# **Understanding Mars from meteorites – the nitrogen and noble gas perspective**

Ratan K. Mohapatra

Mars has inspired our imagination and scientific research. While space missions in the 1960 and 1970s set up a milestone in the study of Mars, discovery of meteorites apparently from the Red Planet led scientific research into a new dimension. Easily identified and linked by their nitrogen and noble gas isotopic signatures, martian meteorites have provided a unique means of acquiring geochemical data about Mars. These in turn, complemented by results from various geophysical studies and cosmochemical modelling, provide important constraints on the planet's origin and evolution, which constitute the subject matter for the present article.

MASS spectrometers aboard Viking Landers (1 and 2) analysed in situ the elemental and isotopic signatures of martian atmosphere 1-3, which were somewhat 'duplicated' in shock glass samples from a meteorite - EETA 79001 - collected from Antarctic ice sheet<sup>4,5</sup>. While concentrations of carbon dioxide, nitrogen and noble gases (Ne, Ar, Kr and Xe) measured in the above samples show a 1:1 correlation (on a log-log plot), their isotopic compositions are often indistinguishable from corresponding martian atmospheric signatures measured by Viking missions (Table 1). This observation together with a host of others provided convincing evidence that linked<sup>6,7</sup> a group of meteorites found on Earth to Mars. A major effort in the study of Mars today involves identification of such meteorites and extracting geochemical information from them about their parent body by a myriad of laboratory techniques. In this article I bring out some of the important results from the study of nitrogen and noble gases in martian meteorites. Although this may sound a bit specific, I have organized the presentation so as to make it legible and useful especially for amateurs (like me) and readers with general scientific interests. At the same time I apologize to specialists in the field for oversimplification and omission of some of the important but rather specialist results. My predilection for this particular line of research is based, besides acquaintance with these elements, on the following reasons. Nitrogen and noble gases uniquely describe Mars in solar system and have been instrumental in the discovery of martian meteorites. Results obtained from studies of these elements in martian meteorites have implications for the origin and evolution of Mars, nature of its interior, atmosphere and hydrosphere, which are of general and broad scientific interests.

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#### **Martian meteorites**

So far only 29 out of about 22,000 meteorites discovered on Earth have been recognized to have originated from Mars. An updated list of these meteorites and relevant general information about them may be found in NASA's web page (www2.jpl.nasa.gov/snc/), while Meyer<sup>7</sup> provides a nice compilation of their petrography, chemical and isotopic characteristics.

Martian meteorites evolve in three stages (Figure 1). Like terrestrial (Earth or earth-like) igneous rocks they crystallize from martian magmas at or near the surface of Mars. Their crystallization ages<sup>8</sup> varying from ~150 Ma to ~4 Ga are however not typical of meteorites. This in turn requires<sup>6</sup>, as explained below, origin from a large (rocky) planetary body (that experienced igneous activities until as recent as ~150 Ma) rather than asteroids. Meteorites, with sizes ranging from a few micro metres (cosmic dust, micrometeorites) to kilometres (such as that blamed for killing dinosaurs ~65 Ma ago) come from a variety of cosmic sources (asteroids, comets, Moon and interstellar medium), although a majority of them can be linked to the 'asteroidal belt' lying between the orbits of Mars and Jupiter. Representing either 'primordial' solar system material (such as chondrites) or the products of igneous activity (such as achondrites) in early solar system, they are much older than martian meteorites except for ALH 84001 (which has a crystallization age of ~4 Ga)<sup>8</sup>.

Some of these meteorites, such as ALH 84001 and Nakhlites (represented by Governador Valadares, Lafayette, Nahkla, Northwest Africa:817 and 998, and Y:000593, 000749 and 000802), show effects of aqueous interaction<sup>7</sup>. For example, ALH 84001 contains significant secondary carbonates believed to contain trace fossils of microscopic martian organisms<sup>9</sup>. Similarly, Nakhlites contain iddingsite – a clay mineral formed by the interaction of olivine with water. The extraterrestrial nature of these secondary phases is verified by various isotopic signa-

Earth<sup>47</sup>

Table 1.	Comparative planetolgy: nitrogen and key noble gas isotopic ratios for the atmosphere and interior of						
More and Earth							

Will and Earth							
	$\delta^{15} N~(\% \it{o})^a$	<sup>38</sup> Ar/ <sup>36</sup> Ar	<sup>40</sup> Ar/ <sup>36</sup> Ar	129	⟨e/ <sup>132</sup> Xe		
Atmosphere							
Mars (Viking)	$620 \ (160)^{1-3}$	_	3008 (1137) <sup>1</sup>		2.51		
(EET 79001)	$300^{44}$	$0.244 (12)^{44}$	2257 (697) <sup>44</sup>		$2.6^{45}$		
Earth	$0^{46}$	$0.188^{44}$	$295.5^{47}$	$0.98^{47}$			
Mantle							
Mars	$-30^{21,24}$	_	$\sim 300^{35}$	$1.03^{23}$ to $1.07^{21}$			
Earth (Upper)	$-15^{48}$	0.188 to	$40000^{49}$	$1.15^{47}$			
(Lower)	$-25^{25,26}$	$0.179^{47}$	10000 <sup>50</sup>	$1.10^{50}$			
Krypton isotopic da	ata <sup>b</sup>						
	$^{78}\mathrm{Kr}/^{84}\mathrm{Kr}$	$^{80}\mathrm{Kr}/^{84}\mathrm{Kr}$	$^{82}{ m Kr}/^{84}{ m Kr}$	<sup>83</sup> Kr/ <sup>84</sup> Kr	<sup>86</sup> Kr/ <sup>84</sup> Kı		
Mars <sup>19,c</sup>	0.637 (36)	4.32 (2)	20.99 (6)	20.58 (8)	29.75 (7)		

 $<sup>^{</sup>a}\delta^{15}N$  (expressed in ‰) =  $(R_{\text{sample}}/R_{\text{air}} - 1) \times 1000$ , where  $R = ^{15}N/^{14}N$  and  $R_{\text{air}} = 3.669 \times 10^{-3}$ .

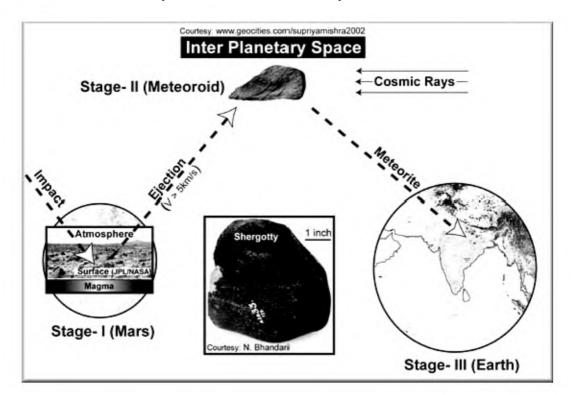
3.96(2)

20.22(6)

20.14(6)

30.52 (6)

0.609(3)



**Figure 1.** Evolution of a martian meteorite (e.g., Shergotty, which fell in Bihar in 1865) consists of three stages (that correspond to different components in it, see text for explanation). Stage I: origin and evolution on Mars (trapping of martian volatiles), II: evolution in interplanetary space as a meteoroid (accumulation of cosmogenic radionuclides) and III: entry into Earth's atmosphere and terrestrial residence (acquisition of terrestrial contamination). During the last stage it also acquires a thin (dark) layer of melt glass coating (due to burning in air) called 'fusion crust', which distinguishes it from terrestrial igneous rocks in field.

tures. Effects of martian secondary processes are also visible in noble gas signatures of these meteorites. For example, it has produced a mass-dependent fractionation favouring heavier noble gas species (Ar, Kr and Xe) in

the trapped martian atmospheric gases<sup>10</sup>. Such effects are consistent with solubility and adsorption behaviour of noble gases, as expected in a secondary process<sup>11,12</sup>. At present water mostly occurs as a frozen subterranean res-

<sup>&</sup>lt;sup>b</sup>Krypton isotopic ratios represent values multiplied by 100. Signatures of martian mantle are not known, while those of Earth's mantle are indistinguishable from corresponding atmospheric signatures.

<sup>&</sup>lt;sup>c78</sup>Kr/<sup>84</sup>Kr ratio is from atmosphere-a while the others are from atmosphere-b of ref. 19.

ervoir in Mars. But topographic features (relict channels and probably a global ocean) and recent discovery of polar ice caps containing both  $CO_2$  and water by Mars Express suggest that water would have played an important role on Mars at some point of its history.

These rocks (precursors of martian meteorites) witness martian geological processes until shock waves (with pressures up to ~50 GPa<sup>13,14</sup>) from asteroidal impacts eject them from the gravitational field (escape velocity ~5 km/s) of Mars. Besides helping them to overcome the planet's gravitational attraction, shock often metamorphoses or even partially melts martian rocks. Shocked plagioclase (maskelynite) from martian meteorites provide estimates of the peak shock pressures 13, while 'glass inclusions' (~1 mm) representing partial melts of the parent rock deliver key geochemical information from Mars. Shock-induced partial melting of martian rocks fairly differs from partial melting of terrestrial rocks (either in mantle or by high grade metamorphism). The former operates under high and directive pressures lasting for a duration (seconds) much smaller than that (years) typical of terrestrial partial melting events operating under hydrostatic pressures. Shock apparently produces melts in a much more localized scale, which cool fast resulting in tiny (~1 mm) 'glass-inclusions' in martian rocks. Although the precise nature of such a process is poorly understood, laboratory shock-experiments on terrestrial basalts reveal that 'shock-implantation' (as it is called) can incorporate ambient volatiles without producing (detectable) effects on their elemental and isotopic compositions<sup>15</sup>. Because of fast cooling, the 'implanted' gas has little time to 'communicate' with volatiles beyond the melt volumes in a rock, which probably enabled shock glasses in EETA 79001 to deliver us a 'sample' of martian atmosphere. At the same time glass-inclusions from no other martian meteorites have been able to trap martian atmosphere so efficiently. For example, shock glasses from SaU 005, a martian meteorite from Oman, show traces of gases both from martian atmosphere and interior 16. This indicates that parent rock for this meteorite might not have been as communicating with martian atmosphere as that for EETA 79001, also understood by its much lower gas content.

The ejected martian rocks spend some time in interplanetary space (as meteoroids in trajectories defined by their initial energy) where they are exposed to cosmic rays (both galactic and solar). The duration that a rock spends in its trajectory, known as 'cosmic ray exposure age', is estimated from the growth of radionuclides by interaction with cosmic rays. Exposure ages of martian meteorites (varying from ~1 to 19 Ma<sup>7</sup>) apparently fall into six groups, believed to represent different 'ejection events' that derived them from Mars.

At some point of time, captured by Earth's gravitational field they fall as meteorites. While a few of martian meteorites are observed 'falls' (e.g., Shergotty, Figure 1), most of them are 'finds'. Till the late 1990s, meteorites

recovered from Antarctic ice dominated the 'martian meteorite collection'. But careful exploration of deserts of the Middle East (e.g., Oman) and Africa (e.g., Algeria, Libya and Morocco) has almost doubled the number of martian meteorites in the last five years<sup>7</sup>. In this context it would probably be useful to extend similar exploratory programmes in the Thar Desert. Interestingly, some of martian meteorites, such as Los Angeles 001, 002 (picked up from a twenty-year-old private meteorite collection) and ALH 84001 (thought to be a common achondrite for almost ten years) had to wait long in our collections before they were correctly identified and brought into the limelight!

Each of the evolutionary stages described above leaves its imprints on a meteorite, readily picked up in different chemical and isotopic signatures in the form of 'components' (Figure 1). The study of martian meteorites essentially tries to track the evolution back in time to derive geochemical signatures acquired from Mars, the success of which depends on efficient resolution of the superimposed components as these can influence indigenous chemical and isotopic signatures of a meteorite.

# A note on experimental approach

Because of their terrestrial residence (e.g., ~13000 years for ALH 84001 (ref. 17), estimated from cosmogenic nuclides) martian meteorites acquire variable amount of terrestrial contamination (e.g., gases from air, carbonates from deserts), which often possesses a major experimental challenge in their study. A commonly employed experimental approach involves simultaneous nitrogen and noble gas isotopic analysis 10, which uses a noble gas mass spectrometer and an ultrahigh vacuum gas extraction line (maintained at  $\sim 10^{-12}$  atm prior to an experiment) such as that at the Physical Research Laboratory (PRL), Ahmedabad (and at six other laboratories in the world). Terrestrial contamination may even reproduce some of the 'martian noble gas signatures', and can be misleading<sup>11,12</sup>. However a carefully planned gas extraction by stepped heating often enables one to isolate terrestrial contamination, even in a fairly weathered martian meteorite (e.g., DaG 476 (ref. 18) and SaU 005 (ref. 16)) from indigenous 'martian components'. A few studies however concentrate on noble gases (for example 19) only and even on a particular species (such as Xe, for example<sup>20</sup>), although utilizing similar piecemeal (stepped heating) extraction of sample gases.

A meteorite during its crystallization from the parent magma (Stage I, Figure 1) traps magmatic volatiles (in the form of inclusions inside the crystal lattice) that are released at temperatures as high as the melting temperatures of its minerals. On the other hand, gases incorporated into it by terrestrial contamination, which are loosely held, are released at low temperatures. Secondary processes in hot deserts often deposit low temperature phases (e.g., carbonates) along fractures inside these meteorites.

Terrestrial contamination in such meteorites often hangs on up to  $\sim 1000^{\circ}$ C<sup>18</sup>. Experience shows that heating in an ultra-pure oxygen environment (known as 'combustion' in contrast to 'pyrolysis' that involves heating in vacuum) efficiently removes atmospheric contamination from a meteorite at a temperature as low as 200°C<sup>21</sup> (but typically 400°C<sup>10</sup>). One may extend the release pattern for terrestrial contamination to low temperature components (from secondary processes) inherited from Mars, which is partly justified except for uncertainty about the effect of shock on any such component. Release of 'martian gases' from these meteorites has been reported from ~400°C<sup>21</sup> to ~1600°C<sup>16</sup>, where the low temperature releases are believed to be contributed by fluid inclusions and the high temperature ones from more retentive sites in a sample. Such release pattern of the meteoritic gas may raise concerns about possible loss of gas during any prior heating events. While gas loss during the exit from Mars and entry into Earth's atmosphere appear insignificant because of the very small interval of time involved, loss by any prolonged 'heating phases' on Mars or interplanetary space (which is somewhat unlikely though) are difficult to evaluate. The uncertainty about gas loss from a martian meteorite (which apparently fails to erase its 'cosmochemical memory', as for many other meteorites) is however overwhelmed by rich chemical and isotopic information about Mars that could not have been obtained by any other means of study so far.

Martian meteorites acquire significant cosmogenic nuclides by interaction with cosmic rays, which often drastically affect the indigenous isotopic signatures. One estimates the 'cosmogenic component' by using certain 'trapped martian' noble gas isotopic ratios (such as <sup>21</sup>Ne/ <sup>22</sup>Ne) and empirically determined 'production ratios' for cosmogenic nuclides. The readers may refer to relevant literatures (for example <sup>10</sup>) for more information regarding the rather involved procedures adopted for resolving various components in a meteorite.

# Martian atmosphere

Mars has a very thin atmosphere with an average pressure of about 7 (varying from 1 to 9 depending on the altitude) millibars ( $\sim 10^{-3}$  atm), but is thick enough to produce strong winds and occasional dust storms. It is composed mostly of carbon dioxide (95.3%); with minor amounts of nitrogen (2.7%), argon (1.6%), and traces of oxygen (0.15%), water (0.03%) and other volatiles<sup>1</sup>. The high concentration of  $CO_2$  (in atmosphere) produces a greenhouse effect only enough to raise the surface temperature by 5° (K) compared to the average martian temperature of 218 K.

# Nitrogen and noble gas signatures

The first-hand information about nitrogen and noble gases in martian atmosphere obtained from the Viking data<sup>1-3</sup>,

although were able to identify martian meteorites, are insufficient to address many specific problems of cosmochemical interests because of large uncertainties (tens of %). But data from martian meteorites have provided a more precise definition (except for He and probably Ne) of martian atmosphere. While martian atmosphere is similar to its terrestrial counterpart in relative concentrations of <sup>20</sup>Ne, <sup>36</sup>Ar, <sup>84</sup>Kr, <sup>130</sup>Xe and overall enrichment of heavier isotopes (except for krypton), it is quite distinct (even in solar system) in the isotopic signatures of nitrogen  $(\delta^{15}N)$ , argon  $({}^{38}Ar)^{36}Ar$  and  ${}^{40}Ar/{}^{36}Ar)$  and xenon  $({}^{129}Xe/$ <sup>132</sup>Xe) some of which even stood out in Viking data (Table 1). Isotopic compositions of krypton in martian atmosphere exhibit a fractionation trend enriching the lighter species (opposite to terrestrial Kr)<sup>19</sup>. Apparent enrichments in 80Kr and 82Kr observed in some martian meteorites indicate the effects of neutron capture on <sup>79</sup>Br and <sup>81</sup>Br, although it is not certain if such enrichments are characteristic of martian atmosphere. Neon (not included in Table 1) isotopic data from some of these meteorites indicate <sup>20</sup>Ne/<sup>22</sup>Ne ratio of about ~11 (compared to 9.8 for Earth's atmosphere) for the martian atmosphere<sup>22</sup>.

#### Martian interior

Martian meteorites are at present the only direct samples to study the interior of Mars. In terms of nitrogen and noble gases, Chassigny (a dunite, composed mostly of olivine) is believed to represent martian mantle, which apparently is indistinguishable from 'solar' in its 129Xe/ <sup>132</sup>Xe (= 1.03) signature<sup>23</sup> but appears quite different from Earth's mantle (Table 1). While terrestrial upper mantle, with  $^{40}$ Ar/ $^{36}$ Ar ~ 40000;  $^{129}$ Xe/ $^{132}$ Xe ~ 1.15 shows significant contributions from radiogenic argon ( $^{40}$ Ar from decay of  $^{40}$ K, half life = 1.26 Ga) and xenon ( $^{129}$ Xe from extinct <sup>129</sup>I, half life = 15.6 Ma), martian mantle is fairly devoid of such in situ radiogenic contributions. On the other hand, nitrogen isotopic composition ( $\delta^{15}N \sim -30\%$ ) of martian mantle<sup>21,24</sup> is not much different from that of its terrestrial counterpart ( $\sim -25\%$ , observed so far<sup>25,26</sup>). It is interesting to note that xenon in martian meteorites often show existence of more than one interior reservoir for Mars, differing slightly in their radiogenic signatures (Table 1). While the precise natures of these reservoirs and their implications for other noble gases are not clear, they may as well refer to a zoning in martian mantle indicated by other geochemical<sup>27</sup> and geophysical data<sup>28</sup>. Earth's upper mantle is more radiogenic than the two martian mantle xenon reservoirs in Table 1, although its lower mantle may not be much different from the 'radiogenic martian mantle reservoir'.

# **Origin of Mars**

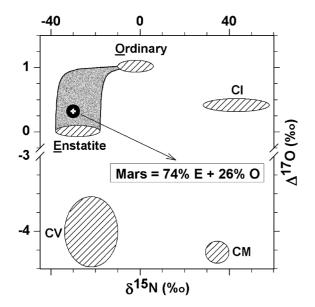
The remarkable similarity observed in chemical compositions between CI carbonaceous chondrites and solar pho-

tosphere has led a number of models to propose a universal carbonaceous-chondrite-like precursor for terrestrial planets<sup>29</sup>. But bulk geophysical properties of Mars such as moment of inertia factor (I/MR<sup>2</sup>), more precisely determined from Mars Pathfinder mission<sup>30</sup>, and mantle structure as imaged from the study of martian meteorites are difficult to explain by significant contributions from carbonaceous (represented by CI, CK, CM, CO, CR, CV) chondrites in Mars<sup>31</sup>. Similarly, isotopic compositions of nitrogen ( $\delta^{15}N$ ) and oxygen ( $\Delta^{17}O$ ) of Mars (Figure 2) require contributions mostly from enstatite (represented by EH and EL chondrites) and ordinary (represented by H, L, and LL) chondrite-like precursors<sup>24</sup> consistent with bulk planet chemical and physical properties of Mars (some of which are difficult to explain by contributions from carbonaceous chondrites). An interesting outcome from the above observation is the prediction that martian core may contain about 7 wt% Si. While at present this seems a bit unconventional, results from recent high pressure melting studies<sup>32</sup> do favour the possibility of accommodating up to 12 wt% Si in metallic cores of terrestrial planets.

#### **Evolution**

#### Interior

With the accumulation of high precision geochemical data from martian meteorites, it has now become possible



**Figure 2.** Nitrogen and oxygen isotopic systematics of Mars<sup>24</sup>.  $\delta^{15}N$  has been defined in the footnote of Table 1.  $\Delta^{17}O = \delta^{17}O + (0.5 \times \delta^{18}O)$  is a special way of expressing oxygen isotopic signatures ( $^{17}O/^{16}O$  and  $^{18}O/^{16}O$ ), where ' $\delta$ 's are defined in a way similar to that for nitrogen. Isotopic compositions of oxygen (forming ~40% by weight of Mars) and nitrogen (a major element in its atmosphere) in Mars, which plot inside the mixing zone (shaded region) of enstatite and ordinary chondrites, suggest origin from these two types of materials and rule out significant contributions from carbonaceous chondrites (CV, CM and CI) commonly invoked as precursors for Mars.

to fairly understand planetary evolution on Mars. A metallic core apparently formed by  $13 \pm 2$  Ma after the beginning of solar system<sup>33</sup>. It is also believed that large scale melting (perhaps associated with the above event) formed a global 'magma ocean' on Mars early in its history. These have important consequences for volatiles, especially noble gases in Mars. For example, if one starts with the reasonable assumption that martian mantle has lost its volatiles to atmosphere during such large-scale melting and remained closed thereafter, from the present <sup>129</sup>Xe/<sup>132</sup>Xe, it is possible to estimate amount of xenon the planet acquired during its accretion<sup>34</sup>. Low radiogenic <sup>40</sup>Ar and almost no (radiogenic) <sup>129</sup>Xe in martian mantle would require either ~ a few orders of magnitude higher (compared to measured concentrations in martian meteorites) amounts of initial argon and xenon in Mars<sup>35</sup> or removal of K and I (from martian mantle) in the early history<sup>36</sup>. On the contrary, radiogenic nature of Earth's mantle requires selective early removal of argon and xenon (from mantle)<sup>37</sup>. Therefore noble gas isotopic signatures of mantles of Mars and Earth reflect differences in planetary evolution.

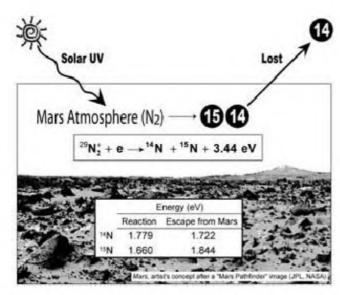
Nitrogen in Earth's mantle indicates, besides the presence of a primordial component, contributions from subducted 'surface-derived' (sedimentary) materials<sup>38</sup>. While 'plate tectonics' is responsible for this surficial nitrogen (and noble gas) component in Earth's mantle, existing data on martian meteorites are unable to evaluate the role of such global tectonic phenomenon in the evolution of volatiles in martian mantle. Low <sup>40</sup>Ar/<sup>36</sup>Ar and <sup>129</sup>Xe/<sup>132</sup>Xe signatures of martian mantle (as compared to atmosphere) may rule out significant recycling of atmospheric volatiles into its mantle. But one must realize that any recycling of contemporaneous (or in past 4.4 Ga, when <sup>129</sup>I was extinct) martian atmospheric volatiles into mantle would hardly be able to affect the isotopic signatures of bulk mantle (which is volatile-rich<sup>29</sup>).

### Atmosphere

The failure of Mariner 6 and 7 missions to detect (by ultraviolet spectrometers) any molecular nitrogen in martian atmosphere together with its much heavier  $({}^{15}N)^{14}N =$  $1.62 \pm 0.16$  times terrestrial) nitrogen isotopic signature indicated the scarcity of nitrogen in martian atmosphere<sup>39</sup>. Although <sup>15</sup>N may also form by cosmic-ray interactions with atmospheric oxygen, such production is too low to account for the observed anomaly. 'Thermal (Jeans) escape' for nitrogen, in ground  $(N_2)$  or ionized  $(N_2^{\dagger})$  states, from Mars is negligible. But a number of 'non-thermal' escape mechanisms, such as 'pick up' by solar wind of planetary ions (from sputtering of neutral atmospheric species), photochemical, ion-molecule and dissociative recombination reactions in martian atmosphere, can cause loss of atmospheric nitrogen<sup>39,40</sup>. Incident solar radiations in the far UV range (>796 A)<sup>39</sup>, with energy comparable

to the first ionization potential of molecular nitrogen (15.58 eV) provide a suitable background for such reactions in martian atmosphere. Figure 3 illustrates the essence of dissociative recombination (of N<sub>2</sub><sup>+</sup> with electrons), apparently the most important escape mechanisms for nitrogen above martian exobase. Ground state molecular nitrogen (N<sub>2</sub>) in martian atmosphere dissociates into two atoms in a series of reactions. The lighter atom (<sup>14</sup>N), with a kinetic energy of 1.779 eV, if directed favourably can overcome martian gravitational attraction. On the other hand, the heavier atoms (15N) with a lower kinetic energy (1.660 eV) are retained by martian atmosphere, and affect its isotopic composition in the long run. Observation of martian atmospheric nitrogen trapped in ALH 84001 (age ~4 Ga) with an isotopic composition ( $\delta^{15}$ N ~+46‰) much lighter than that in EETA 79001 (age ~150 Ma) and measured by Viking provided experimental evidence<sup>10</sup> for loss of martian atmospheric nitrogen in last 4 Ga.

While the above mechanism explains nitrogen isotopic composition of martian atmosphere, its low content of primordial noble gases requires additional explanation. It is believed that intense far-ultraviolet radiations from young Sun were able to ionize lighter gaseous species such as H which formed bulk of the primordial atmospheres in terrestrial planets. 'Thermal loss' of these ionized species exerted upward drag forces on the heavier species occurring in trace concentrations in an atmosphere, which was effective in removing loosely held chemically inert gaseous species, such as molecular nitrogen (N<sub>2</sub>) and noble gases. Known as 'hydrodynamic escape'<sup>41</sup>, such loss mechanism induces a mass-dependent fractionation (both among elements and isotopes) in the remnant



**Figure 3.** 'Non-thermal' loss of nitrogen from martian atmosphere by dissociative recombination<sup>40</sup>. Energies of nitrogen atoms thus produced (as a function of their masses) have been compared with that required for escape from martian atmosphere (see text for discussion).

atmospheric (heavier) species. It should be realized here that presence of a martian magnetic field (indicated by large-scale remnant magnetic lineations) in old martian southern highlands observed by Mars Global Surveyor<sup>42</sup>, and impact of large asteroidal bodies on Mars early in its history<sup>43</sup> may also have helped loss of ionized gaseous species from early martian atmosphere.

None of the above mechanisms ('continuous loss' or 'hydrodynamic escape') can, however, suitably explain isotopic compositions of martian atmospheric krypton, which is poorly understood.

#### Summary

Isotopic compositions of nitrogen and noble gases in martian meteorites not only help in their identification, but provide useful insights into their origin and evolution and that of the Red Planet. While Mars appears pretty much a planet like ours, it has an atmosphere much different in isotopic signatures of nitrogen, argon and xenon, and a mantle that has much less radiogenic noble gas isotopic signatures. These reflect differences in planetary evolution in these two planets. At the same time, similarity in nitrogen isotopic composition of mantles and relative concentrations of noble gases in their atmospheres may indicate some similarity in the nature of precursors and planetary evolution. While conventionally CI carbonaceous chondrites are proposed as a universal precursor of terrestrial planets, the isotopic compositions of nitrogen and oxygen suggest Mars to have formed by the accretion (in a ratio of 74:26) of enstatite and ordinary chondritelike materials.

- 1. Owen, T., Biemann, K., Biller, J. E., Lafleur, A. L., Rushneck, D. R. and Howarth, D. W., The composition of the atmosphere at the surface of Mars. *J. Geophys. Res.*, 1977, **82**, 4635–4639.
- Nier, A. O., McElroy, M. B. and Yung, L. Y., Isotopic composition of the martian atmosphere. Science, 1976, 194, 68–70.
- McElroy, M. B., Yung, Y. L. and Nier, A. O., Isotopic composition of nitrogen: Implications for the past history of Mars' atmosphere. Science, 1976, 194, 70–72.
- Bogard, D. D. and Johnson, P., Martian gases in an Antarctic meteorite? Science, 1983, 221, 651-654.
- Pepin, R. O., Meteorites evidence of martian origins. *Nature*, 1985, 317, 473–475.
- McSween, H. Y. J., What we have learned about Mars from SNC meteorites. *Meteoritics*, 1994, 29, 757–779.
- Meyer, C., Mars Meteorite Compendium, NASA, Houston, 2003, http://www-curator.jsc.nasa.gov/curator/antmet/mmc/mmc.htm.
- Nyquist, L. E., Bogard, D. D., Shih, C.-Y., Greshake, A.; Stöffler, D. and Eugster, O., Ages and geologic histories of martian meteorites. Space Sci. Rev., 2001, 96, 105–164.
- McKay, D. S. et al., Possible relic biogenic activity in martian meteorite ALH 84001. Science, 1996, 273, 924–930.
- Murty, S. V. S. and Mohapatra, R. K., Nitrogen and heavy noble gases in ALH 84001: Signatures of ancient Martian atmosphere. *Geochim. Cosmochim. Acta*, 1997, 61, 5417–5428.
- Mohapatra, R. K., Schwenzer, S. P. and Ott, U., In Lunar Planetatery Institute Conference Abstracts 1532, 2002.

- Schwenzer, S. P., Mohapatra, R. K. and Ott, U., Nitrogen and noble gases in caliche from the martian meteorite SaU 008. Geochim. Cosmochim. Acta, 2002, 66, A693.
- 13. Fritz, J., Greshake, A. and Stöffler, D., In Lunar Planetary Institute Conference Abstracts 1335, 2003.
- Head, J. N., Melosh, H. J. and Ivanov, B. A., Martian meteorite launch: High-speed ejecta from small craters. *Science*, 2002, 298, 1752–1756.
- Wiens, R. C. and Pepin, R. O., Laboratory shock emplacement of noble gases, nitrogen, and carbon dioxide into basalt, and implications for trapped gases in shergottite EETA 79001. *Geochim. Cosmochim. Acta*, 1988, 52, 295–307.
- Mohapatra, R. K., Schwenzer, S. P., Herrmann, S. and Ott, U., Trapped nitrogen and noble gases in a shock-glass from Sayh Al Uhaymir 005 – the Martian meteorite from Oman. *Meteoritics Planet. Sci.*, 2001, 36, A139.
- 17. Jull, A. J. T., Donahue, D. J., Eastoe, C. J., Swindle, T. D., Bukland, M. K. and Herzog, G. F., Isotopic evidence for extraterrestrial carbonates in the SNC meteorites Allan Hills 84001 and Nakhla. *Meteoritics*, 1995, **29**, 479.
- Murty, S. V. S. and Mohapatra, R. K., Cosmogenic and trapped gas components in the Martian meteorite Dar al Gani 476 from hot desert. *Lunar Planet. Inst. Contrib.*, 1999, 997, 57–60.
- Swindle, T. D., Martian noble gases. Rev. Mineral. Geochem., 2002. 47, 171-190
- Gilmour, J. D., Whitby, J. A. and Turner, G., Disentangling xenon components in Nakhla: Martian atmosphere, spallation and martian interior. *Geochim. Cosmochim. Acta*, 2001, 65, 343–354.
- 21. Mathew, K. J. and Marti, K., Early evolution of martian volatiles: Nitrogen and noble gas components in ALH84001 and Chassigny. *J. Geophys. Res.*, 2001, **E1 106**, 1401–1422.
- 22. Mohapatra, R. K., Schwenzer, S. P. and Ott, U., Trapped neon in the martian meteorite SaU 005. *Meteoritics Planet. Sci.*, 2003, 38,
- 23. Ott, U., Noble gases in SNC meteorites: Shergotty, Nakhla, Chassigny. *Geochim. Cosmochim. Acta*, 1988, **52**, 1937–1948.
- 24. Mohapatra, R. K. and Murty, S. V. S., Precursors of Mars: Constraints from nitrogen and oxygen isotopic compositions of martian meteorites. *Meteoritics Planet. Sci.*, 2003, **38**, 225–241.
- 25. Cartigny, P., Boyd, S. R., Harris, J. W. and Javoy, M., Nitrogen isotopes in peridotitic diamonds from Fuxian, China: The mantle signature. *Terra Nova*, 1997, **9**, 175–179.
- 26. Mohapatra, R. K., Harrison, D. and Ottu, U., Nitrogen in OIB mantle. *Geochim. Cosmochim. Acta*, 2002, **66**, A517.
- 27. McSween, H. Y. Jr., Leonard Medal Address: The rocks of Mars, from far and near. *Meteoritics Planet. Sci.*, 2002, **37**, 7-25.
- Zuber, M. T., The crust and mantle of Mars. *Nature*, 2001, 512, 220-227.
- 29. Dreibus, G. and Wänke, H., Mars, a volatile-rich planet. *Meteoritics*, 1985, 367–381.
- Folkner, W. M., Yoder, C. F., Yuan, D. N., Standish, E. M. and Preston, R. A., Interior structure and seasonal mass redistribution of mars from radio tracking of Mars Pathfinder. *Science*, 1997, 278, 1749–1752.
- Bertka, C. M. and Fei, Y., Implications of Mars Pathfinder data for the accretion history of the terrestrial planets. *Science*, 1998, 281, 1838–1840.
- 32. Dobson, D. P., Vocado, L. and Wood, I. G., A new high-pressure phase of FeSi. *Am. Mineral.*, 2002, **87**, 784–787.
- Kleine, T., Munker, C., Mezger, K. and Palme, H., Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature*, 2002, 418, 952–955.

- Mohapatra, R. K. and Gilmour, J. D., Understanding the I-Xe systematics of the Martian mantle. *Meteoritics Planet. Sci.*, 2003, 38, 5196.
- Bogard, D. D., Clayton, R. N., Marti, K., Owen, T. and Turner, G., Martian volatiles: Isotopic composition, origin, and evolution. Space Sci. Rev., 2001, 96, 425–458.
- Musselwhite, D. M., Drake, M. J. and Swindle, T. D., Early outgassing of Mars supported by differential water solubility of iodine and xenon. *Nature*, 1991, 352, 697–699.
- Allegre, C. J., Staudacher, T. and Sarda, P., Rare gas systematics: formation of the atmosphere, evolution and structure of the Earth's mantle. *Earth Planet. Sci. Lett.*, 1987, 81, 127–150.
- Mohapatra, R. K. and Murty, S. V. S., J. Asian Earth Sci., 2002, 20, 867–877.
- Brinkmann, R. T., Mars: Has nitrogen escaped? Science, 1971, 174, 944–945.
- Fox, J. L. and Hac, A., The <sup>15</sup>N/<sup>14</sup>N isotope fractionation in dissociative recombination of N<sub>2</sub><sup>+</sup>. J. Geophys. Res., 1997, 102, 9191–9204.
- Pepin, R. O. and Porcelli, D., Rev. Mineral. Geochem., 2002, 47, 191–246.
- 42. Connerney, J. E. P. et al., Magnetic lineations in the ancient crust of Mars. Science, 1999, 284, 794-798.
- Melosh, H. J. and Vickery, A. M., Impact erosion of the primordial atmosphere of Mars. *Nature*, 1989, 338, 487–489.
- Wiens, R. C., Becker, R. H. and Pepin, R. O., The case for a martian origin of the shergottites, II. Trapped and indigenous gas components in EETA 79001 glass. *Earth Planet. Sci. Lett.*, 1986, 77, 149–158.
- Bogard, D. D. and Garrison, D. H., Relative abundances of argon, krypton, and xenon in the Martian atmosphere as measured in Martian meterorites. *Geochim. Cosmochim. Acta*, 1998, 62, 1829– 1835
- 46. Junk, G. and Svec, H. J., The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. *Geochim. Cosmochim. Acta*, 1958, 14, 234–243.
- 47. Ozima, M. and Podosek, F. A., *Noble Gas Geochemistry*, Cambridge Univ. Press, Cambridge, 2002.
- 48. Mohapatra, R. K. and Murty, S. V. S., Nitrogen isotopic composition of the MORB mantle: A reevaluation. *Geochem. Geophys. Geosyst.*, 2004, 5, doi:10.1029/2003GC000612.
- 49. Burnard, P., Graham, D. and Turner, G., Vesicle-specific noble gas analyses of 'popping rock'; implications for primordial noble gases in the Earth. *Science*, 1997, **276**, 568–571.
- 50. Trieloff, M., Kunz, J. and Allegre, C. J., Noble gas systematics of the Reunion mantle plume source and the origin of primordial noble gases in Earth's mantle. *Earth Planet. Sci. Lett.*, 2002, **200**, 297–313.

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