

## IN MEMORIAM: RAFAEL NAVARRO-GONZÁLEZ (1959-2021)

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### 1. INTRODUCTION

Rafael Navarro-González was born in Mexico City on April 25, 1959, and died on January 28, 2021. He developed his career interest in science since he was a child. He studied Biology at Universidad Nacional Autónoma de México (UNAM). In 1979, when he was in the middle of his studies in Biology, he attended a series of conferences of Prof. Cyril Ponnampertuma at the Centro de Estudios Nucleares, UNAM, now named Instituto de Ciencias Nucleares (ICN). After talking with Prof. Ponnampertuma, he joined ICN as a volunteer in a project related to chemical evolution under Dr. Alicia Negrón (a former Ph.D. student of Prof. Ponnampertuma). Later, as a part of this work related to the behavior under irradiation of hydrogen cyanide (*HCN*) and related compounds, he obtained a B. Sc. degree in 1983 with the B. Sc (biology) dissertation “Identificación de ácidos carboxílicos de interés en la evolución química formados en muestras irradiadas de nitrilos y cianuros sencillos”.

In 1980 he started as an assistant professor at Facultad de Ciencias, UNAM, and he obtained a scholarship from the ICN. In 1983, he published his first article related to his B. Sc. thesis. He got a position at ICN as a research assistant until 1984 when he went to the University of Maryland at College Park to carry out a Ph.D. program with Prof. Ponnampertuma as his thesis advisor. He graduated in 1989, continuing with his studies related to *HCN*. His

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Fig. 1. Laboratory of Chemical Evolution (LCE) University of Maryland (1984), with R. Navarro on the left.

Ph.D. dissertation thesis was: “The role of hydrogen cyanide in chemical evolution”, Later, when he finished his Ph.D., he returned to Mexico and reincorporated in the group of chemical evolution at ICN. In 1994 he inaugurated his laboratory (Química de Plasmas y Estudios Planetarios) thanks to the funding of UNAM and BID, and the technical support of Susana Castillo, who was in charge of the requests and customizations to the laboratory. From his first article in 1983 until 1994, he published 11 scientific articles and three memoirs with the group of Chemical Evolution. Always he showed a broad general interest in many fields in science.

### 2. THE BEGINNINGS OF AN AMAZING CAREER

Alfredo Romero, from Facultad de Química, UNAM, was the first student who joined Rafael Navarro’s research group. Romero performed a series of computational simulations aimed to understand details of the radiolysis processes of the glycine and alanine amino acids in scenarios like cometary nucleic and primitive Earth’s oceans to predict potential enantiomeric excesses useful for the origin of life (Navarro-González & Romero 1996).

In 1996 all the information about Titan came from the studies performed by the instruments on board the Voyager 1 mission. There was a particular interest to fully understand the chemical processes occurring on that extraterrestrial atmosphere that resulted not only in the gas-phase hydrocarbons and nitriles detected by the Voyager missions,



Fig. 2. Members of the Laboratorio de Evolución Química at the Centro de Estudios Nucleares now Instituto de Ciencias Nucleares, UNAM (R. Navarro in the center).

but also in solid aggregates or aerosols, known as tholins, detected in the upper levels of Titan's atmosphere. Graciela Matraj, a B. Sc. student from Facultad de Ciencias, UNAM, was assigned to study the chemical fingerprints of the solid aggregates synthesized by corona discharges in a simulated Titan's atmosphere and its implications on the origin of life on Earth (Navarro-González et al. 1998). In the meanwhile, Sandra Ramírez was at the beginning of her master's degree at Facultad de Química at UNAM with Navarro-González as her advisor. He proposed to initiate a project centered on the role of corona discharges on the atmosphere of Titan. The systematic study of the corona processes developed in the putative methane clouds of Titan needed a careful definition of several technical aspects such as the Titan's lower-atmosphere characteristics, the electrical properties of the aerosols, the satellite's energy inventories and their dissipation mechanisms, and of course, the physical properties of the postulated corona discharges. In parallel, specific glass containers that could hold the simulated atmosphere, and a good number of devices needed for a successful set of experiments, were designed, built, and tested. Since then, each glass instrument has been designed by Navarro's students.

The first results demonstrated that corona discharges could form a variety of hydrocarbons, nitriles and *HCN* (Navarro-González & Ramírez 1997). The encouraging initial corona-discharge results motivated a better representation of the Titan's environment. To this end, an academic collaboration with François Raulin to depict a quantitative comparison of the products arising when a Titan's simulated atmosphere was irradiated by different energy sources was performed. A laser-induced plasma (LIP) represented the entrance of high velocity meteoroids into Titan's atmosphere. Gamma radiation simu-

lated the effect of Saturnian electrons going through Titan's stratosphere and of galactic cosmic rays ionizing neutral molecules on their way to the surface. Arc and corona discharges were used to simulate the development of electrical activity within the tropospheric methane clouds (Ramírez et al. 2001). Besides the identification of different hydrocarbons and nitriles, later confirmed by the Huygens probe instruments, a light-yellow solid deposit, whose optical properties were relevant to the atmospheric radiative processes was also formed (Ramírez et al. 2002). By 2001, José de la Rosa carried out experiments oriented to define the role of another electrical phenomenon, the lightning discharges expected to occur at the methane clouds in Titan's atmosphere. De la Rosa used a laser induced-plasma (LIP) to simulate the lightning discharges (Navarro-González et al. 2001a). These studies allowed de la Rosa to earn his master's degree in chemistry. More recently, Jafet Barreto studied the implications of the presence of oxygenated compounds such as carbon monoxide (*CO*), and carbon dioxide (*CO*<sub>2</sub>) in the atmospheric processes occurring at Titan.

### 3. NITROGEN FIXED ABIOTICALLY BY LIGHTNING PROCESSES ON EARLY EARTH AND EARLY MARS

Rafael Navarro-González together new students investigated, studied the processes of abiotic nitrogen fixation. This orientation becomes from the fact that nitrogen is necessary for life, however this element has to be fixed, that is, to be incorporated in compounds such as *HCN*, ammonia or nitrogen oxides. The ability of nitrogen to be fixed is limited by capacity to break the triple bond of molecular nitrogen *N*<sub>2</sub>, it had already been observed that electrical discharges were able to break this bond, and be a source of energy relevant to prebiotic chemistry, this linked to the famous Miller experiment in 1953. However, Prof. Navarro performed simulations with a more modern device. Using a hot plasma, induced by a pulsed laser that would allow to reproduce both the contribution of shock waves and those of the hot lightning channel, The common goal of the work was to delineate the involvement of storm lightning, of corona processes occurring on the ground, as well as in volcanic lightning in the global deposition of reactive nitrogen necessary for the emergence and evolution of life on early Earth, as well as on early Mars. Results on these experiments on early Mars showed the formation of *HCN* with an annual production rate of  $10^{11}$  g yr<sup>-1</sup>, where volcanic lightning would have been the most important source of *HCN* 3.5 Gy ago.

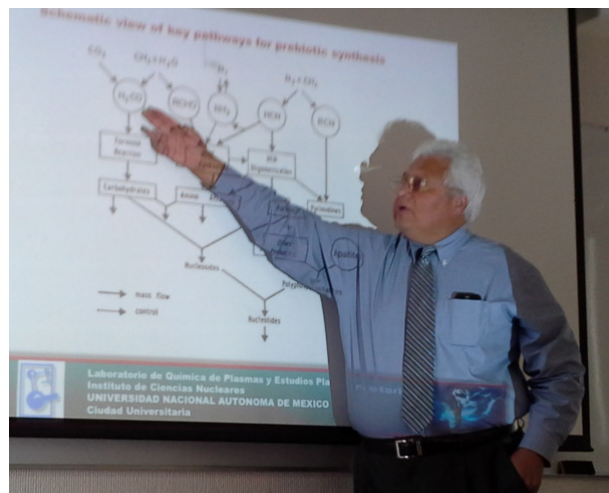


Fig. 3. Prof. Navarro during a lecture.

On the other hand, work on the early Earth, results indicated that in neutral atmospheres nitric oxide ( $NO$ ) was formed, while in the presence of oxygen nitrogen dioxide ( $NO_2$ ) was the predominant nitrogenous form. Also, it was observed that  $NO$  production was very sensitive to the composition of the early Earth atmosphere, being maximum during the Hadean and then declined rapidly with the reduction of  $CO_2$  in the atmosphere. Eventually, this atmospheric kinetics was linked with an interdisciplinary perspective by Rafael Navarro who related it with the biological nitrogen fixation, a key biological process and proposed a “nitrogen crisis”. It implied that the supply of fixed nitrogen for terrestrial microorganisms in the late Archean period was affected by the atmospheric kinetics and may have led to the emergence and proliferation of biological nitrogen fixation. To construct this explanation it was necessary the participation of students from very different fields including chemistry, biology, and astrophysics: Octavio Padilla, Antígona Segura, Leonel Calva, and Delphine Nna-Mvondo. Additional experiments demonstrated the production of  $HCN$ . In reductant and neutral atmospheres it was predicted the hypothesis of a nitrogen crisis, therefore both scenarios would favor the appearance of nitrogen-fixing microorganisms (Navarro-González et al. 2001b).

#### 4. EXPERIMENTAL SIMULATIONS OF HYDROTHERMAL ENVIRONMENTS

The inquisitive personality of Rafael Navarro-González conducted him to participate in the discernment regarding the chemistry prevailing within hydrothermal systems for the origin of life. The research focused on the synthesis of organic molecules

under high temperature and pressure was involved in Astrobiology three years after the discovery of hydrothermal chimneys by John B. Corliss in 1978. The proposal of these environments as chemical reactors came from John A. Baross and John B. Corliss (Corliss et al. 1981). This hypothesis became popular very quickly, though there was a disapproval by the researchers traditionally focused on the origin of life who preferred an atmospheric energy source. During the early 1990s Everett Shock brought the minerals to this hydrothermal proposal.

This paradigm did not remain unnoticed by a pioneer and a natural born scientist like Rafael Navarro-González who planned innovative experiments to recreate hydrothermal systems of the early Earth. Based on his inquiries, iron-sulfur minerals were selected as catalysts for experimental simulations. Besides, this experimental design introduced the fluid circulation and the tracking of physical chemical parameters. At the same time, the planetary missions Voyager and Galileo transported this paradigm to the solar system because of the likely presence of a water ocean in the Galilean satellite Europa. Rafael Navarro-González contributed to this open question by providing support for a biosphere on Europa based on the organics synthesized at hydrothermal systems (Navarro-González et al. 2001c). Fanny Reissman and Lilia Montoya participated as students in these studies and Wanda L. Davis and Christopher P. McKay as collaborators.

The identity of chemical products present in the aqueous phase became a major issue keeping in mind that the first studies analyzed only the gas phase and the chemical reactions take place in aqueous conditions. Several methodological improvements were made with two students involved, Ezequiel Tobón and Paulina Pinedo. The first series of these experiments turned to the initial interest in  $HCN$  which has been one of the most studied and pursued molecules within the research field about the origin of life and Rafael Navarro-González had always had this issue in mind. Their results provided enough evidence of the  $HCN$  synthesis under hydrothermal conditions and allowed them to infer an annual  $HCN$  yield production on early Earth. After a more elaborate method of extraction the team headed by Rafael Navarro showed the synthesis of nitrogen compounds, already detected but in more complex molecules.

#### 5. MARS-LIKE ENVIRONMENT ON EARTH

At the end of the nineties Navarro-González participated in the expedition to the Atacama Desert in





Fig. 4. Prof. Navarro with a model of Mars.

Chile, at the invitation of his colleague and friend Christopher McKay, from NASA Ames. The Atacama desert is considered one of the driest places on Earth. They have collected soil samples from the driest parts of the Atacama Desert to the less arid zones. Rafael Navarro proposed to use a similar method carried out by the Viking missions to search for organic matter on Mars, namely pyrolysis coupled to gas chromatography-mass spectrometry (GCMS). These results indicated that in the core of the desert the content of organic matter is extremely low. As one moves toward the South the precipitation gradient the levels of organics increases but are lower than those found in the Mohave Desert, CA (one of the first places used to test spatial missions in seventies). Therefore, they selected the Atacama Desert to be an analog of Mars for testing future space missions (Navarro-González et al. 2003). Nowadays Atacama Desert is considered the best analog that emulates the main characteristics of Mars.

When, perchlorate was discovered in the Martian Arctic soil by the Phoenix Lander, in 2008, Rafael Navarro reanalyzed the results of the Viking GCMS search for organics. For this, soils of the Atacama Desert were used to which magnesium perchlorate was added. The conclusion was that forthcoming missions will have to incorporate analytical methods to avoid the oxidation of organic matter in Martian soil by thermal volatilization due to iron oxides and perchlorate (Navarro-González et al. 2010).

Most studies carried out by Prof. Navarro's team performed a multidisciplinary methodology, showing that the soils of the Pampas de La Joya desert in

southern Peru have similarities with the Martian regolith. Relevant features in the soil were described such as low amounts of carbon, high oxidant activity, presence of evaporitic minerals, exotic geomorphology, and especially the presence of new habitats for microbial life that were unnoticed for a long time. These findings reinforced the view of Atacama Desert as a Martian analog (Valdivia-Silva et al. 2011). Nowadays, Pampas de La Joya is classified as one of the most exciting places on Earth for astrobiological studies, so much so that this soil has been used to analyze the survival of vegetables such as potatoes and has led to the discovery that four of its varieties can be cultivated in areas such as southern China and India where no other type of food could be grown (Valdivia-Silva et al. 2016; Ramírez et al. 2017).

## 6. MARS TERRAFORMING

Mars has been a subject of interest to search for life for a long time. However, if this planet has no signs of life, one possibility is to terraform Mars, this means to introduce Earth's life. To succeed on this it is necessary to raise the surface temperature by releasing super greenhouse gases in the Martian atmosphere. The raising would sublimate  $CO_2$  and melt the water of the poles and subsurface. This would result in a denser atmosphere and the presence of liquid water on the surface. Under these conditions only anaerobic microorganisms could grow at high  $CO_2$  levels and a low atmospheric pressure. To get an atmosphere breathable to other organisms, including eukaryotes, it would be necessary to introduce cyanobacteria which are known to transform  $CO_2$  to organics through photosynthesis releasing molecular oxygen to the atmosphere as a by-product. On this scheme, a last required step in terraformation would be the introduction of vegetation, including trees.

To obtain better predictions of the terraforming stages described above demands the use of analog sites. To accomplish this objective McKay and Navarro-González proposed the exploration of Pico de Orizaba and presented several pieces of evidence that underlined the advantages of this specific site.

The Citlaltépetl or Pico de Orizaba volcano reaches 5636 masl and is located in the south central zone of Mexico. In this volcano, the alpine vegetation is dominated by *Pinus hartwegii* or pine of the heights which reaches an altitudinal range above 4000 masl. Beyond this altitude, there is an area of bushes and later grasslands. Interestingly, there is no higher region in the world with a treeline than in



Fig. 5. Rafael Navarro at the treeline in Pico de Orizaba the Citlatépetl. Rafael Navarro became interested in this treeline with the initial hypothesis that biological nitrogen fixation would explain this tolerance to high altitudes. To test his hypothesis Aura Palma performed the characterization of a soil profile that included the nitrogen molecules nitrate and nitrite. Unfortunately their results were inconclusive, therefore, a wider characterization was planned to include a forest site quality evaluation. Paola Molina was involved in this soil strategy approach. Their results allowed them to argue that not only biological processes are involved in the treeline. Also, they defined minimal microenvironmental conditions in the soil to use *Pinus hartwegii* in a terraforming process. Beyond the study of Pico de Orizaba with an astrobiological filter Rafael Navarro-González and Cruz Lozano-Ramírez became interested in exploring to what extent soil parameters can help to understand the response of treelines to global warming.

## 7. ACADEMIC ACTIVITIES

Prof. Rafael Navarro-González reached a high production record, since his first article published



Fig. 6. Prof. Navarro accompanied by colleagues and his students during an academic event (from left to right: Alejandro N. Lozada-Chávez, Irma Lozada-Chávez, Luis Cruz-Kuri, Paulina Pinedo, José G. de la Rosa, Frank Drake, Rafael Navarro-González, Tania Eloina Félix, Silvia Palma, Antonieta Bautista, Paola Molina, Sandra Aguilar, and Antígona Segura. Backwards: Student from Universidad Veracruzana, J. Enrique Iñiguez-Pacheco, Cruz Lozano-Ramírez, Julio Valdivia-Silva, and José de la Herrán

in 1983 he contributed to the field with more than a hundred of scientific articles, and a good number of them in high impact journals. He authored or coauthored several books, book chapters, and technical reports. He dictated more than 300 conferences around the world to specialized and outreached audiences. He supervised Ph.D., M.Sc., B.S., and social service projects. He was appointed to the highest academic honors at his *alma mater*, UNAM; likewise, he was awarded internationally he was awarded with the Alexander von Humboldt medal (2009), and the TWAS prize (2009). He was an invited visiting professor at international universities such as the University of Maryland, the universities of Denis-Diderot and Val de Marne (France), and the Massachusetts Institute of Technology. At the latter institution he spent a sabbatical period with Prof. Mario Molina, the 1995 Nobel Laureate in Chemistry, to study chemical processes caused by electrical discharges on the atmosphere.

In 2002 the Mexican Society of Astrobiology (SOMA) officially came into being and Navarro-González participated as co-founder and president of this society. In 2001 with the help of his associated students and the participation of national, and international colleagues and friends, Navarro organized the First Meeting of Astrobiology at ICN, UNAM. He also participated in the organization of the XIII Meeting of the International Society for the Studies of the Origin of Life in 2002 at Oaxaca, Mexico.

Finally, he always was engaged with science outreach activities, e.g., as a member of the Editorial Board of the cultural section of the newspaper *Reforma*. Also he was interviewed in several documentaries for national and international broadcast media, e.g., Discovery Channel, National Geographic, the Japan Broadcasting Corporation, Milenio TV, and news media.

## 8. CONCLUSIONS

The contributions of Prof. Rafael Navarro-González were devoted to almost each Solar System body of interest for Astrobiology, i.e., Mars, Titan, Europa, and the Earth ranging from its early age up to the present. His lines of research were consistent with the name of the laboratory headed by him: “Química de Plasmas y Estudios Planetarios” (i.e., Plasma Chemistry and Planetary Studies), moreover, he certainly had a view more broadly than just planetary chemistry. He seeded a whole generation of astrobiologists in Mexico and his involvement on science can be undoubtedly reflected by his participation on preparing and designing experiments, leading, and guiding students, and planning how to decipher one of the most science essential questions at the time of his leaving: are we alone in the universe?

As one can envisage, the projects developed at the Laboratory of Plasma Chemistry and Planetary Studies required a special level of knowledge and personal skills not only in chemistry or biology, but also in astronomy, physics, computational sciences, geology, and instrumentation. In other words, the stu-

students collaborating in Navarro’s laboratory participated in astrobiological studies even before this term was recognized in the scientific community for the search for extraterrestrial life.

Navarro-González was a leading astrobiologist in Mexico, in the last decades he was a co-investigator on the Sample Analysis at Mars (SAM), a portable chemistry lab aboard Curiosity, as well as Mars 2020, and ExoMars missions. Given all his contributions to the field of Astrobiology he was honored by the team of scientists and engineers behind NASA’s Curiosity by assigning his name to a hill located on Mount Sharp in northwest Gale Crater. His absence represents a great loss to astrobiology and planetary sciences.

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