HYDROGEN ISOTOPIC CONSTRAINTS ON THE EVOLUTION OF SURFACE AND SUBSURFACE WATER ON MARS.

T. Usui[1], H. Kurokawa[1], J. Wang[2], C. M. O'D. Alexander[2], J. I. Simon[3], and J. H. Jones[3], [1]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Meguro, Tokyo 152-8550, Japan (tomohirousui@elsi.jp), [2]Dept. Terrestrial Magnetism, Carnegie Inst. Washington, 5241 Broad Branch Road, NW, Washington, DC 20015, USA, [3]ARES, NASA-Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA.

Introduction: The geology and geomorphology of Mars provide clear evidence for the presence of liquid water on its surface during the Noachian and Hesperien eras (i.e., >3 Ga) [1]. In contrast to the ancient watery environment, today the surface of Mars is relatively dry. The current desert-like surface conditions, however, do not necessarily indicate a lack of surface or near-surface water/ice. In fact, massive deposits of ground ice and/or icy sediments have been proposed based on subsurface radar sounder observations [2]. Hence, accurate knowledge of both the evolution of the distribution of water and of the global water inventory is crucial to our understanding of the evolution of the climate and near-surface environments and the potential habitability of Mars.

This study presents insights from hydrogen isotopes for the interactive evolution of Martian water reservoirs. In particular, based on our new measurement of the D/H ratio of 4 Ga-old Noachian water, we constrain the atmospheric loss and possible exchange of surface and subsurface water through time.

D/H Ratio of 4 Ga-old Noachian Water: We first reported coordinated *in situ* analyses of carbon, oxygen, and hydrogen isotopic compositions of ~4 Ga-old carbonates in Allan Hills (ALH) 84001 [3]. The analyses were conducted using the Cameca NanoSIMS 50L at Carnegie Institution of Washington. The carbon, oxygen, and hydrogen isotopes were positively correlated with each other from the isotopically lighter core ($\delta^{13}C_{PDB}$ = ~10‰, $\delta^{18}O_{SMOW}$ = ~3‰, δD_{SMOW} = ~800‰) to the heavier rim ($\delta^{13}C_{PDB}$ = ~25‰, $\delta^{18}O_{SMOW}$ = ~20‰, δD_{SMOW} = ~1,200‰). This isotopic enrichment was consistent with a widely-accepted formation scenario [e.g., 4] that the ALH 84001 carbonates formed in a Noachian aqueous system that was short-lived and involved small amounts of fluid. A Rayleigh distillation modal based on our new hydrogen isotope data indicates that the original Noachian water should have had a δD range of ~500-1,000‰ (Fig. 1a).

Distribution of Water Reservoirs: The isotopic signatures of three hydrogen reservoirs are now identified based on our analyses of Martian meteorites [this study, 3, 5, 6], telescopic observations [e.g., 7], and Curiosity measurements [e.g., 8]: primordial water, surface water, and subsurface water (Fig. 1a). The primordial water is retained in the mantle and has a D/H ratio similar to those seen in Martian building blocks. The surface water has been isotopically exchanged with the atmospheric water of which D/H ratio has increased through the planet's history to reach the present-day mean value of ~5,000‰. The subsurface water reservoir has intermediate δD values (~1,000–2,000‰), which are distinct from the low-δD primordial and the high-δD surface water reservoirs. We proposed that the intermediate-δD reservoir represents either hydrated crust and/or ground ice interbedded within sediments [5]. The hydrated crustal materials and/or ground ice could have acquired its intermediate-δD composition from the ancient surface water reservoir recorded by 4-Ga ALH carbonates.

Water Inventory at 4 Ga: Our one-reservoir model [9] provides the volume of water loss since 4 Ga using the D/H ratios of the Noachian (500-1,000‰ at 4 Ga) and the present-day (5,000‰) waters. The calculations are performed in two extreme cases for atmospheric escape regimes. Case-1 assumes a Jeans escape-limited regime and employs a minimum net fractionation factor (*f*) of 0.016; this *f* value is interpreted as representing the current Martian condition [10]. Case-2 assumes a diffusion-limited regime of hydrogen from the homopause to the exobase and employs a maximum net *f* of 0.33; this regime approximates ancient Martian conditions with higher solar UV flux than that of today [11]. Although actual atmospheric escape processes have not been fully constrained yet, these two cases provide a probable range of realistic *f* values during the last 4 billion years. Hence, Case-1 and Case-2 yield the water inventory lower- and upper-bounds at 4 Ga (81-270 m global equivalent layer GEL), assuming that polar layered deposits (PLD) dominate the present-day surface water inventory (20-30 mGEL [9]) (Fig. 1b).

Interactive Evolution of Surface/Subsurface Water: The calculated range of water inventory at 4 Ga (81-270 mGEL) is comparable to the water volume estimated from putative Hesperian shorelines (130-156 mGEL [12]), but is distinctly lower than the water volume estimated from putative Noachian shorelines (548 m GEL [13]) (Fig. 1b). At face value, these observations imply that all of the Hesperian surface water was lost to space via atmospheric escape. However, in detail all reasonable escape processes fail to account for the difference in the water volumes between the Noachian surface water and the present-day surface water inventory. Assuming that there was such a large body

of surface water in the Noachian, we propose that a part of the Noachian surface water (≥200 mGEL) has been sequestered underground over geologic time and is a source of the intermediate-δD reservoir.

The geomorphology of Mars suggests that in the Hesperian the surface water might not have existed as long-standing oceans, but occurred episodically as floods and/or ephemeral lakes that once filled in the northern lowlands [1]. The Hesperian surface water might have been sourced from the subsurface, inter-mediate-δD reservoir. This hypothesis is further supported by a recent Curiosity measurement that a Hes-perian-age mudstone has an intermediate-δD value (2,000±200‰ [8]).

References: [1] Carr M. H. and Head J. W. (2010) *EPSL, 294,* 185–203. [2] Mouginot J. et al. (2012) *GRL, 39,* L02202, [3] Usui T. et al. (2016) *LPS XLIIV,* Abstract #1780. [4] Niles P. B. (2013) *Space Sci. Rev., 174,* 301–328. [5] Usui T. et al. (2015) *EPSL, 410,* 140–151. [6] Usui T. et al. (2012) *EPSL, 357–358,* 119–129. [7] Villanueva G. L. (2015) *Science, 348,* 218-221. [8] Mahaffy P. R. (2015) *Science, 347,* 412-414. [9] Kurokawa H. et al. (2014) *EPSL, 394,* 179–185. [10] Krasnopolsky, V. (2000) *Icarus, 148,* 597–602. [11] Kurokawa H. et al. (2016) *Geochem J. 50,* 67–79. [12] Carr M. H. and Head J. W. (2003) *JGR, 108,* 5042. [13] Di Achille G. and Hynek B. M. (2010) *Nature Geosci. 3,* 459–463. [14] Usui T. (in press) in *Volatiles In The Martian Crust* (eds. Filiberoto J. and Schwenzer S. P.).
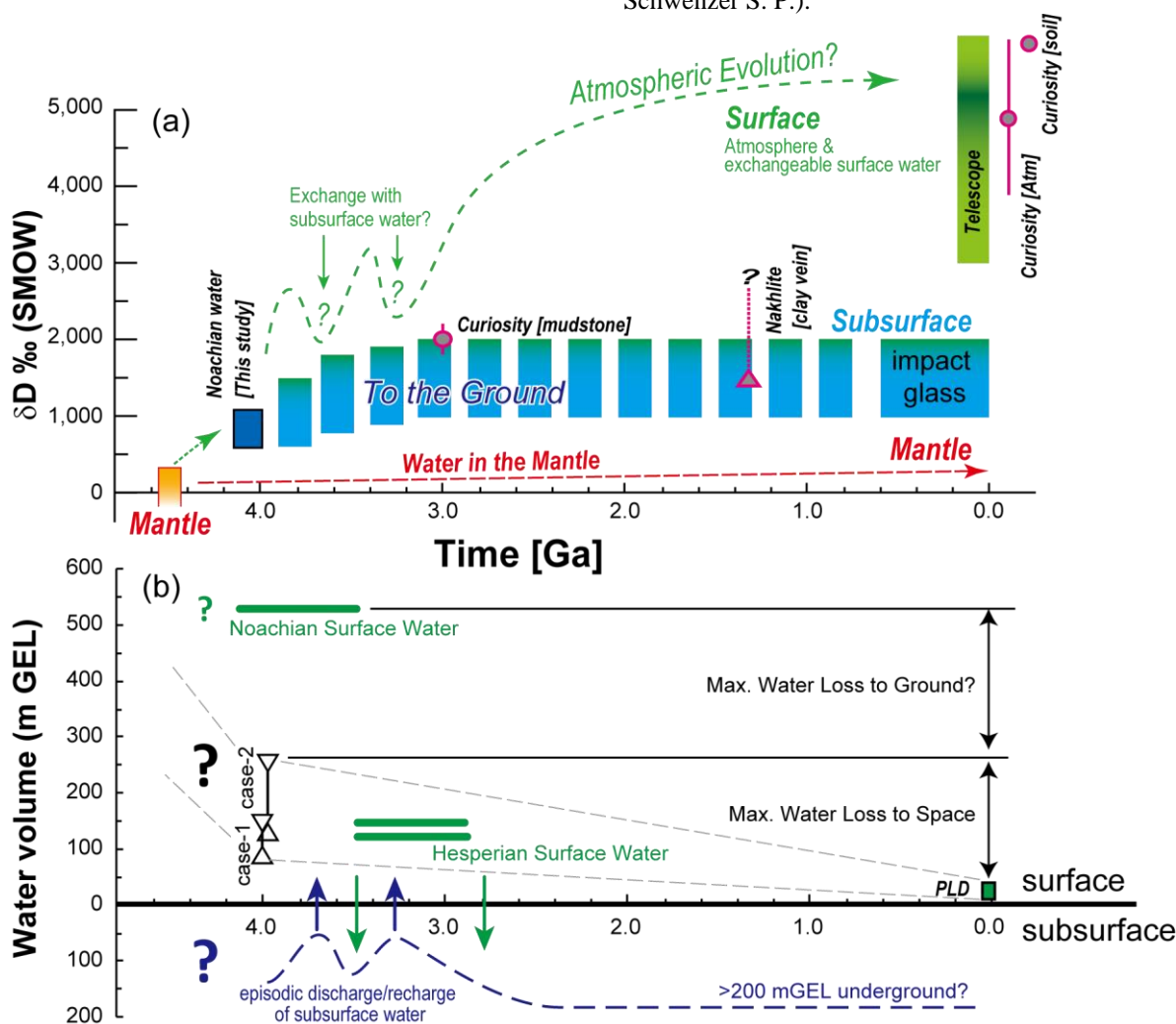

Figure 1: Interactive evolution of (a) hydrogen isotopic compositions of Martian water reservoirs and (b) the surface/subsurface water inventory of Mars. Thick green bars show the volume of paleo-oceans; note that the length of green bar does not indicate the longevity of paleo-ocean but the period of Noachian or Hesperian. Two bars bracketed with open triangles indicate ranges of water volume calculated in Case-1 and Case-2. The data sources of hydrogen isotopic compositions and the size of paleo-oceans are [14] and [9], respectively.