NITROGEN FIXATION BY BOLIDE IMPACTS IN THE EARLY MARS ATMOSPHERE AT THE UNDERGRADUATE LABORATORY. R. Navarro-González[1], K.F. Navarro[1], J. de la Rosa[1], and P. Molina[1]. [1]Laboratorio de Quimica de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Ciudad de México 04510, Mexico, navarro@nucleares.unam.mx.

Introduction: A course on the search for life on Mars with laboratory demonstrations is offered to undergraduate students at the Universidad Nacional Autonoma de Mexico at Ciudad Universitaria in Mexico City. This course is open to any undergraduate student enrolled in space sciences but students majoring in other disciplines can also register (*e.g.*, physics, chemistry, biology, and engineering). Fifty percent of the course work is devoted to laboratory work, which is conducted at the Laboratorio de Química de Plasmas y Estudios Planetarios using state-of-the-art analytical instrumentation. After an introductory session of laboratory safety, the first experiment consists of the preparation of a simulated Martian primitive atmosphere [1]. In the second laboratory demonstration described here, the simulated atmosphere is exposed to shockwaves generated by laser-induced plasmas to recreate the effect of bolide impacts in the Martian atmosphere [2]. The experiment is carried out in one laboratory session of 3 hrs in length.

Nitrogen fixation in the Atmosphere: One of the main goals of the Mars Science Laboratory is to determine whether the planet ever had environmental conditions able to support microbial life. Nitrogen is a fundamental element for life, and is present in structural (*e.g.*, proteins), catalytic (*e.g.*, enzymes and ribozymes), energy transfer (*e.g.*, ATP) and information storage (RNA and DNA) biomolecules. Planetary models suggest that molecular nitrogen was abundant in the early Martian atmosphere, but was rapidly lost to space by photochemistry, sputtering [3, 4], impact erosion [5], and oxidized and deposited to the surface as nitrate [6]. Nitrates (NO_3^-) are a fundamental source for nitrogen to terrestrial microorganisms. Therefore, the detection of nitrates in soils and rocks is important to assess the habitability of the Martian environment. Recently the Sample Analysis at Mars Instrument Suite (SAM) on board the Mars Science Laboratory Curiosity rover detected nitrates in soils and rocks at Gale crater [7]. The origin of these nitrates is sought to have been triggered by bolide impacts in the Martian atmosphere [8] at the end of the heavy bombardment process [5].

Laboratory objective: This demonstration is designed to provide the necessary knowledge for handling a pulsed infrared laser to generate a dense and hot plasma that can be used to simulate bolide impacts in the laboratory.

Procedure: Bolide impacts were simulated in the laboratory by shocks created under a simulated Martian atmosphere by focusing a pulsed laser Nd-YAG beam of 1.06 μm photons inside a closed 1-litre Pyrex flask at 1 bar using a plano-convex optical glass lens with a focal aberration of about 10 mm. The experimental setup is shown in Figure 1. The laser beam had an energy of 250 mJ per pulse in 5-7 ns operating at 10Hz [2]. The energy deposited in the system was determined by the difference between the input laser energy and that transmitted by the plasma, and was measured with an optical power system (Labmaster Ultima, Coheren) using an optical sensor (LM-P10). Figure 2 is a photograph of the laser-induced plasma. The simulated atmosphere is exposed for 10 min to the effects of the laser-induced plasma.

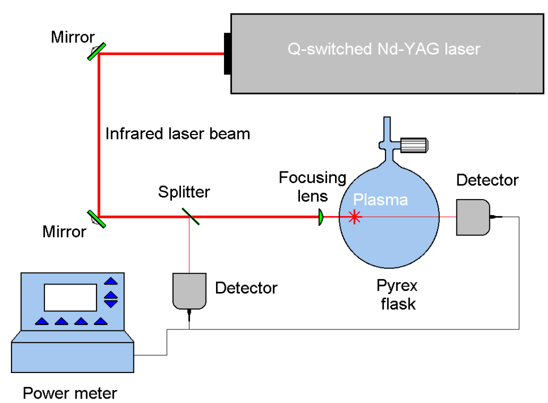

Figure 1. Experimental setup for the simulation of bolide impacts in a simulated Martian atmosphere.

Figure 2. Photograph showing the laser-induced plasma in a contained atmosphere.

The shock wave velocity of this plasma was determined to be >60 km s^{-1} at 20 ns [9], and the electron temperature and density were 17,000 K [9, 10] and 4.0 $\times 10^{17}$ cm^{-3} [10] at 1 μs.

Analysis of the exposed atmosphere to shockwaves: The atmosphere is introduced into the injection port of an Agilent Technologies 7890A GC system held at 250°C by an automatic six-port gas-sampling valve with a gas loop of 5 ml. A styrene-divinylbenzene-based porous polymer column was used (CP-Porabond Q fused-silica) of 50 m x 0.32 mm I.D. with a 5 μm polymer thickness coating. The column program temperature was isothermal at 50°C for 5 min, and then a rate of 10°C min^{-1} up to 240°C and finally isothermal for 6 min. The carrier gas used was helium (chromatographic grade from Praxair, Inc.) with a flow of 1.2 ml min^{-1} and a split ratio of 1:100. The GC was interfaced at 250°C with a mass detector (Agilent Technologies 5975C inert XL EL/CI MSD with Triple Axis detector). The mass spectrometer operated in scan mode from 10 to 150 m/z with a mass resolution of 1 unity using electron impact at 70 eV. The ion source and quadruple were maintained at 230°C and 150°C, respectively.

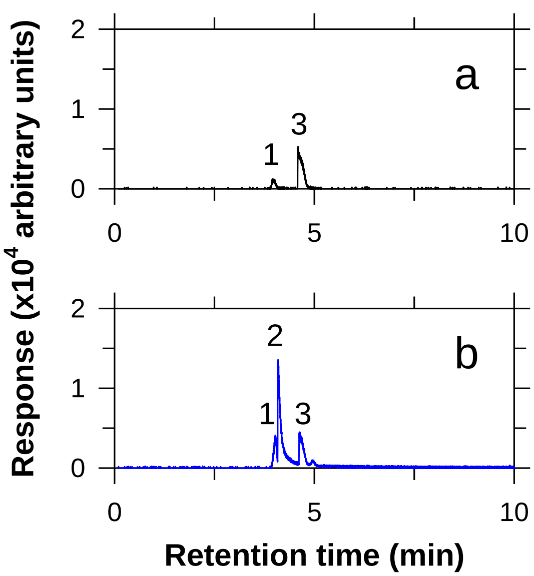

Figure 3. Extracted ion chromatograms using m/z 30 for non-exposed (a) and exposed simulated atmospheres to laser-induced plasmas for 10 min. Peak identifications: 1. NO generated in the mass spectrometer; 2. NO generated by laser-induced plasmas; and 3. $^{12}C^{18}O$ generated from the electro impact ionization of carbon dioxide.

Figure 3 shows extracted ion chromatograms for m/z 30 of the non-exposed and exposed atmospheres to laser-induced plasmas for 10 min. A small fraction of nitric oxide (NO) is produced in the ionization chamber of the mass spectrometer when nitrogen is eluted as shown in figure 2 of reference 1. This is labeled as peak 1 in figure 3. Peak 2 is NO produced by the shockwave of the laser-induced plasma in the simulated Martian atmosphere, and is a distinctive peak only observed in the exposed atmosphere. Peak 3 is $^{12}C^{18}O$ produced by the electron impact fragmentation of $^{12}C^{18}O_2$ present in small fraction in the CO_2 used to prepare the simulated Martian atmosphere (see Figure 2 in reference 1).

NO produced by bolide impacts would have been converted into nitrosyl hydride (HNO) in the atmosphere. The photochemical cleavage of water causes the hydrogenation of the NO, but not directly [11]. It is expected to proceed *via* HCO:

$$H_2O + h\nu \ (190\ \mathrm{nm}) \rightarrow H + OH \quad (1);$$
$$CO + H + M \rightarrow HCO + M \quad (2);$$
$$HCO + NO \rightarrow HNO + CO \quad (3);$$

where M is any third body molecule in the atmosphere.

HNO is soluble in water, and would have been transported to the surface by rain [2], where it is converted into nitrites (NO_2^-) and nitrates. Nitrites and nitrates may have played a key role for the origin and sustainability of life in Mars [2].

Conclusions: This laboratory demonstration can be used to introduce concepts of atmospheric chemistry, prebiotic chemistry, atmospheric evolution, and astrobiology.

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