IMPLICATIONS OF THE IMPACT-DRIVEN NITROGEN CYCLE FOR EARLY AND LATE MARS.

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Introduction: Nitrogen on Mars has been difficult to explain because modeling studies of escape to space suggests it should have effectively escaped [1] unless a thick atmosphere were continually present to suppress its escape. Currently, the atmospheric N/C ratio is 1/18. That this is also the primordial ratio for terrestrial planets is unexpected since N_2 escapes much more readily than CO_2. However, if there were a source of N_2, then it would no longer be anomalous, and instead, perhaps, a tracer of processes and histories we had not anticipated.

In [2] we demonstrated that nitrate minerals could have been produced in large quantities on early Mars as a result of atmospheric impacts, and that nitrogen can be released from near-surface nitrates by impacts. In [3] we investigated the processes determining the production of nitric oxide, a precursor of nitrate minerals.

We have incorporated the modeled processes governing the production and decomposition of nitrates into our numerical model of volatile evolution, the Mars Evolution Code (MEC; [4]), a 1-D forward stepping energy balance code that follows reservoirs of volatiles CO_2 and the isotopes of nitrogen. With it we are able to model both the nitrate production phase on early Mars and the recycling phase on late Mars. We found that on Late Mars, the production of N_2 by impact decomposition of nitrates affects the quantity and isotope ratios of atmospheric nitrogen; observable quantities.

Earlier studies ([2], [3]) suggested that nitrate inventories of order 10^{18} moles (about 10 mbars) would be formed and could still be present today. Our theory is that the impact flux and the nitrate inventory may be large enough to build up the inventory of N_2. However, under current conditions, the escape flux is about twice the predicted decomposition flux. However, the radar observations of Mars' South pole by Phillips et al., [5], and the knowledge that the obliquity was larger in the past [6] provides the opportunity to reduce atmospheric escape by an order of magnitude, as a thicker atmosphere would suppress the escape of nitrogen.

Early Mars: The Early period of Mars lasted about 700 Myr, and involved the accretion of almost 1 km of material [3]. Our simulations with MEC were able to produce large inventories of nitrate minerals as long as the atmospheric pressure during the impact phase of early Mars was over about 2 bars total, with nitrogen present in primordial proportions of 1:18 with carbon. The details of the quantity and the isotope ratio, R_{NO3}, of the nitrates depends on the details of the simulation, as can be seen in Fig. 1. Red squares show variations of initial atmospheric inventory from 0.5 to 3 bars (the 0.5 bar atmosphere collapsed to a permanent CO_2 ice cap – see bottom left); x-symbols vary the gas content of impactors by an order of magnitude; blue triangles adjust suppression of sputtering escape, such as by a geomagnetic field; four-pointed stars show the effect of halving the dissociative recombination (DR) rate, which is a more fractionating means of escape. The highest green point used an initial inventory of 5 bars.

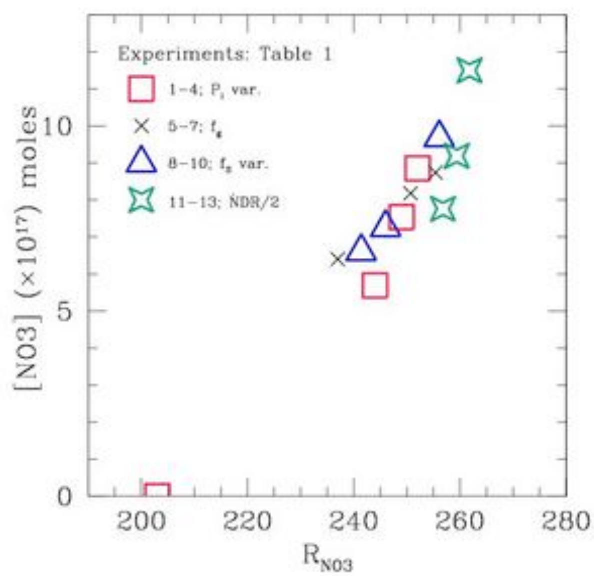

Figure 1. Scatter plots of experimentral nitrarte inventories and isotope ratios under early Mars conditions. A wide range of parameter choices gives a limited range of results; most important is a fairly thick atmosphere of 2 or more bars.

Figure 1 shows a strong correlation between the molar nitrate inventory and its nitrogen isotope ratio, suggesting that the isotope ratio of nitrates on the planet today could be a good indicator of early Mars atmospheric pressure as well as the total nitrate inventory. The figure suggests that about 10^{18} moles of nitrates may have been formed, with a nitrogen isotope ratio of $^{14}N/^{15}N$=250 to 260 under a prevailing atmosphere of 2.5 or 3 bars.

Late Mars: The last half of Mars' history, about 2.28 Gyr is referred to as Late Mars. Let us see how a nitrate inventory would influence the N_2 concentrations today. Figure 2 shows results of experiments run with no starting inventory of nitrates. The legend shows the line types *vs.* combinations of low and high volatile inventory and low and high obliquity. Respective amospheric pressures when no ice cap exists is 30 and 150 mbar, respectively, and low and high obliquities are 29 and 37 degrees. Starting 2.28 Gyr ago with an N_2 inventory equal to the current N_2 inventory (1.6E16 moles), only the high pressure and high obliquity simulation was able to retain much nitrogen. The cause of this behavior is that if the obliquity is low, the atmosphere collapses, and nitrogen is rapidly removed. If the atmospheric pressure is low, nitrogen is more concentrated and will be rapidly eroded even at high obliquity.

If we now assume the presence of 10^{18} moles (~10 mbars) of nitrates on Mars today, then the current impact flux would produce nitrogen at a rate approaching its current escape rate. The experiments in Figure 3 are the same as in Figure 2 except that 10^{18} moles of nitrates are added to the soil. The effect of the nitrates are not seen for a few hundred Myr, but for all models, a relatively strong increase is seen after the first 500 Myr. The current atmospheric inventory (black dot on right) is only reached for the model with high pressure and high obliquity. The eroded models (1-3) might match the current inventory if the reservoir of nitrates were about 1.6 times larger. In short, the more nitrates in the inventory, the smaller the CO_2 reservoir needed to restrain escape enough to allow nitrogen to collect.

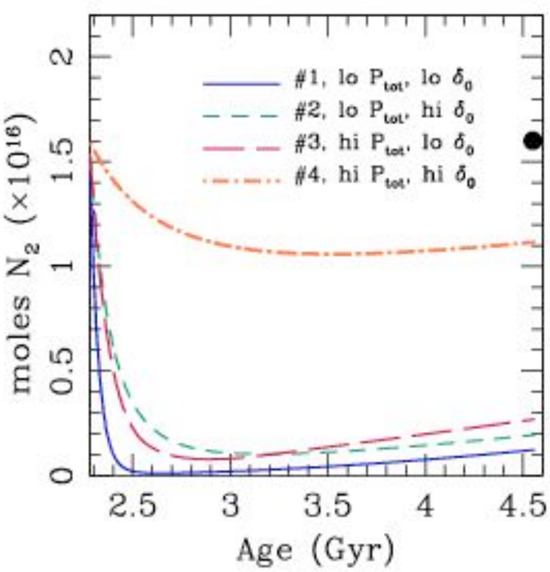

Figure 2. Models with no nitrates. Low maximum pressure is 30 mbars and high is 150 mbars. Low obliquity is 29 deg., and high is 37 deg. Only with high obliquity and high atmospheric pressure is serious N_2 depletion averted.

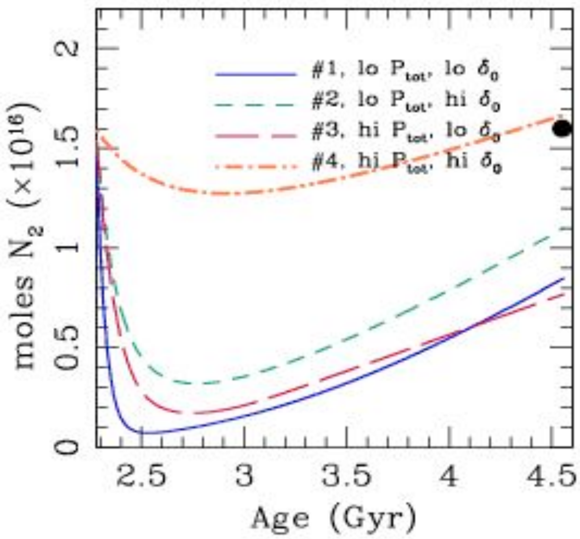

Figure 3. Models of late Mars with 10^{18} moles of nitrates, but otherwise identical to Fig. 2. The increase in inventory with time is due to impact decomposition of nitrates.

Conclusion: The impact-driven nitrogen cycle on Mars appears capable of explaining the regeneration of the nitrogen atmosphere to its current level after a period of strong early atmospheric erosion. However, it takes a thick Early atmosphere (P>2 bars) to make enough nitrates to explain current nitrogn. In addition, it requires either a thick Late atmosphere (up to about 150 mbars) or a nitrate inventory that is greater by a factor of perhaps 2. In any case, it requires a persistently high obliquity for the last 2 Gyr.

We await the arrival of the Mars Sciene Laboratory and the rover *Curiosity* in hopes of learning the isotope ratio of chemically fixed nitrogen, and getting a more accurate value for the atmospheric isotope ratio. With these two parameters accurately known, we should be able to draw more definite conclusions about early and late Mars..

References: [1] Fox, J. L., (1993) *JGR,* 98*,* 3297–3310. [2] Manning, C.V. et al. (2008) *Icarus,* 197*,* 60-64. [3] Manning, C.V. et al., (2009) *Icarus,* 212, 131-137. [4] Manning, C.V., et al., (2006) *Icarus*, 180, 38-59, [5] Phillips, R.J. et al., (2011) *Science*, 332, 838, [6] Laskar, J., et al., (2002) *Nature*, 419, 375-377.