EXPERIMENTAL METHODS TO INFORM MODELLING OF VOLATILE PRESERVATION DURING LUNAR SUBSURFACE ICY SAMPLE COLLECTION: IN SUPPORT OF ESA'S 'PROSPECT' PACKAGE.

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Introduction: ESA's PROSPECT package, due to fly to the south polar region of the Moon on Russia's Luna 27 mission in 2025, consists of two main elements: the ProSEED sample drill, and the ProSPA volatile analysis instrument [1]. After drilling to a depth of up to 1 m, ProSEED will return icy regolith material to the lunar surface, before transferring it to the ProSPA oven carousel, where it will be imaged and sealed, ready for heating and analysis in the ProSPA mass spectrometers. This sample handling chain takes time, during which the sample is exposed to radiative and conductive heat sources, thereby potentially raising its temperature and resulting in ice mass loss via sublimation. It is important to quantify this volatile loss with some confidence in advance of lunar surface operations.

Although significant isotopic fractionation of the remaining water ice is unlikely until >30% of the starting water ice mass has been lost [2], it is necessary to have as much ice content remaining for analysis as possible without forcing corresponding changes to elements such as temperature control and speed of operations. This limit on the amount of permissible mass loss then provides constraints on the maximum temperatures of different parts of the PROSPECT systems and so is of high importance to the thermal design of the entire package. Further work is now being conducted by the PROSPECT Science Team in support of this effort, including groups at Fluid Gravity Engineering Ltd (FGE), Technical University of Munich (TUM), the Italian National Institute of Astrophysics (INAF) and The Open University (OU). From this, an assessment of volatile preservation during lunar surface operations can be made to a high degree of confidence, using a highly detailed model, based on experimentally-defined inputs and verified against experimentally-derived ice loss rates.

Sample Chain Model (FGE): To simulate the loss of water ice during the PROSPECT sampling chain, a model has been developed within FGE's material response code MABLE, named 'KESDRIL' – Knudsen diffusion, Energy transfer, Sublimation and Deposition, Regolith Ice Loss model. This detailed model takes into account: internal energy transfer through conduction and convection; sublimation and deposition of water ice; mass transfer of water through Knudsen diffusion; simple radiative exchange between external surfaces; and a drill interface energy balance model. It can be used to perform end-to-end simulations of the PROSPECT sampling chain (up to the point at which the sample is sealed inside an oven). It has been recently updated to include a cuttings conveyance model and a refined model of thermal contact between the auger and borehole walls. Previous iterations of the KESDRIL model demonstrated that its calculated ice mass loss rates are very sensitive to the diffusion coefficient of the icy regolith. KESDRIL previously used the Dusty Gas Model (DGM) to approximate diffusion coefficients as a function of regolith bulk density and ice mass loading, and this has now been refined by use of experimentally-derived diffusion coefficients and through correlation with sublimation rate experiments.

Diffusivity (TUM): The diffusion coefficient of a gas through porous solid is a macroscopic property of a given solid/gas pair depending, among other factors, on temperature, pressure, pore size, porosity, and tortuosity. In order to investigate the influence of these parameters on the diffusion of water through regolith simulant, a series of experiments with different experimental conditions is performed. The diffusion coefficient of water through the lunar regolith simulant NU-LHT-2M is determined with a fast pulse technique based on temporal analysis of products (TAP) like reactor systems. TAP reactors are commonly used to determine diffusion coefficients as well as sorption parameters in zeolitic materials [3], [4]. The PROSPECT Phase B+ Volatile Extraction Breadboard at TUM [5] was modified to meet the required experimental conditions [6]. Investigating diffusivity values for gas-solid systems with a TAP reactor system has the advantage of obtaining macroscopic diffusivity values that are in good agreement with microscopic values [3].

All tests are performed with water vapour and nitrogen. Each test series are carried out at temperatures between -60 °C and +60 °C, at different sample densities and particle sizes. The pressure response of small gas pulses (~10^{13} molecules) guided through a regolith sample is analyzed with a mass spectrometer. Pore diffusion coefficients as well as adsorption and desorption rate

coefficients are obtained by fitting the single pulse response to a diffusion model. First pulse response measurements (Figure 1) show that diffusion of nitrogen is faster for higher temperatures. Further measurements will provide an empiric temperature-dependent function for the diffusion coefficient of water vapor and nitrogen through the regolith simulant NU-LHT-2M for different sample compactions and particle sizes.

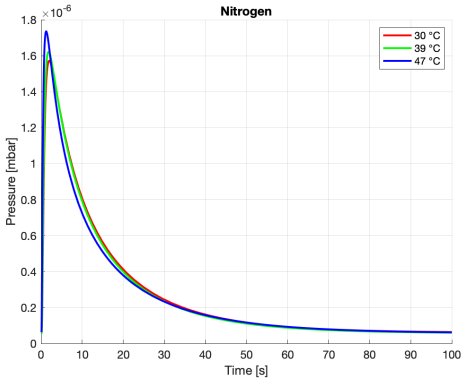

Figure 1: Fast pulse response of nitrogen over a NU-LHT-2M sample at different sample temperatures.

Desorption (INAF): The desorption energies of water molecules from different substrate materials is measured at INAF using a temperature-programmed desorption (TPD) method under high vacuum (~10^{-9} mbar). Firstly, water vapor is introduced to the vacuum chamber and trapped on a cryostat cold finger at 9 K. The cold finger is then heated at a constant rate (1.21 K/s), and as the molecules desorb, they enter a mass spectrometer and are detected. TPD experiments have been performed on a range of natural and synthetic mineral separates (olivine, spinel, enstatite, quartz), as well as on NU-LHT-2M simulant; all materials used are first cleaned, then crushed to 5 µm grain size, and loaded onto the cold finger in a layer of 100 µm. The resulting temperatures of desorption and calculated desorption energies are compared reference measurements without sample (Table 1). Desorption energies will be used to assess ice losses from very low ice content samples (<1% starting ice content) by FGE, where desorption rate dominates loss over diffusion.

	T_{des} [K]	E_{des}/K_b [K]
No sample	141.2	$(4.1 \pm 0.2) \cdot 10^3$
Olivine	128.5	$(3.341 \pm 0.014) \cdot 10^3$
Spinel	128.3	$(3.523 \pm 0.014) \cdot 10^3$
Enstatite	130.9	$(3.551 \pm 0.004) \cdot 10^3$
Quartz	127.8	$(3.410 \pm 0.016) \cdot 10^3$

Table 1: Temperatures and energies of desorption of water molecules from different substrate materials.

Sublimation Rate (OU): Using the existing PROSPECT Phase B+ microbalance vacuum chamber at OU [7], a series of 17 experiments were performed using bulk NU-LHT-2M simulant across a range of ProSPA-relevant temperatures (informed by thermal modeling of ProSPA oven carousel temperatures carried out by the PROSPECT industrial consortium). For each experiment, 300 mg of mixed water and simulant (at an initial ice content of 5 %) was loaded into a 4 mm diameter x 13 mm deep aluminum crucible (to ensure reproducible sample surface area and geometry), frozen using liquid nitrogen to <-180 °C, pumped down to vacuum (~10^{-6} mbar) and heated to the desired setpoint using PID-controlled resistance heating wire. Real-time ice mass loss was recorded alongside temperature using the microbalance software, and the experiment allowed to progress for several hours (~4 h). The resulting mass loss data was then used to calculate sublimation rates for samples held at temperatures between -100 and -30 °C (Fig.2).

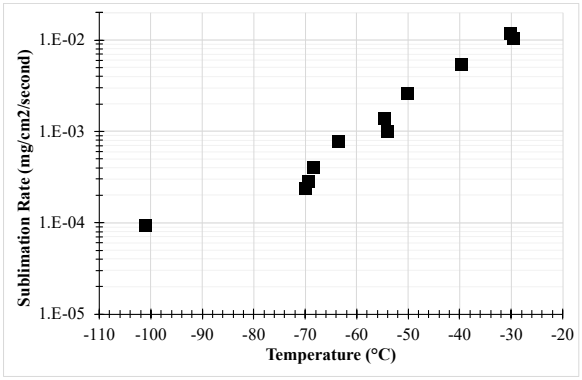

Figure 2: Experimentally-derived sublimation rates for icy NU-LHT-2M samples across a range of temperatures.

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