

TRACING THE OLIGIN AND EVOLUTION OF VOLATILES ON MARS: CONSTRAINTS FROM ELEMENTAL AND ISOTOPIC COMPOSITIONS OF NITROGEN AND NOBLE GASES. Hiroyuki Kurokawa¹, Kosuke Kurosawa², and Tomohiro Usui¹. ¹Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-13 Ookayama, Meguro-ku, Tokyo, 152-8550 Japan (hiro.kurokawa@elsi.jp), ²Planetary Exploration Research Center, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan.

Introduction: Geological and geochemical evidence suggests that the Martian atmosphere and hydrosphere have undergone significant loss throughout the history [1]. The volatiles on Mars would have been removed and replenished by various processes (Figure 1): impact erosion and replenishment by asteroids and comets, atmospheric escape induced by solar radiation and wind, volcanic degassing, and gas deposition by interplanetary dust particles (IDPs).

Contrary to hydrogen, carbon, and oxygen being partitioned into water and rock, nitrogen and noble gases (hereafter called atmophiles) are mainly partitioned into atmosphere, enabling us to trace the history of the Martian atmosphere by using their elemental and isotopic abundances. The Martian atmophiles have two distinct features; i) the uniform depletion of their elemental abundances with respect to Earth implies their chondritic (primitive chondrites and/or comets) origins and nonfractionating loss due to the impact erosion (Figure 2a) [2], and ii) the enrichment of heavy isotopes of N, Ar, and Xe implies substantial loss due to the atmospheric escape driven by solar radiation and wind [3-5]. However, it is unclear how these two features were simultaneously fulfilled in the history.

Using a holistic model of the loss and supply of volatiles (CO_2 , N_2 , H_2O , and noble gases) that has successfully reproduced the isotopic compositions of the Martian atmosphere [6,7] (Figure 1), we simulate the evolution of the elemental compositions of atmophiles to constrain the origin and evolution of the volatiles on Mars.

Model: A Monte Carlo method [8] was used to treat the stochastic nature of impacts. Atmospheric erosion and volatile supply due to each impact were calculated by adapting empirical formulas obtained by hydrocode simulations [9]. We treated the number ratio of comets to asteroids in the impactors after 4.1 Ga (the late heavy bombardment period) as a parameter f_{comet} .

Sputtering and photochemical escape followed the models of [10-12] with some modifications. We adopted the upper atmospheric structures under different EUV levels [10,13,14]. The sputtering is assumed to initiate from 4.1 Ga when the Martian dynamo ceased [15].

The dependence of the volcanic-degassing rate on time was taken from [16], which is based on geologic records of volcanism on Mars. The abundances of the

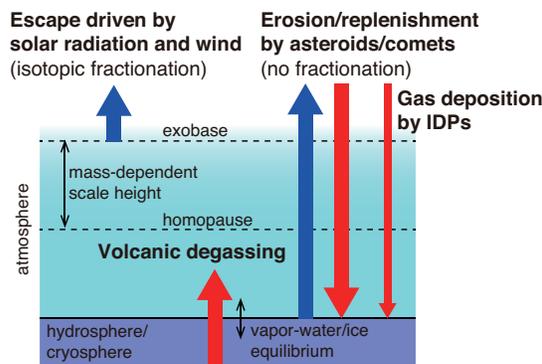


Figure 1: Schematic illustration of our model [6].

noble gases in the volcanic gas were estimated by assuming their ratios to (C+N) to be identical to those of the Earth's depleted mantle [17]. We introduced the volcanic factor C_{vol} , which is a multiplicative factor that accounts for a different volcanic rate. The model of [16] corresponds to $C_{\text{vol}} = 1$.

IDPs are a non-negligible source of the atmospheric Ne in the Martian atmosphere [18]. We adopted a model of gas deposition by IDPs [18] for noble gases.

Phase equilibrium of CO_2 and H_2O between the atmospheric and solid/liquid reservoirs was treated. A threshold of the atmospheric collapse (CO_2 sublimation), $P_{\text{collapse}} = 0.5$ bar, was assumed [19].

Results: We compared the elemental (Figures 2a and 2b) compositions obtained from our model to those of the present-day atmosphere on Mars. We note that the evolution of isotopic compositions in this model has been reported elsewhere [6,7]. Because the atmospheric C (CO_2) abundance in the collapsed cases is determined by the equilibrium with surface reservoirs in our model, the C abundance in the atmosphere always equals the observed value. The model with $C_{\text{vol}} = 1$ and $f_{\text{comet}} = 0\%$ contained lower amounts of N and noble gases than the observed values.

Changing C_{vol} chiefly affected the N abundance (Figure 2b). Increasing C_{vol} to ~ 5 resulted in an adequate amount of N, whereas noble gases were depleted compared with the present-day Mars because the volcanic gas is depleted in noble gases. Noble gas abundances were controlled by f_{comet} (Figure 2c). The suitable value was $f_{\text{comet}} \sim 0.1\%$, which corresponds to $\sim 3 \times 10^{17}$ kg of comets in our model.

Because Ne was rapidly lost from a thin atmosphere due to the sputtering, Ne supplied by impacts has been lost in the present-day Mars in the cases of $f_{\text{comet}} =$

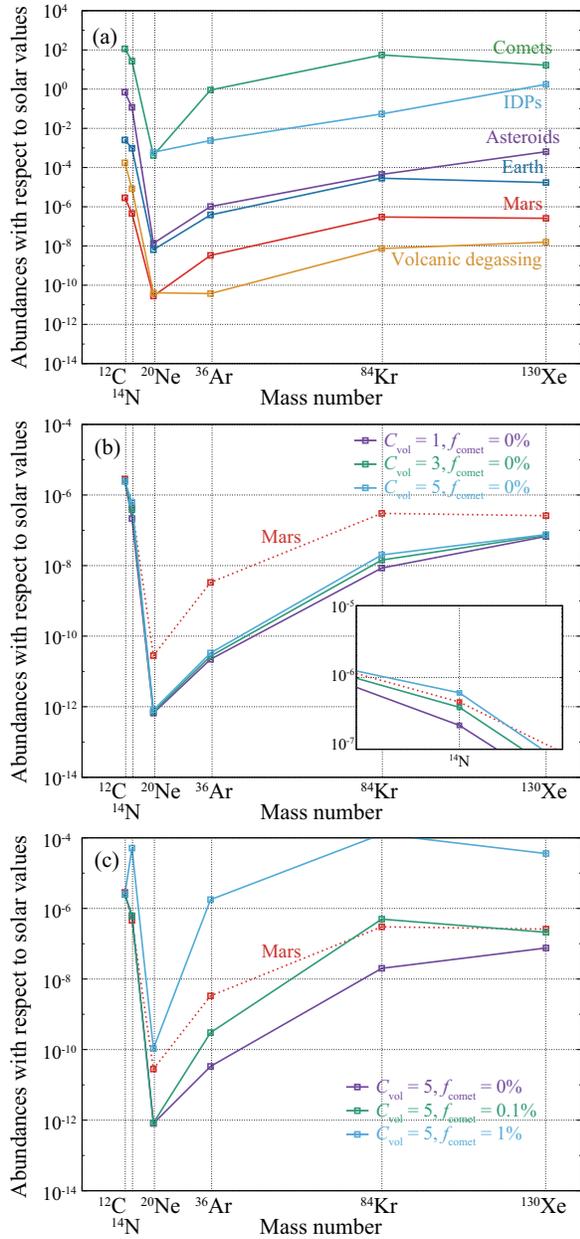


Figure 2: (a) Elemental abundances in asteroids, comets, IDPs, volcanic gas, and the Martian atmosphere, with respect to the solar values. The abundance in the atmosphere is normalized by the mass of solid Mars. Data are from [18,20-23]. (b, c) Simulated elemental abundances in our model with respect to solar values. Averaged values of the collapsed cases in a hundred of Monte Carlo simulations are shown.

0%, 0.1%). The lifetime of Ne in the Martian atmosphere was estimated to be ~ 0.1 Gyrs [10]. The present-day abundance in our model was determined by continuous supply by IDPs.

Discussion: Our model showed that N in the Martian atmosphere originated mainly from volcanic de-

gassing, while the noble gases have exogenous origins: comets and IDPs. Atmospheric escape, which is responsible for the enrichment of heavy isotopes in the Martian atmosphere, inevitably leads to elemental fractionation: depletion in Ne. Even assuming Earth-like, chondritic noble-gas-sources (Figure 2a) resulted in different elemental patterns (Figure 2c). The discrepancy might be explained by additional sources of Ne, such as recent cometary impacts or IDP flux higher than the adopted value. The similarity of Mars to Earth and chondrites in noble gas abundances is coincidence caused by elemental fractionation due to the atmospheric escape in these cases. In addition, reevaluation of Ne abundance in the Martian atmosphere by *in situ* measurements would enable us to test the chondritic abundance retrieved from Martian meteorites.

The origins of atmophiles constrain those of other volatiles (H, C, and O). Given the H_2O abundance in comets $\sim 30\%$ [22], $\sim 3 \times 10^{17}$ kg of comets would supply ~ 1 m global equivalent layers (GEL) of water. The water supply is smaller than the water inventory in polar layered deposits (20-30 m GEL, [24]), suggesting that the origin of Martian surficial water was chiefly chondrites [25] and enriched in deuterium due to the atmospheric escape through time [24,26].

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