

MASS FRACTIONATION OF ATMOSPHERIC XENON ON MARS AND IMPLICATIONS FOR MARTIAN PALEOCLIMATE. W. S. Cassata¹

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Introduction: Constraints on the composition of the early Martian atmosphere are limited, as until 2011, the only sample from early Mars available for study was Allan Hills (ALH) 84001. Initial studies of trapped noble gases in ALH 84001 led to differing interpretations, from evidence for early hydrodynamic escape [1] to evidence of mantle-derived fission Xe [2]. Almost twenty years have passed since these measurements were reported, and since that time a second ancient Martian meteorite, Northwest Africa (NWA) 7034, has been discovered. New measurements of trapped noble gases in ALH 84001 and NWA 7034, recently published in *Earth and Planetary Science Letters* [3], indicate these two meteorites retain a common, ancient trapped atmospheric component. The new measurements indicate that an early episode of atmospheric escape that mass fractionated Xe (selectively removed light isotopes) culminated within a few hundred million years of planetary formation (i.e., more than 4 billion years ago), and little change to the non-iodine-derived atmospheric Xe isotopic composition has occurred since this time [3]. Atmospheric mass fractionation of Xe on Mars differs significantly from Earth, where Xe isotopic fractionation was a gradual process that occurred throughout much of planetary history [4,5], which indicates that atmospheric dynamics on the two planets diverged early in the history of the Solar System [3]. This may have important implications for Martian paleoclimate.

Samples and Methods: Temperature-controlled diode laser heating with a co-aligned optical pyrometer was used to incrementally degas 8-22 mg-sized fragments of NWA 7034 and ALH 84001. During experimental heating, the samples wrapped in high-purity Pt-Ir tubes and held at temperatures between 500 and 1600 °C for durations of 180 seconds. Ar, Kr, and Xe isotopes in the released gas were analyzed using a Nu Instruments *Noblesse* mass spectrometer. A complete description of background, spectrometer discrimination, and cosmogenic corrections is given in [3].

Results: (1) *ALH 84001 and NWA 7034 share a common trapped component.* With increasing temperature, the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio obtained from ALH 84001 increases to a reproducible value of 2.151 ± 0.032 over 86% of the cumulative ^{132}Xe released [3]. Likewise, with increasing temperature, the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio obtained from NWA 7034 increases to a reproducible value of 2.140 ± 0.032 over 78% of the cumulative ^{132}Xe released [3]. The two meteorites also share a

similar trapped $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of ~ 600 , and similar $^{36}\text{Ar}/^{132}\text{Xe}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios [3].

(2) *The trapped component is not consistent with modern Martian atmosphere.* Both $^{129}\text{Xe}/^{132}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ are lower than the modern Martian atmosphere, which has $^{129}\text{Xe}/^{132}\text{Xe} = 2.522 \pm 0.006$ [6] and $^{40}\text{Ar}/^{36}\text{Ar} = \sim 1800$ [7]. $^{36}\text{Ar}/^{132}\text{Xe}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ are also inconsistent with the modern Martian atmosphere.

(3) *The non-iodine-derived Xe isotopes are indistinguishable from the modern Martian atmosphere.* In ALH 84001, $^{130}\text{Xe}/^{132}\text{Xe}$, $^{131}\text{Xe}/^{132}\text{Xe}$, $^{134}\text{Xe}/^{132}\text{Xe}$, and $^{136}\text{Xe}/^{132}\text{Xe}$ are indistinguishable from modern atmosphere [3,6] (Figure 1). It was not possible to accurately constrain the trapped heavy isotopes of Xe in NWA 7034 due appreciable abundances of fission Xe derived from U-rich apatite and zircon crystals [3].

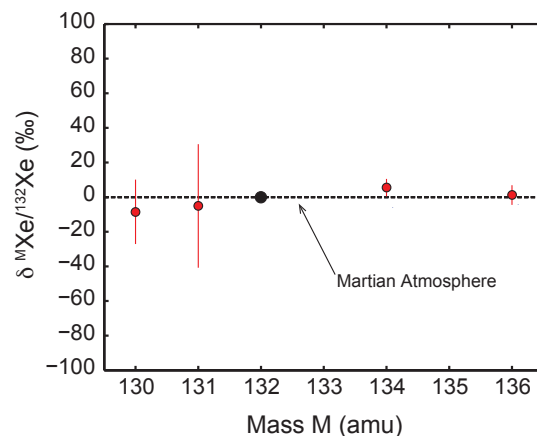


Figure 1: Comparison of modern Martian atmospheric Xe [6] with the trapped atmospheric component in ALH 84001 (red) [3]. The non-iodine-derived Xe isotopic composition identified in ALH 84001 is indistinguishable from modern Martian atmospheric Xe. Figure is modified from [3].

(4) *The trapped components dates to ~ 4.2 Ga or earlier.* The $^{129}\text{Xe}/^{132}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of the trapped component are lower than modern Martian atmosphere and trapped atmospheric gases in the 1.3 – 1.4 Ga Nakhilites [e.g., 8,9] (Figure 2). This indicates the trapped gases in ALH 84001 and NWA 7034 are not associated with shock implantation of modern Martian atmosphere during ejection, and also appear to pre-date the Nakhilites [3]. Additionally, both ALH 84001 and NWA 7034 are Noachian rocks. Incorporation of atmospheric Xe at the time of or nearly coincident with their formation provides an explanation for

the indistinguishable $^{129}\text{Xe}/^{132}\text{Xe}$ ratios that are also lower than modern Xe and that in Nakhrites [3]. If the trapped components were implanted during shock events that occurred after formation, they must have fortuitously occurred at the same time in both samples to explain the similarity in $^{129}\text{Xe}/^{132}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios [3].

Collectively, these observations indicate that ALH 84001 and NWA 7034 retain an ancient atmospheric component that is less evolved than the modern Martian atmosphere in $^{40}\text{Ar}/^{36}\text{Ar}$, $^{129}\text{Xe}/^{132}\text{Xe}$, $^{84}\text{Kr}/^{132}\text{Kr}$, and $^{36}\text{Ar}/^{132}\text{Xe}$, but has indistinguishable non-iodine-derived Xe isotopes [3] (Figure 2). This trapped component likely dates to 4.2 Ga.

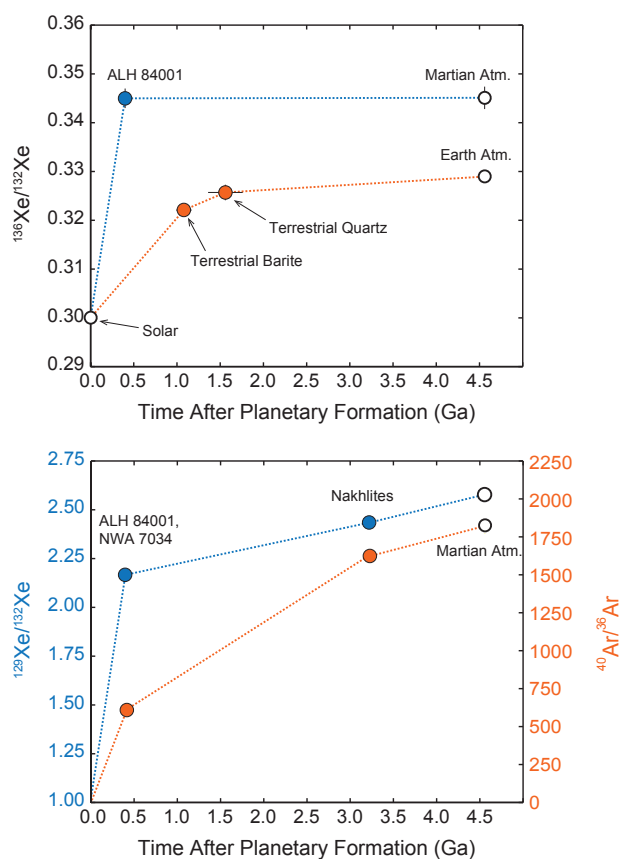


Figure 2: (Upper) Plot of the Martian (blue) and terrestrial (orange) $^{136}\text{Xe}/^{132}\text{Xe}$ ratios as a function of time after planetary formation. Dashed lines linearly connect data points. Data are from: ALH 84001 [3], terrestrial quartz [5], terrestrial barite [12], Martian atmosphere [6], Earth's atmosphere [13], and solar [14]. Panel is modified from [3]. (Lower) Plot of the Martian atmospheric $^{129}\text{Xe}/^{132}\text{Xe}$ (blue) and $^{40}\text{Ar}/^{36}\text{Ar}$ (orange) ratios as a function of time after planetary formation. Dashed lines linearly connect data points. Data are from: ALH 84001 [3,15], NWA 7034 [3,16], Nakhrites [8,9], and Martian atmosphere [6,7].

Discussion and Conclusions: On Earth, mass fractionation of atmospheric Xe was a gradual process that occurred over at least two billion years [4,5] (Figure 2). On Mars, Xe fractionation culminated within 100's of Ma of planetary formation [3] (Figure 2). Why did the evolution of atmospheric Xe on these planets diverge early in planetary history?

Catling and Zahnle [10] and Zahnle [11] proposed that, on Earth, Xe was fractionated throughout the Archean via ionic coupling with escaping H. Ionic hydrodynamic escape requires significantly lower H escape fluxes than neutral Xe escape and therefore operates in the lower EUV environments that existed later in planetary history [11]. The source of H required to drive ionic escape is water [11], which has been abundant on Earth throughout planetary history. The fact that Xe fractionation on Mars ceased by 4.2 Ga therefore suggests that the H escape flux did not exceed the threshold required for Xe escape, possibly because Mars did not have sufficient atmospheric water available to generate H_2 via photodissociation [3]. This in turn suggests liquid water may not have been abundant for persistent durations on the Martian surface after 4.2 Ga, and therefore climate conditions associated with hydrated mineral assemblages and water-related geomorphic features may have been transient [3]. A detailed investigation of the relationship between surface water availability and ionic hydrodynamic escape on Mars is required to better understand the implications of this comparison [3].

References: [1] Murty S. and Mohapatra R. (1991) *GCA*, 61, 5417-5428. [2] Mathew L. and Marti K. (2001) *JGR*, 106, 1401-1422. [3] Cassata W.S. (2017) *EPSL*, 479, 322-329. [4] Srinivasan B. (1976) *EPSL*, 31, 129-141. [5] Pujol M. et al. (2011) *EPSL*, 308, 298-306. [6] Conrad P. et al. (2016) *EPSL*, 454, 1-9. [7] Bogard D.D. et al. (2001) *SSR*, 96, 425-458. [8] Gilmour J. et al. (2001) *GCA*, 65, 343-354. [9] Cohen B.E. et al. (2017) *Nature Comms.*, 8, 640. [10] Catling C. and Zahnle K.J. (2009) *Sci. Am.*, 300, 24-31. [11] Zahnle K.J. (2015) *LPS XLVI*, Abstract #1549. [12] Pujol M. et al. (2009) *GCA*, 73, 6834-6846. [13] Valkiers S. et al. (1998) *JMSIP*, 173, 55-63. [14] Meshik A. et al. (2014) *GCA*, 127, 326-347. [15] Cassata W.S. et al. (2012) *Icarus*, 221, 461-465. [16] Cassata W.S. et al. (2018) Unpublished data.

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