WATER ICE BEHAVIOR UNDER LUNAR POLAR HARSH ENVIRONMENT - THEORETICAL AND EXPERIMENTAL O-H WATER ICE KINETIC ISOTOPE FRACTIONATION DURING SUBLIMATION.

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Introduction: A better understanding of the lunar water cycle is essential for a sustainable water exploitation and management (SDG6) on the Moon and beyond, for determining the availability of water for ISRU and for help constraining the theories about the Earth-Moon system's history. However, the heterogeneous distribution of water on the Moon surface and subsurface and the poor knowledge about its abundance, distribution and form make the study of the water cycle more challenging, the estimation of water reserves and the design of its extraction and purification techniques. Among the international forthcoming lunar polar missions for volatiles *in-situ* analyses stand those within the NASA CLPS program, with payloads on board for analyses of the lunar surface - PROSPECT [1] - and for monitoring the near-surface lunar exosphere - PITMS [2].

Lunar water isotope signature: O-H water ice isotope signatures are key for determining water origin and the mechanisms controlling water storage, distribution and redistribution on the Earth-Moon system and beyond. However, the only existing data concerning lunar water isotope signatures relates to Apollo samples and meteorites. Those δD signatures suggest the contribution of various reservoirs with different origins for lunar water, and/or secondary processes [3], [4]. The potential lunar water origins include: i) Magmatic or primordial lunar water dating back to lunar accretion and assumed to have the same origin than water on Earth, or the parent bodies of primitive meteorites [5]; ii) later addition water by asteroid and/or cometary impacts [6], [7]; iii) water created by solar wind H^+ implantation [3]; iv) mixed origin (solar wind H^+ implantation/inclusion within meteorite impact glasses or volcanic glasses [8]).

Isotope fractionation: sublimation plays a relevant role on the mass balance of the Moon's cryosphere, and together with other physical and chemical processes creates kinetic isotope fractionation altering the isotope signature of lunar polar ice. Thus, a better understanding of the kinetic isotope fractionation during those processes will help to better understand the lunar water cycle and better interpret the isotope signature of water molecules released to the near-surface exosphere. Furthermore, a more robust interpretation of the raw data derived from future lunar missions requires the study of the physical processes triggering any potential water ice mass loss and related isotope fractionation during the sampling chain. Besides, those studies under lunar harsh environment will serve as a laboratory for better understanding the complex Earth's cryosphere.

Up to date, there is no theoretical model for kinetic isotope fractionation for ice sublimation under high to ultra-high vacuum and low to cryogenic temperatures considering the expected physical processes at the Moon poles. Also, experimental studies on isotope fractionation during ice sublimation in nonequilibrium conditions are scarce and conclude on different trends: i) no relevant isotope fractionation up to 40% water ice mass loss [9], ii) relevant Rayleigh-like fractionation trend [10]. 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.

Theoretical kinetic isotope fractionation model: We have developed a theoretical isotope fractionation model derived from concepts developed by Criss (1999) [11] and adapted to the physical processes expected under lunar conditions. Our model conclude in a relevant isotope fractionation for water ice mass loss greater than 10%, following a Rayleigh-like trend more pronounced at lower temperatures. More experimental studies are needed to benchmark the isotope fractionation trend and solve this lack of consensus, either supporting the trend shown by the theoretical model and one of the experimental studies [10] or the trend of the other experimental study [9].

Sublimation/desorption prototype for kinetic isotope fractionation studies under lunar environment:

We have developed and patented a prototype and method [12, 13] for the study of water ice mass loss (i.e., sublimation, desorption) and related kinetic isotope fractionation under high to ultra-high vacuum and low to cryogenic temperatures. The temperature range for the sublimating volume is 93 to 473 K (-180 to 200 °C) and the base pressure is high 10^{-9} mbar. The actual version is an off-line version and it allows to carry out sublimation down to 10^{-7} mbar (153 K / -120°C). All over the sublimation, the evacuation rate is higher than the sublimation rate, avoiding creating an equilibrium between the solid and the gas phase within the sublimation volume and the temperature stable and homogeneous within the sublimation volume. This configuration allows to study on the same specimen the physical process (i.e sublimation) and the related isotope fractionation, since all the released water vapor can be collected or directed to the analyzer. This is possible because there are no colder points on the chamber's walls where the released water vapor could deposit. The homogeneous temperature within the sublimating volume controlled by the thermal management system and monitored with the different temperature sensors ensures that the studied water ice mass loss and related isotope fractionation will not be altered by creating equilibrium, or by creating gradients of temperature within the sublimating volume. The pressure is continuously monitored with time in different compartments of the prototype and registered with the prototype's software. Likewise, the temperature is continuously monitored with time in 8 different zones of the sublimating volume and thermal management system and registered. The sublimated water ice and the remaining water ice fractions are collected in different cold traps and further analyzed with a Laser spectrometer (Picarro L2140-I WS-CRDS; δD, $\delta^{18}O$, $\delta^{17}O$). In a near to mid-future we target also the collection and analyses of different forms of water and an in-line version. The experimental data will lead to a new theoretical framework and modelling tools for pure ice and ice/regolith mixtures, which will contribute to i) a more robust interpretation of water ice behavior 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 and natural resources management.

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