

Investigation of martian surface history: NanoSIMS analyses of D/H ratios and U-Pb chronology of martian meteorites

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Introduction: Water is an important volatile for environments of terrestrial planets as well as their habitability. A number of recent studies have identified strong evidence for liquid water on past Mars, such as clay minerals and fluvial geomorphological features (e.g. [1][2]), whereas a comprehensive history of the martian environment remains complicated. The isotopic compositions of hydrogen (D/H) of present martian atmosphere is highly elevated (~5 times that of terrestrial water; [3]), which results from the extensive atmospheric escape. Martian meteorites are useful as they potentially provide valuable records including D/H of the past surface water and the mantle primitive water (e.g. [4][5][6][7][8]). However, due to their complicated history on Mars, it is challenging to understand their isotopic records accurately. Phosphates are helpful, for they can preserve both U-Pb chronology and D/H information. Here, we report D/H ratios and U-Pb ages of phosphates in two martian meteorites; an ancient orthopyroxenite, ALH 84001 (ALH), and a young enriched shergottite, LAR 06319 (LAR). In addition, we have also measured D/H ratio of melt-inclusion glass (MIs) in LAR.

Analytical methods: For ALH, 3 merrillite grains with known U-Pb ages [9] were selected for D/H analyses. For LAR, several phosphate grains and MIs were found in a thin section, using a SEM-EDS. Both U-Pb and D/H analyses were carried out using a NanoSIMS 50 installed at AORI, Univ. of Tokyo. Before SIMS analyses, the samples were baked at ~100 °C in a SIMS air-lock overnight before/after gold coating to remove adsorbed water. The analytical methods of U-Pb dating were the same as the previous study [9]. The D/H analyses were conducted on the phosphates in ALH and LAR and MIs in LAR. A Cs⁺ primary ion beams with 200pA/1nA was used for phosphates and MIs, respectively. An electron gun was used for charge compensation. Negative secondary ions of ¹H⁻, ²D⁻, ¹²C⁻ and ¹⁸O⁻ were collected. A natural terrestrial apatite from Morocco and NIST SRM 610 were used as standards. To avoid terrestrial H contamination, most of which are background H in the analysis chamber and hydrocarbon in the sample cracks, careful analytical protocols following a previous study [7] were conducted.

Results & Discussion: The δ D values of ALH merrillite varied from -300 to 1970 ‰ (Fig). The obtained highest value is similar to those of ALH carbonates and maskelynite [4]. The U-Pb age of the same grains, 3990Ma, can be interpreted as an impact-induced reset age [9]. It is likely that their D/H ratios reflect 3990Ma surface water, incorporated during the impact and/or a later hydrous metamorphism. The high D/H mainly supports a previously proposed two-stage evolution [5]. On the other hand, phosphates in LAR yielded a total Pb/U age as 167±57 Ma. This is consistent with other radiometric ages within uncertainty, suggesting the U-Pb system in the phosphates has been preserved since crystallization of the host rock. δ D values of LAR apatite, merrillite and MIs were 3340-4380 ‰, 1070-5260 ‰ and 1150-6830 ‰, respectively (Fig). The D/H may have mineral trends: MIs > merrillite > apatite. A similar trend was reported previously [7]. While apatite possibly recorded the magmatic water at the timing of crystallization, MIs might have incorporated water from another reservoir with extremely high D/H ratios.

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