EPSC Abstracts
Vol. 11, EPSC2017-164, 2017
European Planetary Science Congress 2017

What stable nitrogen-bearing minerals could be stored in the surface during early Noachian Mars and what are the constraints in terms of temperature and pH?

I. van de Burgt (1,2), E. Sefton-Nash (2), I.L. ten Kate (1)
(1) Utrecht University, Utrecht, the Netherlands, (2) ESA ESTEC, Noordwijk, the Netherlands, (vdburgt.i@gmail.com)

Early Noachian Mars, nitrogen adsorption, habitability, ExoMars Rover mission

Abstract

Nitrogen plays an important role in many biomolecules and is significant in biological activity on Earth. While nitrogen remains the dominant component in Earth's atmosphere, the nitrogen content of the early Mars atmosphere is ill-constrained, yet fundamental to understanding the habitability of early Mars [16]. The objective of this study is to determine the feasibility and role of nitrogen fixation in clays in conditions that may have prevailed on early Mars. We model fixation as well as loss rates of the nitrogen in phyllosilicates within temperature and pH bounds plausible for ancient Mars surface conditions. We find that ~0.3 – 2.3 teragram (Tg, 10^{12} gram) of nitrogen per Myr may be fixed into the clay phases that are observed on Mars' surface, and that only ~3% of this would be released back to non-fixed reservoirs (aqueous, atmospheric).

1. Introduction

The atmosphere of early Mars contained more than ten times the amounts of free nitrogen than it does today [9, 10]. Before Mars' early and dense atmosphere was lost, this nitrogen was free for interaction with surface minerals and liquids. This study aims to shed light on processes involved fixation of nitrogen into the clays of Mars and what major constraints were involved in this process. Mars' abundant clay minerals may have served as a nitrogen sink due to their excellent capacity of storing cations in their negatively charged interlayers [10].

2. Methods

2.1 Model description

We present a nitrogen box model, as in [17], but with four reservoirs (Figure 1). N_2 (first reservoir) reduces to NO (second reservoir) by lightning [7, 12]. A second flux describes the reduction of NO to ammonium (NH_4^+, third reservoir) by FeS [18]. NH_4^+ (aqueous) may then be adsorbed into clays (fourth reservoir). We used montmorillonite and nontronite as these are the two widely occurring clays on Mars [2, 5]. Their layered structure allows inorganic cations, e.g., NH_4^+ or K^+, to be fixed in the negatively charged interlayers [10].

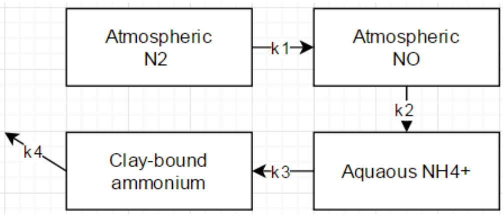

Figure 1. Schematic of the box model. Fluxes are described in the text. The initial reservoir size of N_2 was $8x10^5$ TgN.

This model was run for a time-span of 2 Myr for maximum and minimum bounds of input parameters to produce a plausible envelope of nitrogen fixation.

2.2 Calculations

The adsorption of NH_4^+ into clay minerals was calculated after the work of Boatman and Murray, 1982 [1]:

$$N_{clay} = a_{NH4+} / \left(\left(\frac{1}{K_{ads}} + a_{NH4+} \right) * \Gamma * M_N \right) \qquad (1)$$

a_{NH4+} is the activity of NH_4^+. This is the multiplication of the molar concentration by the activity coefficient of 0.57 for seawater [6, 17]. M_N is the molar mass of nitrogen (14.01 g/mol). K_{ads} is the adsorption constant (12 and 11.7 for nontronite and montmorillonite [1], respectively), and Γ is the cation exchange capacity (0.94 mmol/g and 0.69 mmol/g for nontronite and montmorillonite [1, 14], respectively).

To calculate temperature dependence, the Arrhenius equation (2) was used:

$$\frac{v1}{v2} = \exp(10b * (T_1 - T_2)/(T_1 * T_2) \quad (2)$$

v_1/v_2 is the rate of reaction for a new temperature (T_2) versus the rate of reaction of the reference temperature (T_1). The constant *b* is the product of the activation energy and the gas constant and equals 6352 K [14]. Upper and lower temperature bounds for the model are set 263 K and 283 K informed by warm and wet early Mars assumptions of previous studies [4, 11].

pH dependence of the loss rate from adsorbed NH_4^+ to volatile NH_3 was calculated using equation (3) and the equilibrium constant $K_{NH3} = 10^{-9.25}$ [17]:

$$pH: (NH_3) = ((NH_4) * K_{NH3})/H^+ \quad (3)$$

The stability field of both phyllosilicate minerals are weakly acidic to alkaline [3]. The pH boundaries in this model are set to 6 - 9.

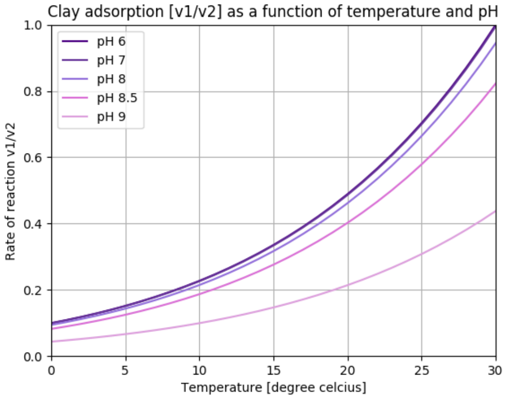

Figure 2: The v_1/v_2 dependence of pH as a function of temperature.

3. Results

The calculation of ammonium adsorption into phyllosilicates without any constraints, pH < 6 and temperature = 303 K, is equivalent to fixing $10.25\text{x}10^{12}$ g N/Myr.

However, pH and temperature both have an effect on the rate of adsorption of nitrogen into different phyllosilicates (Figure 2). For the upper boundary (pH 6 and temperature 283 K) we calculate a v_1/v_2 of 0.23. For the lower boundary (pH 9 and temperature 263 K) a v_1/v_2 of 0.034. Consequently, provided that reactions are not supply-limited we estimate that plausible rates of N fixation in nontronite and montmorillonite lie in the range of ~0.3 – 2.3 Tg N/Myr.

4. Summary and Conclusions

Given the current knowledge about surface conditions and atmospheric composition on early Noachian Mars, we use constraints in pH and temperature and a hypothetical box model to gain a better understanding of nitrogen fixation with respect to phyllosilicates thought to have formed on early Mars. We find that pH is only a meaningful constraint when very alkaline conditions prevail, but a decline in temperature results in a strong decline of nitrogen fixation. Nonetheless, even at the lowest rates of fixation it is possible to lock a large amount of nitrogen in clay minerals that are prevalent on the surface of Mars today. Clues to Mars' ancient atmospheric inventory, and the consequence for early habitability, may therefore lie in rocks that will be targeted by ESA's upcoming ExoMars Rover, which is intended to sample Noachian-aged clay-bearing rocks.

Acknowledgements

I would like to thank the University of Utrecht for providing funds. I further thank my co-workers for constructive criticism.

References

[1] Boatman, C. D., and J. W. Murray. Limnology and Oceanography 27.1 (1982): 99-110. **[2]** Carter, J., et al. Icarus 248 (2015): 373-382. **[3]** Chevrier, V., F. Poulet, and J.-P. Bibring, Nature 448.7149 (2007): 60-63. **[4]** Craddock, R. A., and A. D. Howard. Journal of Geophysical Research: Planets 107.E11 (2002). **[5]** Ehlmann, B. L., and C. S. Edwards. Annual Review of Earth and Planetary Sciences 42 (2014): 291-315. **[6]** Fairén, A. G., et al. Nature 431.7007 (2004): 423-426. **[7]** Kasting, J. F., and J. C. G. Walker. Journal of Geophysical Research: Oceans 86.C2 (1981): 1147-1158. **[8]** Mancinelli, R. L., and A. Banin. International Journal of Astrobiology 2.03 (2003): 217-225. **[9]** Manning, C. V., C. P. McKay, and K. J. Zahnle. Icarus 197.1 (2008): 60-64. **[10]** McBride, M. B. (1994). **[11]** McKay, C. P., and W. L. Davis. Icarus 90.2 (1991): 214-221. **[12]** Navarro-González., R., M. J. Molina, and L. T. Molina. Geophysical Research Letters 25.16 (1998): 3123-3126. **[13]** Rodrigo, A., et al. Ecological Modelling 102.2 (1997): 325-339. **[14]** Sayles, F. L., and P. C. Mangelsdorf.. Geochimica et Cosmochimica Acta 41.7 (1977): 951-960. **[15]** Squyres, S., and J. F. Kasting. Science 265.5173 (1994): 744-749. **[16]** Stern, J. C., et al. Proceedings of the National Academy of Sciences 112.14 (2015): 4245-4250. **[17]** Stüeken, E. E. Astrobiology16.9 (2016): 730-735. **[18]** Summers, D. P., et al. b Astrobiology 12.2 (2012): 107-114.