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D/H isotope fractionation during H diffusion loss from clinopyroxene evidenced in martian nakhlites

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Knowing the distribution and origin of water in terrestrial planets is crucial to understand their formation, evolution and the source of their atmospheres and surface water. Mantle D/H ratios may be used to determine what type of material contributed water to the terrestrial planets [1]. However, other processes, magmatic or surface alteration processes, can also modify D/H ratios, and for Mars, we only have samples from the crust, as meteorites. The D/H ratio of igneous phases of Martian meteorites is generally explained in terms of the mixing contributions of two reservoirs: surficial with high D/H ( $\delta D > 700 \%$ ) related to interaction with the martian atmosphere ( $\delta D \sim 5000\%$ ), and mantle-derived with lower D/H ( $\delta D < 500\%$  but the exact value is still debated)[2]. However, our present study evidences that H loss in clinopyroxene during degassing can significantly fractionate H isotopes and increase their D/H ratios. In situ analyses of H isotopes, and of water, major and trace element contents were performed on the pyroxenes of 5 nakhlites. Nakhlites are clinopyroxenites that likely originated from the same lava flow or shallow magma chamber. Water contents decrease (380 to <5 ppm H<sub>2</sub>O) with increasing  $\delta D$  (-268 to 4860 ‰). Significant influence from spallation, exchange with the martian atmosphere, shock, surface alteration, and hydrothermal processes is ruled out. Together with the evidence of less water at the edge of individual pyroxene grains compared to their interior, we interpret this correlation as the result of preferential diffusive loss of H relative to D from the already crystallized pyroxenes during ascent of the partially-crystallized magma. Similar H isotope fractionations have been observed in another nominally anhydrous mineral, garnet, during experimental dehydration [3]. These results emphasize that caution is warranted when interpreting H isotope analyses of igneous, nominally anhydrous minerals in terms of planetary processes.

[1] Peslier *et al.* (2017) *SSR* **212**, 743-811. [2] Usui *et al.* (2012) *EPSL* **357-358**, 119-129. [3] Roskosz *et al.* (2018) *GCA* **233**, 14-32.