

Abiotic input of fixed nitrogen by bolide impacts in CH4+CO2+N2 and H2+CH4+CO2+N2 atmospheres. Comparison with nitrate levels measured by the curiosity rover's sample analysis at mars instrument

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ABIOTIC INPUT OF FIXED NITROGEN BY BOLIDE IMPACTS IN CH_4+CO_2+N_2 AND H_2+CH_4+CO_2+N_2 ATMOSPHERES. COMPARISON WITH NITRATE LEVELS MEASURED BY THE CURIOSITY ROVER'S SAMPLE ANALYSIS AT MARS INSTRUMENT. R. Navarro-González[1], K. F. Navarro[1], P. Coll[2], C. P. McKay[3], B. Sutter[4], J. C. Stern[5], P. D. Archer[4], A. C. McAdam[5], C. Szopa[6], C. Freissinet[6], H. B. Franz[5], A. Buch[7], B. D. Prats[8], M. Millan[9], J. L. Eigenbrode[5], D. Coscia[10], S. Teinturier[5], J.-Y. Bonnet[10], D. P. Glavin[5], A. J. Williams[11], F. Raulin[2], M. Cabane[6], D. W. Ming[12], C. A. Malespin[5], P. Mahaffy[5], F. J. Martín-Torres[13], M.-P. Zorzano-Mier[13], S. Atreya[14], A. Fraeman[15], and A. R. Vasavada[16], [1]Universidad Nacional Autónoma de México (navarro@nucleares.unam.mx), [2]Université Paris-Est Créteil, [3]NASA Ames Research Center, [4]Jacobs, NASA Johnson Space Center, [5]NASA Goddard Space Flight Center, [6]Université Versailles Saint-Quentin, [7]Ecole Centrale Paris, [8]NASA GSFC/eINFORMe, Inc., [9]Georgetown University, [10]Université Paris-Saclay, [11]University of Florida, [12]NASA Johnson Space Center, [13]University of Aberdeen, [14]University of Michigan at Ann Arbor, [15]NASA Jet Propulsion Laboratory, and [16]California Institute of Technology.

Introduction: The evidence for liquid water on early Mars implies that the atmosphere was denser and contained greenhouse gases that allowed for a wet and warmer climate with a faint young Sun [1]. A possible solution for the martian climate puzzle is the presence of 10–20% molecular hydrogen (H_2) from volcanic emissions that would have warmed the atmosphere episodically by collision-induced absorption (CIA) with CO_2 [2-6] or N_2 [6-7]. An alternative warming scenario is the presence of methane (CH_4~10%) or CH_4-H_2 mixtures due to CO_2–CH_4 CIA in the 250–500 cm^{-1} spectral window [3,7-8]. The N_2–CH_4 CIA is significantly weaker than with CO_2 [7]. CH_4 could have been outgassed by volcanoes if the mantle was oxygen-poor [9,10]. Additionally, serpentinization of ferromagnesian minerals could have led to localized subsurface sources of CH_4 and H_2 [11,12] and contributed to episodic outbursts during chaotic transitions of the mean obliquity of the planet leading intermittent excursions to a warm and wet climate [13].

In addition to its greenhouse effect, CH_4 may have had a role in nitrogen (N) fixation in the martian atmosphere, *e.g.*, the conversion of N_2 into fixed and reactive forms of N, such as nitric oxide (NO) and hydrogen cyanide (HCN) by high energy processes. The key parameters determining the type of N species formed and their rates of fixation are the ratios of carbon (C), oxygen (O), and hydrogen (H) atoms in the atmosphere [14-17]; for example, a CH_4-H_2-rich atmosphere (high C and H) produces reduced forms of fixed N, such as HCN [14,15], while neutral (CO_2) or oxidized atmospheres (O_2) generate oxidized forms of fixed N, such as NO [16]. We have previously investigated the efficiency of N fixation by bolide impacts in CO_2-N_2 martian atmospheres with or without H_2. Surprisingly, NO was produced more efficiently in 20% H_2 in spite of it being a reducing agent and not likely to increase the rate of nitrogen oxidation [17]. Here we present experimental data and theoretical calculations that investigate the efficiency of N-fixation by bolide impacts in 10% CH_4 and 5% CH_4-5% H_2 in CO_2-N_2 atmospheres. In addition, we compare the N-fixation rate by bolide impacts with the levels of nitrates present in the rocks examined by the Curiosity rover along the stratigraphic column from John Klein to Mary Anning.

Laboratory simulations: Simulated atmospheres were prepared with a mixture composed of CH_4 (10%) or CH_4 (5%)-H_2 (5%) in CO_2 (0-100%) and N_2 (0-100%) using a computerized gas-blending system [17]. Bolide impacts were simulated in the laboratory using a pulsed laser Nd-YAG beam at 1 bar [18]. The gases were analyzed by gas chromatography (GC) coupled to mass spectrometry (MS) using electron impact [17].

Theoretical modeling: The energy yield for the production of NO generated by bolide impacts was estimated following the model of Chameides *et al.* [19] according to the following equation [17]:

$$E_{\mathrm{NO}} = \frac{0.5 \times \mathrm{N_A} \times f_{\mathrm{NO}}(\mathrm{T_F})}{\mathrm{T_F} \times (n\mathrm{CO_2} Cp\mathrm{CO_2} + n\mathrm{N_2} Cp\mathrm{N_2} + n\mathrm{CH_4} Cp\mathrm{CH_4} + n\mathrm{H_2} Cp\mathrm{H_2})}$$

Where, E_{NO} is the number of NO molecules produced per joule; N_A is the Avogadro constant; $f_{NO}(T_F)$ is the nitric oxide equilibrium mixing ratio at the freeze-out temperature (T_F); n is the mole fraction of the gas in the mixture; and Cp is the specific heat at constant pressure. $f_{NO}(T_F)$ was computed using FactSage, a thermodynamic-based equilibrium speciation program [20].

Martian samples: Evolved gas analyses of the drilled rock samples by the Sample Analysis at Mars Instrument were conducted from 40°C to ~860°C with a ramp rate of 35°C/min under reduced pressure (~25 mbar) using a He flow of ~0.8 cm^3/min, and the evolved gases were analyzed by electron impact MS.

Results and Discussion: Figure 1 shows the experimental and predicted E_{NO} values as a function of CO_2/(CO_2+N_2) ratio by shockwaves in simulated

primitive martian atmospheres in the absence and presence of CH_4 and/or H_2.

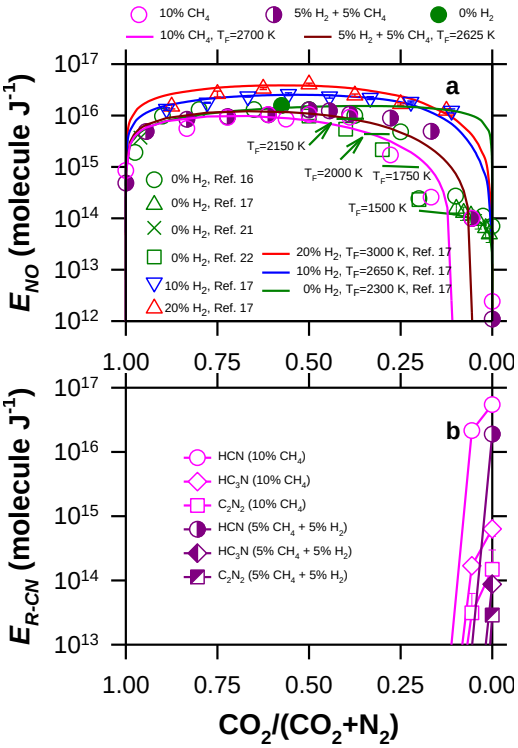


Fig.1. The efficiency in the energy yield (E) of production of fixed N by shockwaves in simulated primitive martian atmosphere. Panel (a) shows the production of NO combining experimental data (symbols) as well as predictions (lines) derived in this and previous studies. Panel (b) shows the experimental production of cyano compounds (R-CN) consisting of HCN, C_2N_2 and HC_3N.

NO was the main form of fixed N in CH_4 and H_2–CH_4 mixtures; HCN, cyanogen (C_2N_2), and cyanoacetylene (HC_3N) were produced only when the $CO_2/(CO_2+N_2)$ ratio was ≤0.06. E_{NO} (10^{16} molecules/J) increased from ~1.0 in 10% CH_4, to ~1.3 in 5% H_2 + 5% CH_4, to ~1.5 in 0% H_2, to 2.5 in 10% H_2 and finally to 3.8 in 20% H_2 at $CO_2/(CO_2+N_2)$=0.5. E_{NO} increased in H_2 rich atmospheres because the shockwave cooled faster, trapping NO at higher mixing ratios at T_F ≥2600K. T_F in CH_4 and H_2-CH_4 mixtures was similar than in H_2 mixtures (Fig. 1); however E_{NO} was lower because atomic oxygen (O), produced by the dissociation of CO_2, was consumed in the oxidation of CH_4 (reaction 1) rather than in N_2 (reaction 2) that led to NO:

$$CH_4 + O \rightleftarrows CH_3 + OH \quad (1)$$

$$N_2 + O \rightleftarrows NO + N \quad (2)$$

Figure 2 shows the variation of amount of fixed nitrogen present in the form of nitrites and nitrates in the sedimentary rocks surveyed by Curiosity to date, and the estimated N accumulation (N_A) rate from the lowest to the highest stratigraphic column. Figure 2 also shows the N deposition (N_D) by bolide impacts and UV irradiation under various conditions. A possible explanation to account for the variation of fixed N is a change in the rate of N_D by fluctuations in the type and amount of greenhouse gases in the atmosphere although leaching of fixed nitrogen is also likely [17, 23]. Perchlorate on Mars roughly tracks nitrate [24], and if the hypothesis suggested here is correct, this may point to an atmospheric chemistry source for perchlorate as well.

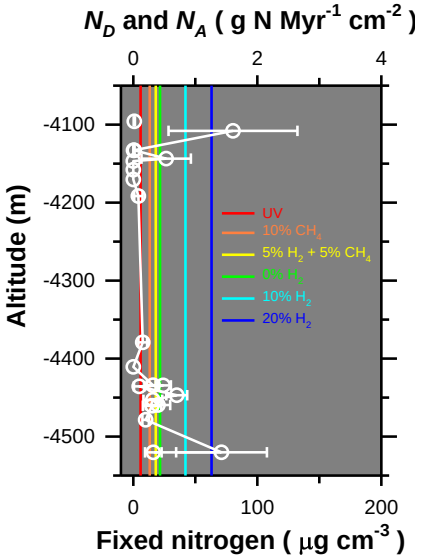


Fig.2. Variation of fixed N evolved as NO in the sedimentary record of Gale crater. N_D and N_A are the rates of fixed N deposited over the entire surface of Gale crater that was transported into the lake [17].

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