D/H Fractionation during Sublimation of Water Ice at Low Temperatures into a Vacuum

James Mortimer¹, Christophe Lécuyer², François Fourel³, James Carpenter³

¹School of Physical Sciences, The Open University, Walton Hall, Milton Keynes, Buckinghamshire, United Kingdom, MK7 6AA, UK. (James.Mortimer@open.ac.uk),
²Laboratoire de Géologie de Lyon, CNRS UMR 5276, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France,
³ESA ESTEC, Keplerlaan 1, 2401 AZ, Noordwijk, The Netherlands.

1: Context:
- ESA’s PROSPECT package and Luna 27 (Luna-Resurs) see poster #1271 for further background information.
- Icy regolith samples will be drilled, transferred to a carousel of ovens, imaged, and heated to measure water ice and other volatiles present.
- Sample drilling, transfer to oven carousel, and imaging all takes time and may result in small temperature increases, so:
  - What happens to any water ice during this time?
  - Is it all lost to sublimation, or is the residual ice heavily fractionated?

2: Experimental Approach: carried out at the Laboratoire de Géologie de Lyon: Terre Planètes Environnement (Lyon, France) using an existing experimental set-up and proven method [1].

- A 0.5 mL aliquot of starting water of a known isotopic composition was introduced, frozen using liquid nitrogen (LN), pumped down to vacuum, then heated with a heat gun to transfer it into the temperature-controlled cryotrap as water vapour, wherein it formed the initial water ice sample.
- The temperature-controlled cryotrap was set to the desired temperature of sublimation (in these experiments, -75°C and -100°C) and the manual valve to the rest of the vacuum line was opened to allow the sublimate to leave the cryotrap.

3: Rate of Water Loss to Vapour Phase:

-75°C at 10⁻³ mbar
Between 30-40% of the initial ice mass was lost within the first 10 minutes. After this time, the rate decreased due to inefficient water vapour removal resulting in saturation of the vacuum system (although water removal was more efficient in this study than in [1], where this effect is more pronounced).

-100°C at 10⁻⁵ mbar
Only 1% of the initial ice mass was lost within the first 10 minutes, and even after 60 minutes, only 8% water ice loss had occurred. With such a low rate of sublimation, the loss of water here is unaffected by retarding factors like inefficient water removal and so this linear relationship reveals the true physics of sublimation.

4: Isotopic Composition of Sublimate:

-75°C at 10⁻³ mbar
Measured isotopic compositions of the residual water ice samples remain close to or within error of the starting water composition, suggesting that the ice will not undergo significant fractionation until almost half of its original mass has been lost via sublimation.

-100°C at 10⁻⁵ mbar
Initial εD of water sample = -75.69 ± 0.29 %

5: Isotopic Composition of Residual Water Ice:

-75°C at 10⁻³ mbar
-100°C at 10⁻⁵ mbar
Isotopic compositions of both sublimate and residue samples are almost identical at small increase in % of water in vapour phase, but similar rate after initial increase.

6: Effect of Changing Pressure at Constant Temperature: -75°C at 10⁻³ mbar and 10⁻⁵ mbar

-100°C at 10⁻⁵ mbar
Only a negligible increase in the amount of sublimation is seen when the pressure is reduced by two orders of magnitude at constant temperature (left panel), which results in essentially no difference in the fractionation behaviour as measured in the residual water ice. This implies that temperature is a more critical factor for sublimation than pressure; so long as the pressure is low enough for sublimation to occur, sublimation will progress in the same way and have the same isotopic effects at any given pressure.

7: Conclusions:
- Up to approx. 35% of total water in the vapour phase, residual ice is not significantly fractionated relative to the initial isotopic composition (for experiments with pure water ice only).
- Data for experiments with >35% water in the vapour phase are compromised by saturation of the vacuum line volume by previously released water vapour.
- Incomplete trapping of water vapour/trapping is too slow compared to speed of sublimation.
- Keeping T constant at -75°C but changing P from 10⁻³ mbar to 10⁻⁵ mbar
  - small increase in D/H ratio at initial increase
  - Isotopic compositions of both sublimate and residue samples are almost identical at both pressures (residue is within error of initial isotopic composition i.e. no additional fractionation caused by lower pressures).
- The results of this work will help to inform modelling which will extrapolate the data down to lunar-relevant conditions.

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