EXPERIMENTAL SIMULATION OF CHEMISTRY INDUCED BY HYPERVELOCITY IMPACTS ON ICY MOONS SURFACES: LASER-INDUCED SHOCKS IN ICES. D. Nna-Mvondo[1], B. N. Khare[2,3] and C. P. McKay[2], [1]Centro de Astrobiologia (CAB) / CSIC-INTA, Ctra. de Ajalvir, km 4, Torrejon de Ardoz, Madrid, Spain, nnamvondod@inta.es, [2]NASA Ames Research Center, Moffett Field, CA 94035-1000, USA, Bishun.N.Khare@nasa.gov, cmckay@mail.arc.nasa.gov, [3]SETI Institute, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA.

Introduction: In planetary bodies, the chemical effects of impact by extraterrestrial objects may be related to atmospheric changes such as atmospheric erosion, i.e. substancial losses of the atmosphere [1, 2], to atmospheric shock synthesis [3, 4] and to local or global endogenic chemical transformations of the surface depending on the scale of an impact [5].

When impacting the surface, part of the kinetic energy of the impactor is imparted to the atmosphere as kinetic energy in the high-velocity ejecta plume and other part is transferred to the ground [6, 7], liberating a great deal of stress energy in the atmosphere and into the surface. The chemistry induced during the surface impact is basically triggered by this stress energy released in the form of shock vaporization of the impacting body and the solid targets generating a vapor plume, high-temperature melting and heating of the surface material [8]. It has been suggested that post-impact shock synthesis of organics may occur [1, 9]. And particularly, for some icy satellites, it is proposed that meteorite impacts could be a source for organic synthesis in ices [7, 10]. Such hypothesis is motivated upon recent observations of the surfaces of the jovian satellites like Europa, Metis, Almalthea, Thebe which exhibit visible colour variation (dark and bright coloration) in their surface material, at the impact sites or between the leading and trailing sides. A possible mechanism which is proposed for these common variation is the strong effect from preferential impact of meteoroids bombardment [7, 11]. Here we have developped a new experimental approach to examine the hypothesis by testing in laboratory the chemical synthesis induced by hypervelocity impacts on planetary ices using the pulsed laser ablation technique with GC-MS and FTIR analytical methods [12].

Experiments: The configuration of our experimental system is shown in Fig 1. A solid-state Q-switched Nd-YAG pulsed laser (model DCR-1A, Quanta-Ray) was used to simulate hypervelocity meteoritic impacts. The correspondence of high irradiance in pulsed laser ablation (>1 GWcm^{-2}) with hypervelocity impacts up to 10^2 km s^{-1} has been confirmed recently by Kadono et al. [13] and Sugita et al. [14]. The pulsed laser delivers a beam at a wavelength of 1064 nm with a pulseduration of 10 ns and pulse repetition rate of 10 Hz. The laser beam was directed and focused via mirrors and lenses onto the surface of the ice which was located inside a closed Pyrex flask maintained at 77 K during the entire irradiation time (Fig. 1)

Ices with different chemical compositions (see Table 1) were ablated with the laser at different spots on the icy surface material, with an input energy of each laser pulse of 200 mJ, and a total ablation time of 30 min. The focused spot size was determined to be 400 µm in diameter which leads to an energy deposition rate (or irradiance) of about 1.6×10^{10} Wcm^{-2}.

Previously, icy samples were prepared inside a glass flask by freezing 30 ml aqueous solutions slowly at 77 K, using a liquid nitrogen bath. Frozen aqueous solutions were then pump-thaw degassed at 10^{-3} Torr at 77 K, then backfreezed at 77 K and ultimately pumped down to approximately 10^{-5} Torr so as to remove any oxygen and nitrogen from the water ice.

In order to follow the chemical behaviour when ablating the icy material, we decided to study for each ice (1) the nature of the gas phase formed above the icy solid phase at low temperature (77 K) due to simulated shocks, (2) the nature of volatiles evaporated at room temperature (293 K) when the ablated ice has melt, and (3) the nature of dissolved trace volatiles in the liquid melt. Such chemical study was able using two powerful analytical techniques, GC-MS and FTIR. The samples after ablation were extracted with a gas-tight syringe for injection in the GC-MS instrument containing a fused silica capillary chromatographic column (Agilent GS-Q, 30 m × 0.32 mm ID). For the analysis by FTIR, samples were transferred in a detachable infrared single pass gas cell, with 10 cm path length and ZnSe windows (25 mm O.D.) at each extremity. The measurement conditions of the FTIR spectrometer were set up in the spectral range from 400 to 4000 cm^{-1}, with a resolution of 2 cm^{-1} and 128 scans.

Results and Discussion: The icy compostions and the products detected after irradiation are reported in Table 1. Each experiment with a different ice composition was repeated three times resulting in unchanged GC chromatograms and FTIR spectra, which confirms the reproducibility of our results.

H_2O/CO_2 ice. Laser ablation of 10:1 icy mixture of H_2O/CO_2 at 77 K shows the synthesis of the oxidants CO, CH_3OH and H_2O_2. Comparing our results to other experiments using other energy sources applied to H_2O/CO_2 ices in the laboratory, i.e., UV and ionizing radiations, we observe that in these radiations experiments CH_3OH is not formed but rather carbonic acid and formaldehyde [15, 16]. This suggests that impact shock simulated by laser ablation implies different chemical reactions than in other irradiations. This is expected, since in our simulations we are dealing with shock effects (shock wave compression and shock heating) and not with electron bombardment or the photon absorption process. Also energetic ion irradiation onto pure water ice, H_2O/O_2 and H_2O/CO_2 ices produces hydrogen peroxide [16]. Such results have supported the hypothesis that H_2O_2 detected by space observations on the Galilean moons, e.g. Europa, is very probably formed by ion energies characteristics of magnetospheric ions from Jupiter.

The production of hydrogen peroxide in our new experiments may give rise to new ideas regarding the chemistry occurring at the surface of icy satellites such as Europa which shows various cratering features. Impact processing could be another local source of H_2O_2 on Europa.

H_2O/Na_2CO_3 ice. The only new species detected from ablated H_2O / Na_2CO_3 ices were carbon monoxide in the gas phase at 77K by FTIR and carbon dioxide in the gas phase at 293K by GC-MS. Laser ablation of frozen sodium carbonate in ice results primarily in the destruction of the salt into CO and CO_2. This leads us to suggest that impacts into ice containing Na_2CO_3 could have provided a local source of carbon monoxide released locally around craters on Europa. For the case of carbon dioxide, under Europa's low temperature surface (100-120K), CO_2 released may be trapped by the icy crust.

H_2O/CH_3OH ice. The laser ablation of H_2O/CH_3OH (10:1) resulted in the formation of CH_4 and CO in the gas phase at 77K, then CO_2 was evaporated at 293K. The three molecules are decomposition products of methanol. Acetone (CH_3COCH_3), methyl formate ($HCOOCH_3$) and dimethyl formal ($CH_3OCH_2OCH_3$) are also synthetized. Compare our results with experiments done with other energy sources applied to ices, the UV photolysis of H_2O + CH_3OH ices shows the formation of CO, CO_2, CH_4, HCO radical and H_2CO at < 20K [17]. The same products are identified from ion irradiation at < 20K with the new production of ethanol and acetone [18]. In both cases, formaldehyde was the dominant volatile species identified.

CO_2 is seen in the ice on the leading side of Europa where micrometeoroid infall is greater than on the trailing side. We propose that, apart from ion irradiation as currently suggested, CO_2 could also be formed around craters sites of Europa from impacts into ice containing methanol.

$H_2O/CH_3OH/(NH_4)_2SO_4$ ice. Laser ablation of this ice leads to a rich variety of new compounds. It produces in the gas phase CH_4 and CO at 77K, CO_2 and N_2O are released from the melted ice in the gas phase at 293K and more complex molecules containing alkyl, carbonyl and nitrile groups. Among them, methane, ethane, acetone (CH_3COCH_3), methyl formate ($HCOOCH_3$) and dimethyl formal ($CH_3OCH_2OCH_3$). Two nitrogen compounds were also detected: acetonitrile (CH_3CN) and hydrogen cyanide (HCN).

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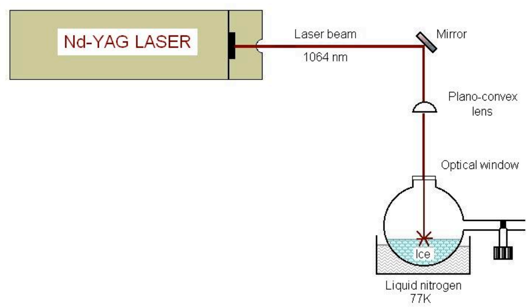

Figure 1. Schematic diagram of our experimental system

Table 1. New molecular species identified by GC-MS and FTIR after laser ablation of different icy compositions. Ratios of components in icy mixtures are indicated in parenthesis.

Initial Ice	FTIR gas phase 77K	GC-MS volatiles evaporated 293K	GC-MS Dissolved trace volatiles extracted from aqueous phase
$H_2O + CO_2$ (10:1)	CO	CH_3OH	H_2O_2
$H_2O + Na_2CO_3$ (10:1)	CO	CO_2	—
$H_2O + CH_3OH + (NH_4)_2SO_4$ (10:1:1)	CH_4, CO	CO_2, N_2O	C_2H_6, CH_3COCH_3 $HCOOCH_3$ $CH_3OCH_2OCH_3$ HCN, CH_3CN
$H_2O + CH_3OH$ (10:1)	CH_4, CO	CO_2	CH_3COCH_3, $HCOOCH_3$ $CH_3OCH_2OCH_3$ CH_3CHO