligonucleotides and oligosaccharides) produce such an intense mass distribution in the low-molecular-weight region that they mask the signal of small molecules present in the sample. This is of course a significant issue for planetary science objectives on Europa. The key to utilizing a TOF MS on Europa will be to produce an instrument capable of both small and large molecular determinations.

The task at hand is to identify MALDI agents that do not proliferate in the low-molecular-weight range and can be applied in as simple a manner as possible. The use of nanometer-sized metallic particles is very interesting in this regard. By virtue of their small size, these particles have very large optical absorption cross sections, effecting their efficient laser vaporization and ionization. The contribution of this type of MALDI agent to the mass spectrum is merely its atomic weight (or the molecular weight of small clusters) and can be readily separated from other species in the mass distribution. Cobalt particles 20 nm in diameter have been shown to be useful as MALDI agents (Tanaka *et al.*, 1988; Kawabata *et al.*, 1998), since the result is the contribution of only the Co^+ ion at $m/z = 58.9332$. It should also be noted that there have been attempts, unpublished to our knowledge, to utilize mid-IR lasers to do MALDI involving water–ice as the agent.

On Europa, the lack of a significant atmosphere and the ~125°K temperature make it possible to manufacture nanophase MALDI metal agent deposits directly onto the sample simply by vaporizing the metal onto the cold surface. This permits the use of easily evaporated metals such as aluminum, magnesium, sodium, or potassium as MALDI agents (other metals are of interest as well). Evaporating a metal onto a cryo-ice would result in a surface deposit of small "islands" in the nanometer size range rather than a mirror finish, producing dramatically high optical absorption. Almost 40 years ago, in an industrial setting, one of the authors (Wdowiak) experimented with the vaporization of magnesium–barium alloys onto liquid nitrogen–cooled substrates, which were then shown to display an increased rate of hydrogen uptake relative to those prepared on room-temperature substrates. This was an early application of small-size island clustering to produce nanoparticles.

More recently, others have produced nanophase materials, including iron, through a similar procedure. Methods of dispensing metallic species, such as Co, and other potential MALDI agents mentioned previously onto cryo-ice, by vaporization and other means, are now being explored in our laboratory. MALDI, as used in biomolecular laboratory measurements, involves mixing intimately the MALDI agent and the sample prior to placing it on the platen. A metal agent, through its optical absorption, serves to couple the laser energy to the material under interrogation. Although applied to the surface, upon the laser pulse, both the metal MALDI agent and the sample underneath are vaporized and mixed in an extremely rapid manner. This simplifies sample preparation relative to what is currently done in the laboratory. The cryogenic conditions on Europa provide a unique opportunity to implement this technique, one that would not be normally used in a room-temperature laboratory. A potentially significant issue to be addressed is the interaction of the MALDI agent and the Europan cryo-ice, which has been processed by radiation and photolysis to produce, among other species, resident oxidants.

Any atmosphere on Europa is likely due to the evaporation of H_2O from its icy surface, and therefore depends upon the temperature of the ice, which itself depends upon the IR flux from Jupiter and the Europan latitude in consideration. According to the literature (e.g., Orton *et al.*, 1996), a value of $T \leq 125°K$ is appropriate. At least, this implies a good fore-pumping pressure that only needs to be augmented by one of several options: (a) a turbomechanical pump, (b) a sorption pump with thermal recycling, (c) a getter pump (the MALDI agent material supply could also be applied as a chemisorption agent in this case), or (d) an ion pump (simpler than a turbomechanical pump, but requires a special high-voltage power supply).

NEED FOR INSTRUMENT-SCALE FAMILIARITY WITH THE SURFACE OF EUROPA

Current experience with surface conditions of solar system bodies has been obtained by landings on the Moon, Mars, and Venus. Prior to a Europa lander, experience will likely arise from landed missions to Titan, comets, and asteroids (as with NEAR-Shoemaker on Eros). Europa is without a significant atmosphere, like the Moon, and its temperature is similar to that on Titan, which has a very significant atmosphere. Europa is covered with water–ice, of which comets are composed, but, unlike comets, it has significant gravity for compressing the ice. Most of all, it is immersed in the high-radiation environment of the Jovian magnetosphere, a condition quite unlike the radiation environment experienced by the Moon, Mars, Titan, comets, or asteroids. Thus, from the standpoint of experience on-hand and to be expected in the near future, Europa (and the other icy Galilean satellites) is a unique kind of landing site. For a landed spacecraft to function successfully on Europa, it will have to be able to withstand the conditions on that body and other icy satellites orbiting within an energetic magnetosphere.

Placing a spacecraft onto the Europan surface will be similar to the task of robotic landings on the Moon, given that there is no atmosphere of significance on either body. Prior to the lunar robotic missions, there was considerable conjecture as to the nature of the lunar surface and the consequences for landing operations. It is to be expected that similar discussions and controversies will arise as the first landing on Europa is being planned. From the standpoint of doing *in situ* science, it will be important to arrive at a reasonable model of the Europan surface to ensure that the arrival of the spacecraft or the deployment of instruments does not perturb the nature of what we wish to assess.

When preparing for missions to the Moon or to Mars, a researcher can exercise instruments and instrumental protocols in the field at terrestrial sites that represent reasonable analogs of extraterrestrial geologies. In the case of Europa (or other icy Jovian or outer-planet satellites) the situation is quite different in that terrestrial field site analogs are nonexistent even at Arctic or Antarctic sites because of the radiation environment of the Jovian magnetosphere as well as the cryogenic temperatures and the vacuum of the icy Galilean satellites. In terms of deep probing through an ice cap and into a hydrosphere, Lake Vostok should provide useful ground upon which to begin to build an experience base for such operations on Europa. However, that kind of outer-planet operation, by virtue of energetics and technological complexity, is not realistic for the first or early follow-up missions directed to the Europan surface. On the basis of current knowledge, the general nature of the immediate accessible Europan surface is known to be largely composed of water–ice, to have cryogenic temperatures (~125°K), to have no significant atmosphere (effectively a vacuum), and to suffer a high bombardment flux of charged particles over a wide energy range (~10^3–10^7 eV) that results in processes including sputtering, implantation, and radiation-driven chemistry (see, e.g., Cooper *et al.*, 2001).

Realistically, there are only two options for predicting the nature of the surface environment with which the first Europan landed spacecraft will have to contend: (a) theoretical models based upon current knowledge of physical and chemical properties of likely cryosphere constituents on the basis of observations and (b) laboratory simulations. We take the viewpoint that theoretical modeling, while useful for initiating the issue, has one major drawback: namely, the requirement for sufficient imagination or foresight on the part of the modeler when confronting a situation such as is found on Europa—one that can only be regarded as extreme in terms of the human experience or, indeed, is absolutely outside of direct human experience. Laboratory experiments done on the small scale, while important in understanding the chemistry issues, in actuality do not address the problems encountered when developing a full-scale instrument for deployment on a full-scale surface, particularly one of a largely unknown nature like that of Europa.

The inability to "take a field trip" makes meaningful laboratory experiences necessary, at the simulator level, for deriving the factors involved in the deployment of an instrumental technique on Europa and for formulating the protocols for its successful and efficient utilization. The technical complexities and economic consequences of placing instruments on Europa for *in situ* measurements would seem to make this route a mandatory one. It is the contention here that radiation chemistry and particle bombardment are the likely drivers of the physical and chemical processes in the topmost surface layer of Europa, which will be first accessible in the exploration effort. Therefore, these environmental elements must play significant roles in laboratory investigations.

We also argue that, because of the expected complexity of the Europan situation, creation of Europan surface analogs should result in area and depth of material that is comparable to the footprint of instrumental interrogation or sufficient to assess any perturbation induced by the vehicle itself. This expectation means that activities involving charged-particle bombardment of cryo-ices in a vacuum would have to be carried out on a scale that is much greater than has been done in the past. Prior research involved irradiation of millimeter- to centimeter-sized areas by experimenters utilizing MeV accelerators most often set up for other purposes (e.g., Moore *et al.*, 1983; Pirronello *et al.*, 1988; Strazzulla, 1988) or ~100 keV systems built for such investigations (e.g., Wdowiak *et al.*, 1985, 1988; Strazzulla *et al.*, 1991).

It is ironic, given the interest in and significance of Europa to both planetary science and exobiology, that only one accelerator-based cryo-ice study in the United States is being carried out in a continuing manner, under the direction of Marla Moore at NASA's Goddard Space Flight Center. It uses a 1960s-era Van de Graaff proton accelerator (originally acquired for engineering studies of radiation effects on electronic components) for the purpose of studying radiation-driven chemical reactions (see, e.g., Moore and Hudson, 2000). This laboratory also employs Lyman-α photolysis for the study of ice photochemistry (Gerakines *et al.*, 2000). While such a facility provides essential physiochemical research information, it cannot be considered an adequate simulator for instrument and protocol development or a significant provider of engineering-level information, since this system was designed for the study of specific cosmic-ice issues with irradiation areas only ~1–2 cm across. The surface composition of Europa will likely vary over larger size ranges. An *in situ* instrument capable of "scanning" a large surface area, because of expected textural variation, will provide a chemical map of the Europan surface ice, permitting study relevant to planetary science in that lessons learned from such fields as geophysics may be employed to come to a full understanding on the Europan surface.

A facility is required that permits the deposit of spacecraft/instrument-scale areas of cryo-ice and the energetic processing of significant fractional areas of the overall deposit so that edge effects and depth issues become insignificant. For a Europan mission, this calls for (nearly) industrial-scale irradiation by charged particles and UV radiation (typically Lyman-α) during and after the production of ice deposits. The means for sample production must be varied, in order to account for all possibilities likely in the Europan scenario. The irradiations must also be performed at elevated levels and over compressed time scales such that the total dose expected on Europa is delivered to the laboratory ice in a manageable time span for Earth-bound scientists.

While sputtering of simple surfaces can be estimated using data derived from small-scale experiments, it can be expected that removal rates will vary across larger areas because of inhomogeneities in composition (the likely situation on the Europan surface). This "etching" will yield a varying surface texture that must be taken into account when developing *in situ* instrumentation and testing its deployment and operational protocols. Bombarding meter-sized cryo-ices with keV-energy ions in a large-scale laboratory facility, without contending with "edge effects," would allow these issues to be overcome well before a Europa surface mission.

In the Introduction, we pointed out that it might be necessary to shield from the radiation environment certain key portions of the spacecraft or instruments by covering them with Europan surface material to a sufficient depth. This would of course require the design and development of technical mechanisms that must be based upon a realistic model of Europan surface textures on scales considerably greater than the 1-cm scale available in a typical laboratory setting. This again argues very strongly for the need of a large-scale (tens of centimeters to several meters) Europan surface simulator. We stressed the point that carrying out such activities is compatible with a system that will also yield basic science.

SIMULATING THE EUROPAN SURFACE RADIATION-CHEMISTRY–DRIVEN ENVIRONMENT ON SPACECRAFT INSTRUMENT FOOTPRINT SCALES

The interaction of the landed vehicle with the footprint of an instrument deployed from the platform, and hence the area of potential perturbation, is key to configuring a simulator. Obviously, from the standpoint of acquiring engineering information and protocol development, larger testing areas are more desirable. If one did not have to consider bombardment by energetic particles and/or electromagnetic radiation, production of large areas and sufficient depths of $T \geq 77°K$ cryo-ices is relatively easy. A possible solution is to form a sufficiently large mass of cryo-ice that incorporates smaller segments bombarded either during or after ice deposition [photolysis during ice deposition provides higher levels of processing in the bulk of the sample (Gerakines *et al.*, 2000)]. However, available particle or photon source luminosity will be the principal determining factor. A 1-m^2 ice sample with a processed section 10 cm wide at a specific location should provide a realistic result in most cases of interest. The cryo-ice could also be "salted" with specific molecular species such as H_2O_2 or SO_2 during formation of the mass in order to reproduce the observed Europan ice composition.

To simulate the high energy (MeV) range of charged-particle irradiation from the Jovian magnetosphere, an electrostatic accelerator capable of producing beams of either H or He ions will be the principal cost driver of such a facility and the determining factor as to the maximum practical size of an irradiated segment. Because the need is just for an irradiation source, it may be possible to make use of an accelerator normally utilized for other purposes (i.e., nuclear studies, Rutherford scattering analyses, MS), with associated economic savings expected. MeV-level H/He ion irradiation is relevant because of the environment of the Jovian magnetosphere and makes possible studies of the formation of prebiotic molecules, destruction of prebiotic molecules, destruction of organic biomarkers, formation of small molecular species (i.e., H_2CO_3, H_2O_2), formation of oxidants for sustaining a biosphere, and alteration of surfaces—including coloration of brine deposits formed during surface ice breaching. Importantly, it would bring into focus those issues that impact the use of instruments at the Europan surface environment.

At $E > 1$ MeV, the penetration depth of H or He ions into water ice is ≤ 0.5 m. Given that at Europa, the Jovian magnetosphere provides an H^+ flux ($E > 2.5$ MeV) of 1.9×10^9 m^{-2} s^{-1} (Vogt *et al.*, 1979) and 1 μA of accelerator current translates to 6.2×10^{12} H^+ s^{-1}, a 100 μA m^{-2} beam is equivalent to 3.3×10^5 times the H^+ ($E > 2.5$ MeV) flux at Europa. Taking as a practical consideration that the maximum target area of an irradiated segment would be ~0.1×0.1 m (~0.01 m^2), an accelerator flux of 100 μA over that area would be 3.3×10^7 times the actual H^+ flux at Europa, and hence 1 s of accelerator time is equivalent to ~1 year at Europa. In ~24 hr, it would then be possible to duplicate 10^5 yr of irradiation at Europa. This ought to be adequate, considering that other processes such as sputtering, deposition, and transport could be taking place on similar (or shorter) timescales. This short laboratory timescale also bodes well for the ability to manipulate areas in excess of 0.01 m^2 (either directly or by "tiling").

Currently, National Electrostatics Corporation has products capable of 50–100 μA beam currents (their Pelletron line of devices), including a 5 MV tandem (18.8 m long and 2.2 m in diameter) for H^+ and a 10 MV single-ended machine (12.2 m tall and 4.3 m in diameter) for both H^+ and He^+ ions. Costs range from \$2 to \$3.5 million, respectively. However, it must be kept in mind that significant concrete vaults are required for radiation safety.

Because the Jovian magnetospheric flux is largely composed of ions, not only of H and He, but species including C, N, O, F, and S, a simulation facility should have the ability to irradiate the cryo-ice mass surface with many different ionic species. In the vacuum of an ice-capped Europa, ion bombardment would cause sputtering of H_2O as well as ion implantation into the ice.

Possible consequences include the destruction of prebiotic molecules, the destruction of biomarkers, the loss of a means to detect such species by *in situ* instruments (unless interrogation strategies take these effects into account prior to such a mission), or the removal of molecular species prior to being transported downward to a sub–ice-cap biosphere.

Workers at the University of Virginia (e.g., Johnson, 1990) and elsewhere (e.g., Wdowiak *et al.*, 1985, 1988; Pirronello *et al.*, 1988; Strazzulla, 1988; Strazzulla *et al.*, 1991) have utilized mid-energy range accelerators ($E < 1$ MeV) to study physiochemical processes including sputtering. Machines developed to serve as injectors of high-energy particles or for species implantation in the integrated circuit industry are available to cover this range of interest. Coverage of the lowest energy range (0.1–1 keV) is readily accomplished through commercial Kaufman-type ion sources originally developed for ion propulsion of spacecraft. Ion Tech, Inc., a subsidiary of Veeco, offers a range of accelerators operating in the 0.05–2 keV range and from 3 to 21 cm in diameter (this company also sells linear devices). These are typically used to accelerate Ar ions but can be fed other species as well. The relatively high currents involved permit the bombardment of larger areas than the smaller, lower-current high-energy machines discussed previously. The inferred chemistry in cryo-ices under ion bombardment in the 0–100 keV energy range has been described by Delitsky and Lane (1997, 1998) and recently by Cooper *et al.* (2001).

In addition to charged-particle irradiation, a Europan surface chemistry simulator should have a source of UV radiation, specifically illuminating the surface with Lyman-α of hydrogen (λ = 1,216 Å, E = 10.2 eV), which is sufficient to break almost all chemical bonds (exceptions include N_2 and CO). At 1 AU, the Lyman-α flux is $\sim 3 \times 10^{15}$ photons m^{-2} s^{-1} (Ajello *et al.*, 1987), meaning that at Jupiter it would be $\sim 1.1 \times 10^{14}$ photons m^{-2} s^{-1} (in terms of energy $\sim 1.1 \times 10^{15}$ eV m^{-2} s^{-1}). As with charged particles, Lyman-α-induced photochemistry will be significant in the formation and destruction of prebiotic molecules, the destruction of biomarkers should they be transported to the surface, the formation of oxidants (including those for sustaining biospheres through downward transport), and alterations (including coloration).

Given a Lyman-α flux at Jupiter of $\sim 1.1 \times 10^{15}$ eV m^{-2} s^{-1}, the time to break 1 mole of 10 eV molecular bonds per square meter is $t = N_A\ m^{-2} / 1.1 \times 10^{14}\ m^{-2}\ s^{-1} \sim 5.5 \times 10^{8}$ s = 170 years, where N_A is Avogadro's number. The thickness of an ice composed of 1 mole (18 g) of H_2O evenly distributed over an area of 1 m^2 (0.018 kg m^{-2}) is $\sim 20\ \mu$m. Thus, one concludes that Lyman-α photochemistry's primary significance will be at the topmost surface layer [or at a deeper level when coincident with deposition processing (see, e.g., Gerakines *et al.*, 2000)]. Simulating the relevant doses of Lyman-α photolysis (i.e., 170 years of exposure on Europa) is more difficult than charged-particle irradiation. If a practical time for photolysis in the simulation is 100 h (360,000 s), the Lyman-α flux necessary to break 1 mole of 10.2 eV molecular bonds m^{-2} in this time span is 1.7×10^{18} photons m^{-2} s^{-1}. This translates into 2.8 W m^{-2} in Lyman-α. Although current lamp technology has improved such that luminosity levels have risen from $\sim 10^{10}$ Lyman-α photons cm^{-2} s^{-1} obtainable 10–20 years ago to $\sim 10^{15}$ cm^{-2} s^{-1} today, this still falls short of what is desirable. As for MeV ion irradiation, a smaller selected area can be irradiated. Again, a solution to the problem could be the "salting" of larger areas during ice formation with species shown to result from experiments on smaller samples.

CONCLUSIONS

We have presented the use of TOF MS as a robust and efficient technique for achieving success in both planetary science and exobiology goals at the surface of Europa. New methods for making low- and high-molecular-weight measurements compatible in a single system have been presented. We assert that TOF MS on Europa will provide the means necessary to identify biomarkers that may be present in the surface ices due to extant life in the hypothesized hydrosphere, as well as serving planetary science goals through small-molecule analysis.

As one progresses into the issues arising from doing *in situ* measurements on Europa with practical spacecraft systems, it becomes apparent that there is a need for a large-scale Europan surface environment simulator. Taking into account all of the considerations discussed here, it appears that a Europan surface environment driven by photo- and radiation chemistry can be simulated on scales sufficient for the "field testing" of actual flight instruments or demonstration units. This would not only provide development/test information, but, importantly, also permit protocol development under conditions relevant to the Europan surface chemistry environment. In this work, we have focused on radiation chemistry aspects, but it is also obvious that because the facility can also function at irradiation levels experienced in real time at Europa (they are much lower than those desired in the laboratory), it can test an instrument system's resilience to the Jovian magnetospheric environment.

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ABBREVIATIONS

MALDI, matrix-assisted laser desorption ionization; MS, mass spectrometry; TOF, time of flight.

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