

SEQUESTERING NOBLE GASES IN EARLY HYDRATED CRUSTS ON MARS. J. A. Krantz¹, K. M. Cannon², and S. W. Parman¹. ¹Brown University, Department of Earth, Environmental and Planetary Sciences, Providence, RI, 02912. ²University of Central Florida, Department of Physics, Orlando, FL, 32816. Email: john.krantz@brown.edu

Introduction: Noble gases serve as tracers of planetary processes, including accretion and differentiation, mantle outgassing, and atmospheric loss. Of particular interest is xenon, with 9 stable isotopes, that on Earth and Mars shows depletion and mass-dependent fractionation relative to Solar Wind (SW) [1-3]. Xenon reservoirs are usually thought of in terms of mantle and atmosphere, but noble gases have solubilities 2-3 orders of magnitude higher in layered phyllosilicates than in mantle minerals [4-6], and so could act as another source. Here, we use Mars to explore the possibility of sequestering significant amounts of noble gases, including Xe, in early hydrated crusts formed during a steam atmosphere phase on terrestrial planets [7,8].

Current models have difficulty explaining Mars's Xe isotopic system. Atmospheric loss and mantle outgassing may not be able to account for the overabundance of I-derived ¹²⁹Xe and the lack of Xe from ²⁴⁴Pu fission [1-3]. These constraints imply the products of early ¹²⁹I decay ($t_{1/2}=15.7$ Myr) were retained through atmospheric loss, while the later decay products of ²⁴⁴Pu ($t_{1/2}=80.0$ Myr) were not.

During magma ocean solidification, a significant fraction (70-99%; [7]) of mantle volatiles are outgassed to build up a dense atmosphere (Fig. 1a; [7]). On Mars, this atmosphere likely consisted mostly of H₂, H₂O and CO [10], where water began as a vapor or supercritical fluid, and could have rapidly condensed to form hot lakes or oceans at the surface, although impact-heating might have prevented this [9]. In either case, these conditions were ripe for significant aqueous alteration of the early crust [7,8], potentially forming a thick layer of phyllosilicates (primordial clays) that on Mars may have survived to the present day [8].

Experimental studies have demonstrated that mineral structures with ring sites, including phyllosilicates, have high noble gas solubilities compared to other silicates [4-6]. Further, the noble gas composition of hydrous phyllosilicates has been shown to reflect the composition of the alteration fluid and the experimentally determined solubility. This allows for the trapping and storage of noble

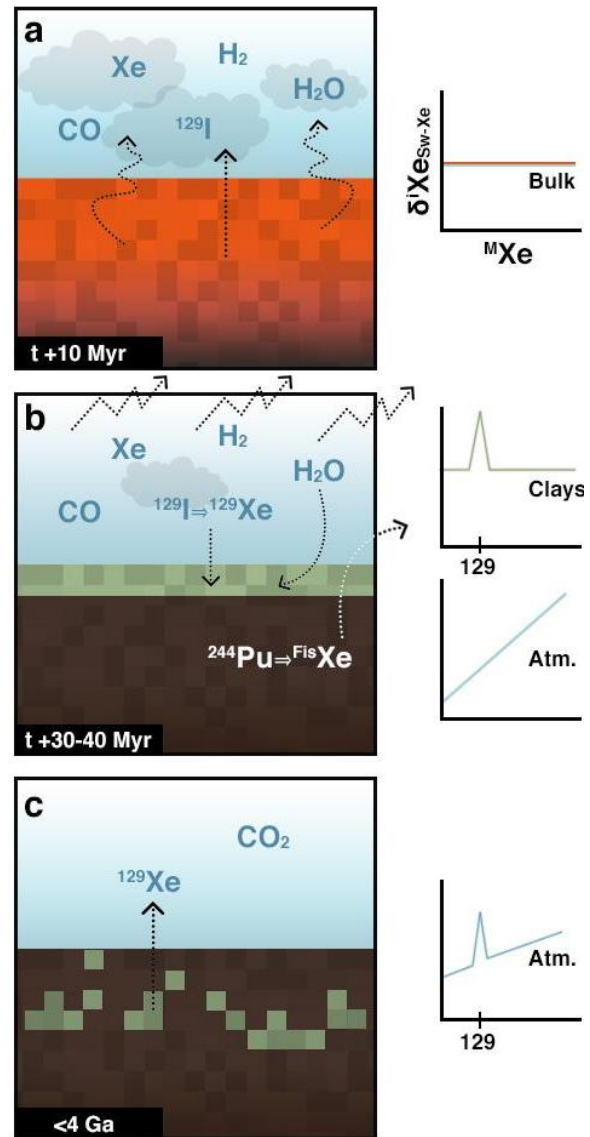


Figure 1. Diagram of Xe sequestration model. a) Outgassing of volatiles to form a thick, steam atmosphere with chondritic Xe during magma ocean phase b) Hydration of early crust sequesters Xe into clays with I-derived ¹²⁹Xe anomaly, but without Pu-derived Xe; atmospheric loss produces mass-fractionation slope c) Later degassing from clay-bearing crust reintroduces I-Xe anomaly to atmosphere.

gases without isotopic fractionation. Due to the high solubility of noble gases in layered phyllosilicates, significant amounts of these species, including Xe, could be sequestered into an early hydrated Martian crust (Fig. 1b) and may have produced the seemingly contradictory Xe isotopic fractionation patterns observed in the modern atmosphere (Fig. 1c). Noble gas sequestration during the steam atmosphere should have taken place in the first 40 million years, when ^{129}I -derived Xe was abundant in the atmosphere, but before substantial production of ^{244}Pu -derived Xe. Thus, the I-Xe would be sequestered in the phyllosilicate layer, while the Pu-Xe would be lost.

Model set-up: A box model was used to assess the potential of an early, hydrous crust to trap and store Xe. Values for the I, U, and Pu content and isotopic ratios of modern Bulk Silicate Mars, as well as the initial $^{129}\text{I}/^{127}\text{I}$ ratio, were used to back-calculate the abundances at 4.56 Ga [11-14]. The decay products of ^{129}I and ^{244}Pu were calculated for fully degassed mantle 40 Myr after solar system formation, with all Xe produced in the first 10 Myr assumed to be lost from the system during accretion (Fig. 2). The total mass of phyllosilicates, partial pressure of Xe in the atmosphere, and solubility of Xe in phyllosilicates were then used to calculate the total mass of Xe stored in the hydrous crust [6,9].

Results: For the full range of input parameters, the amount of ^{129}Xe stored in modern phyllosilicates is 6.8×10^3 - 3.0×10^4 times higher than in the atmosphere. Likewise, the ratio of stored $^{132,134,136}\text{Xe}$ to that in the modern atmosphere is 6.7-30. Thus, a primary clay layer would sequester more than enough Xe to affect the current atmosphere. As production of these isotopes is independent of retention, and there is no isotopic fractionation induced by trapping in phyllosilicates, the excess Xe in the model is assumed to be additional loss of trapped Xe via later impacts and incomplete degassing of the hydrous crust. In the case where all ^{129}Xe in the modern atmosphere has been degassed from the clays, at most 4% of the ^{136}Xe is derived from ^{244}Pu fission. Even in this most conservative case, the results are consistent with observations of the modern atmosphere.

Discussion: Fig. 1 shows a sketch of the early evolution of the Martian crust and atmosphere, with the associated Xe fractionations expected for this scenario. Early outgassing from the magma ocean releases gases with a chondritic Xe isotopic pattern.

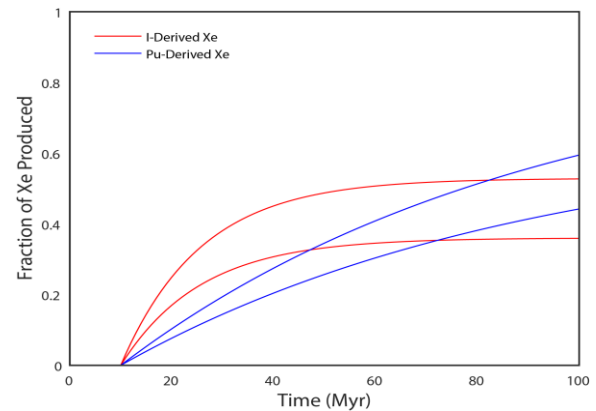


Figure 2. Fraction of total I-derived (red) and Pu-derived (blue) Xe modeled through time. All Xe produced prior to 10 Myr is lost during accretion. This early loss accounts for roughly half of the I-derived Xe, but only 10% of the Pu-derived Xe in the system.

Ingrowth of ^{129}Xe from I-decay rapidly increases $^{129}\text{Xe}/^{132}\text{Xe}$ in the atmosphere. Hydration of the crust and growth of clays traps and stores the chondritic Xe and anomalously high ^{129}Xe during atmospheric loss. This loss also causes mass-dependent fractionation in the atmosphere. Subsequent degassing of Xe from the hydrated crust reintroduces chondritic Xe with excess ^{129}Xe , matching the current atmosphere.

Mass balancing the sequestration of Xe in phyllosilicates indicates that they have the potential to trap and store Xe that has been outgassed to an early, dense, wet atmosphere. In the case of Mars, this may explain the observation of an I-derived Xe anomaly in the atmosphere, without a corresponding Pu-derived Xe anomaly.

References: [1] Marty B. et al. (2016) *EPSL*, 441, 91-102. [2] Cassata W. S. (2017) *EPSL*, 479, 322-329. [3] Musselwhite D. S. et al. (1991) *Nature*, 352, 697-699. [4] Jackson C. R. M. et al. (2015) *GCA*, 159, 1-15. [5] Jackson C. R. M. (2013) *Nat. Geosci.*, 6, 562-565. [6] Krantz J. A. et al. *in prep.* [7] Elkins-Tanton L. T. (2008) *EPSL*, 271, 181-191. [8] Cannon K. M. et al. (2017) *Nature*, 552, 88-91. [9] Maindl T. L. et al. (2015) *A&A*, 574, A22. [10] Pahlevan K. et al. (2017) *AGU Fall Meet.*, P31F-02. [11] Dreibus G. and Wänke H. (1985) *Meteoritics*, 20, 367-381. [12] Hudson G. B. et al. (1989) *LPS XIX*, 547-557. [13] Crabb J. et al. (1982) *GCA*, 46, 2511-2525. [14] Porcelli D. et al. (2002) *RIMG*, 47, 1-19.