A LOWER LIMIT OF ATMOSPHERIC PRESSURE ON EARLY MARS INFERRED FROM NITROGEN AND ARGON ISOTOPES.

H. Kurokawa[1], K. Kurosawa[2], and T. Usui[3]. [1]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-13 Ookayama, Meguro-ku, Tokyo, 152-8550 Japan (hiro.kurokawa@elsi.jp), [2]Planetary Exploration Research Center, Chiba Institute of Technology, [3]Department of Earth and Planetary Sciences, Tokyo Institute of Technology.

Introduction: Geomorphological evidence (valley networks, outflow channels, deltas, etc.) has suggested that Mars once sustained a large amount of liquid water [e.g., 1]. A dense atmosphere (at least ~ 1 bar) is required to sustain a permanent ocean on Martian surface [e.g., 2]. On the contrary, geochemistry of clay minerals discovered to be widespread in Noachian terrains indicates that aqueous environments were limited to be in the subsurface and that surface water existed only episodically [3]. Therefore, constraining atmospheric pressure on early Mars is crucial to understand the ancient climate.

Whereas there are several constraints on an upper limit of the atmospheric pressure on early Mars [4,5], a lower limit has been poorly constrained. We calculated the evolution of volumes and isotope compositions of the Martian atmosphere and hydrosphere taking into consideration asteroid impacts, atmospheric escape induced by solar radiation and wind, and volcanic degassing. Comparing our results with N and Ar isotope ratios of trapped gas in Allan Hills (ALH) 84001 gave a lower limit of the atmospheric pressure at 4.1 Ga when ALH 84001 formed.

Model: We constructed a model of the loss and supply of volatiles (CO_2, N_2, H_2O, and noble gases) to simulate the evolution of their isotope ratios (Figure 1).

Asteroid impacts were included by a stochastic bombardment model [6]. Impact erosion and supply of volatiles by asteroids were calculated with the scaling laws obtained from recent numerical simulations [7]. The total volatile abundance in asteroids was treated as a parameter (1 wt. % is assumed in our nominal model).

Atmospheric escape induced by solar radiation and wind was modeled based on [8,9] with some modifications. We adopted ion pick-up and sputtering rates interpolated and extrapolated from [10]. Photochemical escape rate of nitrogen was taken from [11] with an EUV-flux dependence proposed by [8]. We assumed that the solar-wind-induced escape was absent before 4.1 Ga because the Martian magnetic field would protect the atmosphere from the solar wind during this period [12].

Contrary to the impact erosion process, the atmospheric escape induced by solar radiation and wind fractionate isotopes because it removes the atmosphere from exobase where lighter species are relatively enriched. The mass-dependent fractionation factors of N and Ar for early and present Mars were taken from
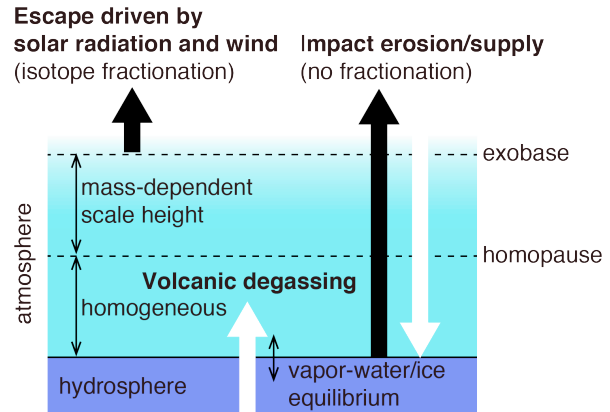

Figure 1: Schematic illustration of our model.

[13] and [8], respectively. The processes that dissociate N_2 and eject high-speed atoms can also cause fractionation. This fractionation factor was adopted from [14].

Volcanic degassing rate is treated as a parameter based on a minimum estimate from geologic records [15]. A three-fold degassing rate of [15] is assumed in our nominal model.

The decrease in the atmospheric pressure may induce atmospheric collapse [16]: CO_2 ice forms and the partial pressure of atmospheric CO_2 is determined by equilibrium with the CO_2-ice reservoir. We assumed that the CO_2 partial pressure decreases to 6 mbar when the atmospheric pressure becomes lower than 0.3 bar as suggested from recent 3D GCM simulations (for obliquity = 25°) [17].

We adopted the initial δN = -30 ‰, the value estimated for the Martian mantle [18], and the initial $^{38}Ar/^{36}Ar$ = 1/5.3, the value estimated for CI chondrites [19]. Volcanic degassing and asteroids were assumed to supply the same isotope ratios for simplicity.

Results: The atmospheric pressure evolved stochastically because of frequent impacts for the first ~0.5 billion years (Figure 2a). In some cases, impact erosion prevailed supply of volatiles and the atmosphere collapsed during this period.

Whereas the N and Ar isotope ratios kept unfractionated values before the collapse, they increased stochastically after the collapse (Figures 2b and 2c). Asteroid impacts in a thinner atmosphere increased abundances of N and Ar. It resulted in higher escape rates of these species and consequently increased their isotope ratios. In the same way, the case started from a
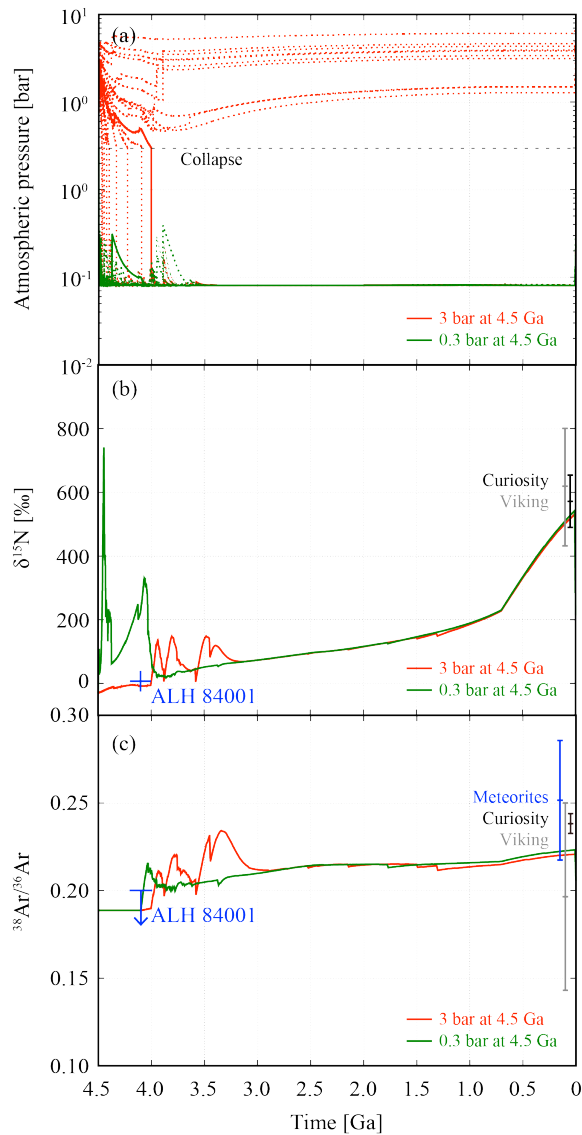
Figure 2: Evolution of (a) atmospheric pressure, (b) nitrogen isotope ratio, and (c) argon isotope ratio. 20 simulations are shown for the cases where atmospheric pressure = 3 bar and 0.3 bar at 4.5 Ga, respectively, in (a). Typical examples are shown in (b,c) (corresponds to the cases of solid lines in panel (a)). Exploration and meteorite data are from [18, 20, 21].

thin atmosphere (< 0.3 bar, a pressure lower than the threshold to collapse) underwent the random increase of the isotope ratios.

The cases of a moderately dense atmosphere (> 0.3 bar) at 4.1 Ga is consistent with unfractionated N and Ar isotope ratios recorded in ALH 84001 [18]. This lower limit of the atmospheric pressure is valid regardless of the presence/absence of the Martian magnetic dynamo at 4.1 Ga because the atmospheric nitrogen

was removed by photochemical escape driven by solar radiation.

Discussion: Simulated argon isotope ratios at present were slightly lower than the value obtained by *Curiosity* measurements (Figure 2c). As the present $^{38}Ar/^{36}Ar$ ratios are determined by sputtering, the discrepancy may indicate that the isotope fractionation is more efficient than the assumption in our model. Even if we adopt an efficient fractionation, it does not change our conclusion that moderately dense atmosphere (>0.3 bar) is required to explain unfractionated $^8Ar/^{36}Ar$ ratios at 4.1 Ga because an efficient isotope fractionation yields a larger value of the lower limit of the atmospheric pressure.

The data on the trapped-nitrogen-isotope composition of ALH 84001 vary significantly (∼7 ‰ [18] to >200 ‰ [22, 23]) in the literature. Identification of the actual nitrogen isotope ratio at 4.1 Ga would help to constrain the evolution of the Martian atmosphere.

Our results provided a lower limit of the atmospheric pressure at 4.1 Ga. If we combine our results with an upper limit at 4.1 Ga (< 0.4 bar) [5], a moderately dense atmosphere (0.3-0.4 bar) at 4.1 Ga is suggested. A permanent warm climate due to a dense atmosphere, if existed, may have ceased at this period.

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