

EGU22-8169

<https://doi.org/10.5194/egusphere-egu22-8169>

EGU General Assembly 2022

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A more robust interpretation of water ice isotope signature from lunar polar missions: theoretical model for isotope fractionation during water ice sublimation in very low pressure systems at cryogenic temperatures.

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Targeting the deployment of sustainable human and robotic exploration on the Moon by the end of this decade, there is a pressing need for better understanding the lunar water cycle and the availability of water for ISRU. The O-H isotope signatures in lunar water are key for determining the water origin in the Earth-Moon system and the mechanisms controlling water distribution and redistribution on the Moon. This has profound implications for understanding the Earth-Moon system's history and the stability and renewability of water deposits.

Lunar volatiles are involved in a largely unconstrained and complex system of input, transport, trapping, recycling, and loss. The water origin on the Earth-Moon system remains poorly understood. The δD signatures from Apollo samples and meteorites suggest various contributing reservoirs of different origins for lunar water, and/or secondary processes [1], [2]. The different origins include: i) Magmatic (primordial) [3]; ii) asteroidal/cometary impacts [4], [5]; iii) solar wind H+ [1]; iv) mixed origin (solar wind H+/inclusion within meteorite impact glasses or volcanic glasses [6]).

The Roscosmos/ESA Luna 27 mission [7] is one of several international lunar polar missions for in-situ analyses of lunar surface, targeting pressing scientific and industrial knowledge gaps. To interpret the results derived from those polar missions it is critical to understand the extent and nature of any potential water ice loss and related isotope fractionation during the sampling chain. Experimental studies on isotope fractionation during ice sublimation in nonequilibrium conditions are scarce. These studies concluded on different trends: i) no relevant isotope fractionation up to 40% ice mass loss [8], ii) relevant Rayleigh-like fractionation trend [9]. There is no kinetic isotope fractionation model (theoretical or experimental) for ice sublimation in low pressure systems at cryogenic temperatures, which considers the expected physical processes. Thus, the calculation of water ice isotope signatures remains highly uncertain, hindering the assessment of potential lunar water resources and the interpretation of scientific planetary data.

Here we present a theoretical isotope fractionation model derived from concepts developed by Criss (1999) [10] and adapted to the physical processes expected under lunar conditions, which

will contribute to i) more robust interpretations of water ice behaviour in lunar environment and/or extra-terrestrial and/or extreme terrestrial environments; ii) mission operational planning, data processing, extraction/processing techniques; iii) exploration/exploitation roadmap, space mining business plan, natural resources management. [1] B. M. Jones et al., 2018. *Geophys. Res. Lett.*, 45(20), 10,959-10,967; [2] F. M. McCubbin and J. J. Barnes, 2019. *Earth Planet. Sci. Lett.*, 526; [3] A. E. Saal et al., 2013. *Science*, 340(6138), 1317-1320; [4] J. P. Greenwood et al., 2011. *Nat. Geosci.*, 4(2), 79-82; [5] J. J. Barnes et al., 2016. *Nat. Commun.*, 7(1), 11684; [6] C. I. Honniball et al., 2021. *Nat. Astron.*, 5(2), 121-127; [7] D. J. Heather et al., 2021. *Lunar Planet. Sci. Conf. LPI*, Abstract #2111; [8] J. Mortimer et al., 2018. *Planet. Space Sci.*, 158(Feb), 25-33; [9] R. H. Brown et al., 2012. *Planet. Space Sci.*, 60(1), 166-180 [10] R. E. Criss, 1999. USA: Oxford University Press.