COORDINATED IN SITU NANOSIMS ANALYSES OF H-C-O ISOTOPES IN ALH 84001 CARBONATES.

T. Usui[1], C. M. O'D. Alexander[2], J. Wang[2], J. I. Simon[3], J. H. Jones[4]. [1]Dept. of Earth & Planet. Sci., Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan (tomohirousui@geo.titech.ac.jp). [2]Dept. of Terrestrial Magnetism, Carnegie Institute of Washington, Washington, DC 20015, USA. [3]Center for Isotope Cosmochemistry and Geochronology, ARES NASA/JSC, Houston, TX 77058, USA, [4]ARES, NASA/JSC, TX 77058, USA.

Introduction: The surface geology and geomorphology of Mars indicate that it was once warm enough to maintain a large body of liquid water on its surface, though such a warm environment might have been transient [e.g., 1, 2]. This study reports the hydrogen, carbon, and oxygen isotope compositions of the ancient atmosphere/hydrosphere of Mars based on *in situ* ion microprobe analyses of ~4 Ga-old carbonates in Allan Hills (ALH) 84001. The ALH 84001 carbonates are the most promising targets because they are thought to have formed from fluid that was closely associated with the Noachian atmosphere [e.g., 3, 4]. While there are a number of carbon and oxygen isotope studies of the ALH 84001 carbonates, *in situ* hydrogen isotope analyses of these carbonates are limited and were reported more than a decade ago [5, 6]. Well-documented coordinated *in situ* analyses of carbon, oxygen and hydrogen isotopes provide an internally consistent dataset that can be used to constrain the nature of the Noachian atmosphere/hydrosphere and may eventually shed light on the hypothesis of ancient watery Mars.

Method: A 1-inch round thin section of ALH 84001 (,81) was examined by optical microscopy and electron microprobe at Tokyo Institute of Technology before the C-O-H isotope analyses. Isotopic compositions of carbon, oxygen and hydrogen in carbonates were determined using the Cameca NanoSIMS 50L at Carnegie Institution of Washington (CIW), following the technique of [7] and [8]. The isotopic compositions of carbon and oxygen were measured simultaneously, followed by the hydrogen isotope analyses on the same spots. Natural carbonates and silicate glasses were used as standards for calibration of the carbon and oxygen, and the hydrogen isotopic measurements, respectively.

We could reduce and assess the effect of contamination of volatiles by following the method developed previously at CIW and JSC [9, 10]. The thin section was dried in a vacuum oven (~50 °C) before being coated with gold for ion microprobe analysis. The sample and standards were stored for ~1 week in a sample chamber of the CIW NanoSIMS, prior to the analysis at high vacuum ($<10^{-10}$ torr).

Results and Discussion: Carbonate occurs as globules (Fig. 1) and veins within host pyroxene crystals in the studied thin section. The carbonate globules are chemically zoned from relatively Ca-rich in the core (calcite $[\mathrm{Cal}]_{\sim 45}$, magnesite $[\mathrm{Mag}]_{\sim 40,}$ siderite $[\mathrm{Sid}]_{\sim 15}$) to Ca-poor in the rim ($\mathrm{Cal}_{\sim 10}\mathrm{Mag}_{\sim 60}\mathrm{Sid}_{\sim 30}$), surrounded by a pure magnesite outermost rim ($\mathrm{Mag}_{>95}$). This chemical variation consistently falls within the range of the ALH 84001 carbonates reported in previous studies [e.g., 4, 11].

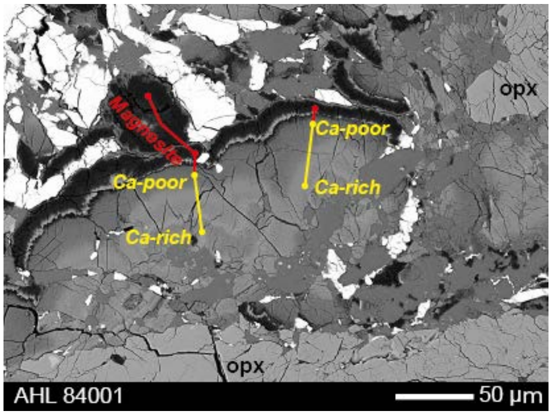

Figure 1: Back-scattered electron image of carbonate globules in ALH 84001. Traverses of ion microprobe analyses are shown as yellow and red lines.

Carbon and oxygen isotopic compositions of ALH 84001 carbonates are positively correlated with each other (Fig. 2a). They range from isotopically light cores (δ^{13}C = ~10 ‰ relative to PDB, δ^{18}O = ~3 ‰ relative to SMOW) to heavy rims (δ^{13}C = ~25 ‰, δ^{18}O = ~20 ‰). The outermost magnesite rims have distinctly higher δ^{13}C values than the inner carbonate globules. These results reconstruct the reported variability of δ^{13}C and δ^{18}O values in the ALH84001 carbonates and are consistent with previous bulk analyses (see [4], references therein).

Hydrogen isotopic compositions are also positively correlated with the carbon and oxygen isotopic compositions (Fig. 2b). The inner carbonate globules have δD values (relative SMOW) ranging from ~800 ‰ (core) to 1,200 ‰ (rim), whereas the magnesite outermost rims have more scattered and slightly lower δD values than the inner carbonate globules. The δD values are negatively correlated with ^{12}C/^{1}H ratios (Fig. 3). These negative correlations clearly indicate that the measured hydrogen isotopic compositions are not significantly disturbed by contamination of terrestrial water.

Only two papers reported *in situ* analyses of hydrogen isotopic compositions of carbonates in ALH 84001 [5, 6]. In contrast to our observation (Fig. 3), the reported δD values (182-2,092 ‰ for [5] and 331-1,196 for [6]) are positively correlated with C/H and 1/H_2O ratios. Thus, these studies concluded that δD in the ALH 84001 carbonates reflect the effects of mixing with varying amount of terrestrial water. Our study appears to be the first report of uncontaminated hydrogen isotopic compositions for ALH 84001 carbonates.

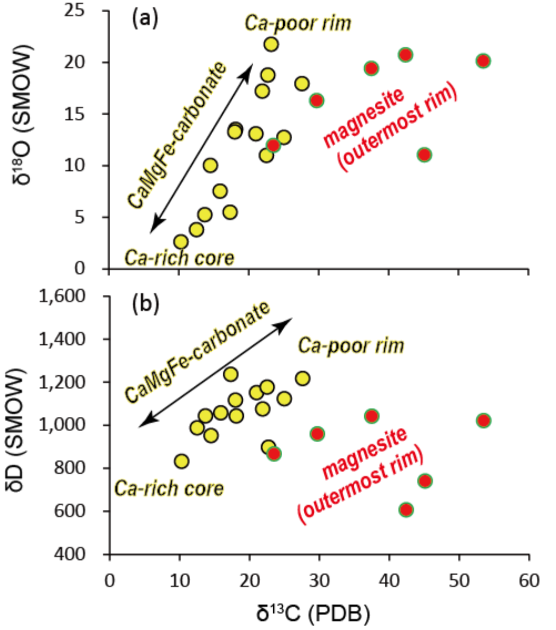

Figure 2: Hydrogen, carbon, and oxygen isotopic compositions of ALH carbonates: (a) $\delta^{18}O$-$\delta^{13}C$ and (b) δD-$\delta^{13}C$.

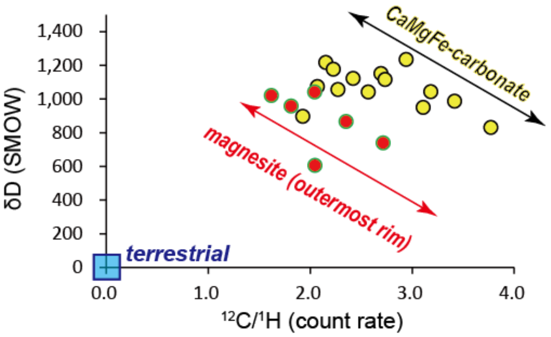

Figure 3: δD vs. $^{12}C/^{1}H$ diagram of ALH 84001 carbonates. A conceivable terrestrial water component (blue) is plotted near the origin.

A large number of studies have focused on the formation environment of the ALH 84001carbonates leading to two competing hypotheses: The first suggests a relatively constant, low-temperature environment (≤100 °C) [e.g., 12] and the second a rapidly cooling environment (initially at high temperature of ≥100 °C) [e.g., 13]. Both scenarios imply that the ALH 84001 carbonates formed in an aqueous system that is short-lived and involves small amounts of fluid. These scenarios are further supported by our hydrogen isotope data that exhibit strong positive correlations with the carbon and oxygen isotopic compositions (Fig. 2).

A Rayleigh distillation modal based on our new data (δD = 800-1,200 ‰, Fig. 2b) indicates that the original Noachian water should have had a δD range of ~500-1,000 ‰ (Fig. 4). This δD range is lower than the upper-bounds for the previously reported δD values of carbonates (2,092 ‰ [5]) and apatites (2,998 ‰ [14]) in ALH 84001. These upper-bounds probably represent highly fractionated waters (e.g., F = <0.1 in Fig. 4) from the original Noachian water reservoir. Our new estimate (~500-1,000 ‰) suggests that the Martian water would not have escaped in the Noachian era as much as previously determined based on the fractionated high δD values of ~3,000 ‰ [15].

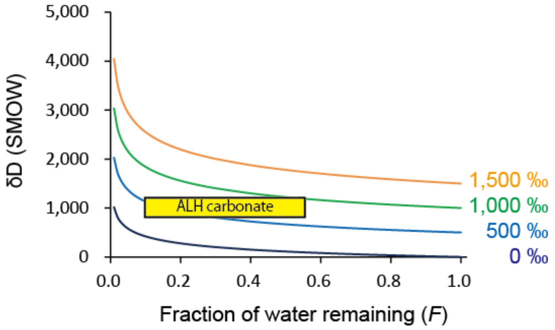

Figure 4: A Raleigh distillation model for the hydrogen isotope compositions of Noachian water forming the ALH 84001 carbonates. The ALH 84001 carbonates (yellow box) are plotted on the water evolution curves with the original δD of 500-1,000 ‰. The ranges of δD values (800-1,200 ‰) and water factions (0.08-0.58) of the ALH 84001 carbonates are from this study (Fig. 2) and [12], respectively. A fractionation factor is from [16].

References: [1] Carr M. H. and Head J. W. (2010). *EPSL*. *294*, 185-203. [2] Ehlmann B. L. and Edwards C. S. (2014). *Annu Rev Earth Planet Sci Lett*. *42*, 291-315. [3] Borg L. E. et al. (1999). *Science*. *286*, 90-94. [4] Niles P. B. et al. (2013). *Space Sci Rev*. *174*, 301-328. [5] Sugiura N. and Hoshino H. (2000). *Meteoritics & Planet Sci*. *35*, 373-380. [6] Boctor N. Z. et al. (2003). *GCA*. *67*, 3971-3989. [7] Saal A. E. et al. (2013). *Science*. *340*, 1317-1320. [8] Wang J. et al. (2015). *25th Goldschmidt Conference*. Abstract #3330. [9] Usui T. et al. (2015). *EPSL*. *410*, 140-151. [10] Usui T. et al. (2012). *EPSL*. *357–358*, 119-129. [11] Bridges J. C. et al. (2001). *Space Sci Rev*. *12*, 365-392. [12] Halevy I. et al. (2011). *PNAS*. *108*, 16895-16899. [13] Eiler J. M. et al. (2002). *GCA*. *66*, 1285-1303. [14] Greenwood J. P. et al. (2008). *GRL*. *35*, L05203. [15] Kurokawa H. et al. (2014). *EPSL*. *394*, 179-185. [16] Kurokawa H. et al. (in press). *Geochem J*.