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curiosity rover's sample analysis at mars instrument**

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Rafael Navarro-González, Karina F. Navarro, Patrice Coll, Christopher P. Mckay, Brad Sutter, et al.. 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. 52nd Lunar and Planetary Science Conference, Mar 2021, Virtual Meeting, Unknown Region. pp.LPI Contribution No. 2548, id.1365. insu-03563684

HAL Id: insu-03563684

<https://insu.hal.science/insu-03563684>

Submitted on 9 Feb 2022

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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. R. Navarro-González¹, K. F. Navarro¹, P. Coll², C. P. McKay³, B. Sutter⁴, J. C. Stern⁵, P. D. Archer⁴, A. C. McAdam⁵, C. Szopa⁶, C. Freissinet⁶, H. B. Franz⁵, A. Buch⁷, B. D. Prats⁸, M. Millan⁹, J. L. Eigenbrode⁵, D. Coscia¹⁰, S. Teinturier⁵, J.-Y. Bonnet¹⁰, D. P. Glavin⁵, A. J. Williams¹¹, F. Raulin², M. Cabane⁶, D. W. Ming¹², C. A. Malespin⁵, P. Mahaffy⁵, F. J. Martín-Torres¹³, M.-P. Zorzano-Mier¹³, S. Atreya¹⁴, A. Fraeman¹⁵, and A. R. Vasavada¹⁶, ¹Universidad Nacional Autónoma de México (navarro@nucleares.unam.mx), ²Université Paris-Est Créteil, ³NASA Ames Research Center, ⁴Jacobs, NASA Johnson Space Center, ⁵NASA Goddard Space Flight Center, ⁶Université Versailles Saint-Quentin, ⁷Ecole Centrale Paris, ⁸NASA GSFC/eINFORMe, Inc., ⁹Georgetown University, ¹⁰Université Paris-Saclay, ¹¹University of Florida, ¹²NASA Johnson Space Center, ¹³University of Aberdeen, ¹⁴University of Michigan at Ann Arbor, ¹⁵NASA Jet Propulsion Laboratory, and ¹⁶California 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 (H₂) from volcanic emissions that would have warmed the atmosphere episodically by collision-induced absorption (CIA) with CO₂ [2-6] or N₂ [6-7]. An alternative warming scenario is the presence of methane (CH₄~10%) or CH₄-H₂ mixtures due to CO₂-CH₄ CIA in the 250–500 cm⁻¹ spectral window [3,7-8]. The N₂-CH₄ CIA is significantly weaker than with CO₂ [7]. CH₄ 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 CH₄ and H₂ [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, CH₄ may have had a role in nitrogen (N) fixation in the martian atmosphere, *e.g.*, the conversion of N₂ 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 CH₄-H₂-rich atmosphere (high C and H) produces reduced forms of fixed N, such as HCN [14,15], while neutral (CO₂) or oxidized atmospheres (O₂) generate oxidized forms of fixed N, such as NO [16]. We have previously investigated the efficiency of N fixation by bolide impacts in CO₂-N₂ martian atmospheres with or without H₂. Surprisingly, NO was produced more efficiently in 20% H₂ 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% CH₄ and 5% CH₄-5% H₂ in CO₂-N₂ 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 CH₄ (10%) or CH₄ (5%)-H₂ (5%) in CO₂ (0-100%) and N₂ (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]:

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

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 C_p 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 cm³/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 CO₂/(CO₂+N₂) ratio by shockwaves in simulated

primitive martian atmospheres in the absence and presence of CH₄ and/or H₂.

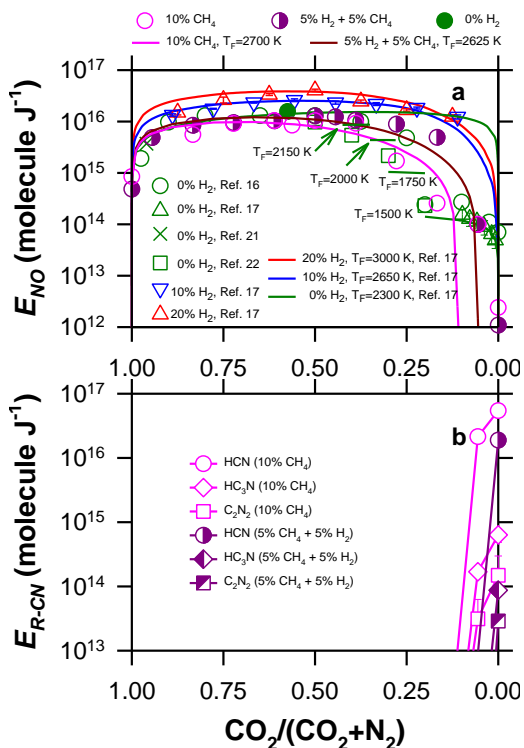


Fig. 1. The efficiency in the energy yield (E) of production of fixed N by shockwaves in simulated primitive martian atmosphere. Panel (a) shows the production of NO combining experimental data (symbols) as well as predictions (lines) derived in this and previous studies. Panel (b) shows the experimental production of cyano compounds (R-CN) consisting of HCN, C₂N₂ and HC₃N.

NO was the main form of fixed N in CH₄ and H₂-CH₄ mixtures; HCN, cyanogen (C₂N₂), and cyanoacetylene (HC₃N) were produced only when the CO₂/(CO₂+N₂) ratio was ≤ 0.06 . E_{NO} (10¹⁶ molecules/J) increased from ~ 1.0 in 10% CH₄, to ~ 1.3 in 5% H₂ + 5% CH₄, to ~ 1.5 in 0% H₂, to 2.5 in 10% H₂ and finally to 3.8 in 20% H₂ at CO₂/(CO₂+N₂)=0.5. E_{NO} increased in H₂ rich atmospheres because the shockwave cooled faster, trapping NO at higher mixing ratios at $T_F \geq 2600$ K. T_F in CH₄ and H₂-CH₄ mixtures was similar than in H₂ mixtures (Fig. 1); however E_{NO} was lower because atomic oxygen (O), produced by the dissociation of CO₂, was consumed in the oxidation of CH₄ (reaction 1) rather than in N₂ (reaction 2) that led to NO:

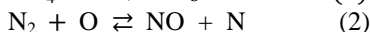
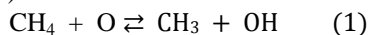


Figure 2 shows the variation of amount of fixed nitrogen present in the form of nitrites and nitrates in the sedimentary rocks surveyed by Curiosity to date, and the estimated N accumulation (N_A) rate from the lowest to the highest stratigraphic column. Figure 2 also shows the N deposition (N_D) by 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.

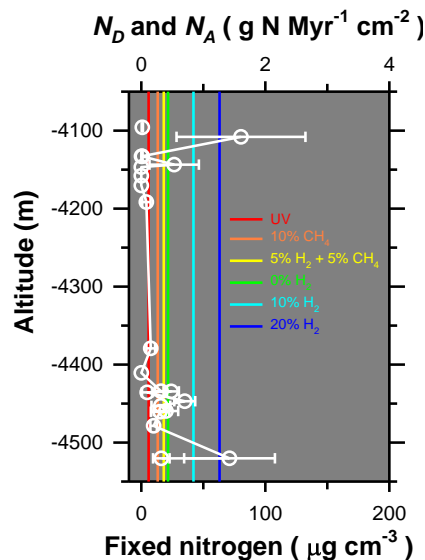


Fig. 2. Variation of fixed N evolved as NO in the sedimentary record of Gale crater. N_D and N_A are the rates of fixed N deposited over the entire surface of Gale crater that was transported into the lake [17].

Acknowledgments: We acknowledge NASA, CNES, and UNAM (PAPIIT IN111619 and PAPIME PE102319) for their financial support.

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