

A setup for studying fractionation of D/H isotopes under low-temperature water sublimation in vacuum

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The paper presents a setup for studying fractionation of D/H isotopes during water ice sublimation under the lunar surface conditions. We have examined the influence of the source water volume on the parameters of analytical signal from the mass spectrometric complex. Water vapor loss and isotopic composition variation during the sample motion from the experimental setup reactor to the mass spectrometric complex were assessed. Optimal parameters of vapor accumulation under water ice sublimation were determined. The experimental procedure was verified.

Keywords: stable isotopes, fractionation, sublimation, mass spectrometry, water, ice, minerals, regolith, Moon.

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The presence of water on the Moon was for the first time confirmed by the Lunar Prospector spacecraft; using a neutron detector, it has revealed in the lunar polar regions the presence of hydrogen that may be regarded as a water component [1]. The phase state of water has not yet been determined: both chemically bound water in the form of hydroxyl groups —OH(D) and water ice mixed with lunar regolith are possible. However, ice accumulation on the lunar surface has to be accompanied by (re)sublimation with separation of stable D/H isotopes. Furthermore, water itself may be of different origins (endogenous, exogenous, implanted), and, therefore, understanding the features of water's hydrogen and oxygen isotopes fractionation under the lunar surface conditions will help answer the question of its source. The water isotopic composition is a key criterion for life support of planned lunar missions.

In global practice, the process of isotope fractionation is investigated by using closed systems where reduced pressure and temperature matching those on the lunar surface are created. For instance, in France they used a glass reservoir to which there were attached via vacuum joints the pre-weighed source water containers with traps for the sublimate and residue, as well as a container into which the source water was directly loaded and where sublimation subsequently occurred at a given pressure and temperature. The typical volume of consumed water was 0.5 ml. The disadvantage of this system is the necessity of using high-precision analytical scales for a small volume of sublimate or residue. In that case, pure monocrystalline water ice was sublimated from the glass vessel surface, which is incredible under the lunar surface conditions [2,3].

In another experiment which took into account impurities, as well as shape and size of water ice particles, there was used a cryostat connected to a mass spectrometer and

equipped with a helium closed-cycle cooling system; on the cryostat, a sample holder in the form of a cylinder 3.6 cm in diameter and 20 cm in depth was mounted [4]. The sample layer was 10 cm. Vacuum in the system was maintained by the turbomolecular vacuum pump of the mass spectrometer. Heat was supplied through a quartz glass by the heat flow from a halogen lamp (50 W) located on top of the working chamber. The temperature on the chamber surface was kept at -73°C with slight variations, while temperature at the base was kept equal to -123°C . That setup was used to study fractionation of hydrogen isotopes under long-term sublimation of fine (0.1–1 mm) and coarse (1–10 mm) water ice fractions either enriched or not enriched in deuterium, as well as of ice mixed with dust. It was noted that sublimation of water ice with dust differed significantly from that of pure water ice because of isotope effects.

It is worth highlighting an experiment conducted on the above-described experimental setup but through a different procedure [5]. A characteristic feature of this experiment was mixing water ice with mineral powder in liquid nitrogen. The same medium was used in transportation and loading the reactor; later, liquid nitrogen was removed from the reactor. As the mineral powder, titanium and silicon oxides and similar soils with particle sizes of 1–50 μm were used; the source water volume was 50 ml. Vacuum was provided by the mass-spectrometer's turbomolecular pump; temperature of the base was maintained at -123°C . Along with this, the authors noted that, in the case of a porous sample, the base temperature should be about -213 to -153°C so as to maintain the surface temperature of -73 to -63°C , which gave rise to measurement inaccuracies.

Note that the cited experimental works were either aimed at studying water vapor sublimation from the pure ice

surface or considered sublimation of water vapor only in a mixture with mineral powders of various compositions. However, with regard to extraterrestrial objects, it is possible to consider in the presence of a mineral composition not only water vapor sublimation through a certain layer of mineral powder that covers this ice or is mixed with it, but also frost sublimation from the surface of openly laid mineral grains.

Experiments with water ice sublimation from the surface of various minerals have not been widely performed; available are only theoretical studies in which a similar situation was simulated [6]. The models have shown that in the presence of irregularities water vapor accumulation in shaded areas is possible, as well as the natural trap boundary motion following the shadow during the lunar day. Note that no real-condition studies have been performed.

To overcome the mentioned difficulties, the RAS Geochemistry and Analytical Institute has created a setup for studying the D/H isotopic fractionation in vacuum under water ice sublimation at low temperatures and pressures, which allows performing experiments of all the necessary types (Fig. 1) [7].

The setup's basic component is a cryovacuum chamber within which a thermostatically controlled base is located. The base temperature may vary from -150 to 200°C . All the surfaces (except the thermostatically controlled base) are heated to 200°C . A specific feature of this setup is direct injection of water sublimated in the trap into the Delta Plus XP isotope-ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, Bremen, Germany) through pyrolytic attachment TC/EA-IRMS (Thermo Fisher Scientific, Bremen, Germany), which allows avoiding contamination and side isotopic effects in the course of analysis.

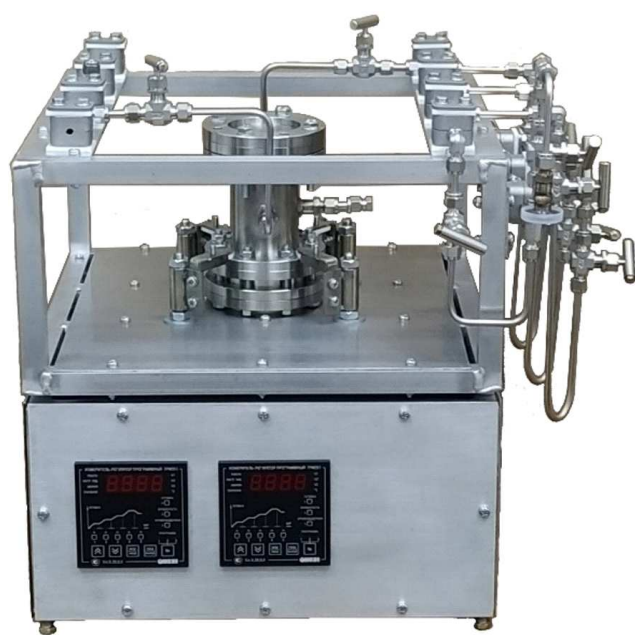


Figure 1. General view of experimental setup GEOKHI RAS.

In the TC/EA pyrolytic attachment, decomposition of water molecules into hydrogen and oxygen takes place on the surface of glassy carbon chips at the temperature of 1450°C ; oxygen forms with carbon the CO compound. Then gas molecules are ionized in the mass spectrometer ion source, and ion currents are measured. Using ratios $2\text{H}^+/\text{H}^+$ and $\text{C}^{18}\text{O}^+/\text{C}^{16}\text{O}^+$, isotopic compositions of the sample's hydrogen $\delta^2\text{H}_{\text{sample}}$ and oxygen $\delta^{18}\text{O}_{\text{sample}}$ relative to the international water standard VSMOW are calculated.

In preparing the experiment, it is necessary to prevent the closed experimental setup from invasion of ambient air moisture. Every time prior to starting the experiment, all the pipeline parts and setup units and components, including the thermostatically controlled base, were heated to 200°C to avoid sorption on the inner surface. The system was pumped out for a few hours until the pressure decreased to maximum $5 \cdot 10^{-2}$ mbar.

The experimental procedure involves injecting into the system a fixed volume of water of known isotopic composition (-72.6‰). For this purpose, the thermostatically controlled base surface is cooled to about -150°C , and the reactor is isolated from the fore-pump. After that, the entire volume of water is injected into the reactor with a syringe through a special inlet with a septum (Fig. 2); in the reactor, all the water condenses on the cooled thermostatically controlled base. The completeness of water vapor condensation was monitored via readings of the vacuum pressure sensor. The vapor condensation zone was monitored through a sight window.

Then the fore-pump is connected to the reactor through a cryotrap. Temperature of the base rises to a preset value; when the cryotrap is cooled with liquid nitrogen, sublimated water vapor accumulates inside it. On expiration of the preset accumulation time, the trap is isolated from the system, the flows are transferred from the bypass line to the line with trap by using a multiport valve, and it is filled with carrier gas. The sublimation process in the reactor did not stop simultaneously with fore-pumping. An isolated from the reactor trap containing frozen sublimated water is heated by abruptly supplying a high-intensity heat flow, and the accumulated sample moves in the carrier gas flow to the isotope-ratio mass spectrometer through a pyrolytic attachment.

After the completion of measuring the sample isotopic composition, the multiport valve returns the flows to their initial state. The carrier gas is removed from the trap and pipelines by the fore-pump; after heating and desorption, the trap is connected to the reactor. The process of accumulating the next portion of the sample may be repeated.

In the course of experiments, side isotopic effects not associated with the water ice sublimation may arise. To verify the experimental procedure, there was examined variation in isotopic composition $\delta^2\text{H}_{\text{sample}}$ of the source water that was injected through the septum, passed through the reactor and all communications, and underwent concentration in the

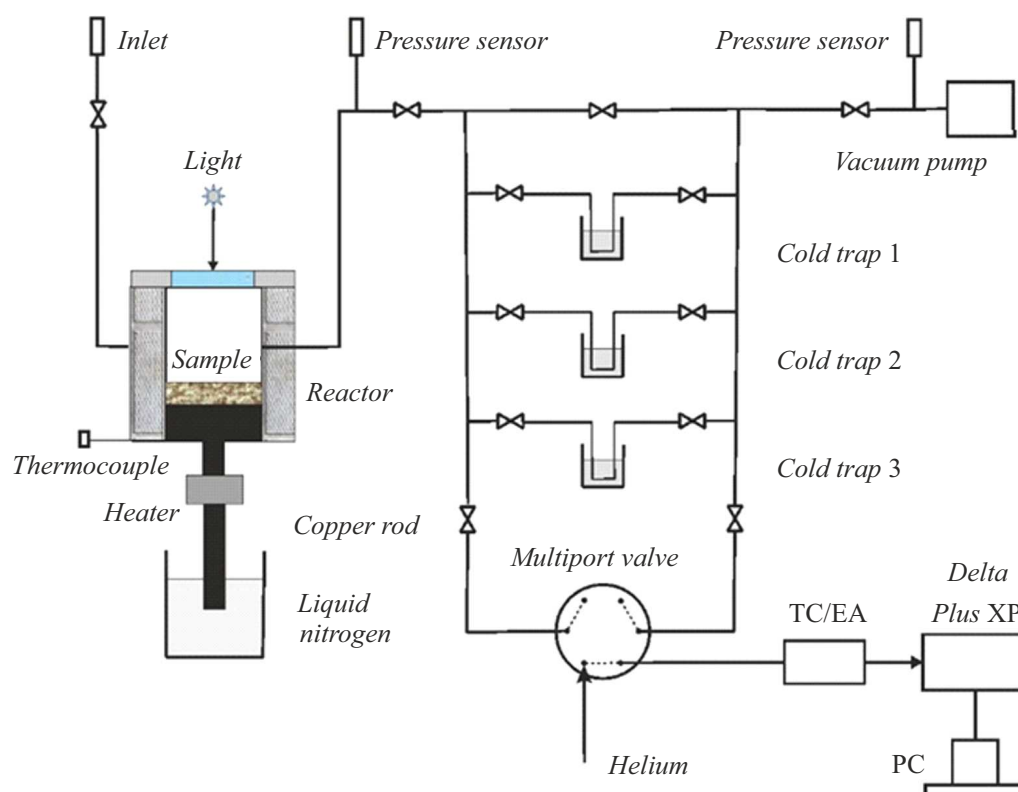


Figure 2. Schematic diagram of experimental setup GEOKHI RAS.

nitrogen trap, as compared to $\delta^2\text{H}_{ref}$ of the source water injected directly into pyrolyzer TC/EA.

For this purpose, source water samples 0.1, 0.2, 0.3, and 0.4 μl in volume were fed into the reactor with a 0.5 μl microsyringe (Hamilton). Reproducibility of the analytical signal measurements was controlled prior to injecting each sample from the experimental setup into TC/EA-IRMS by

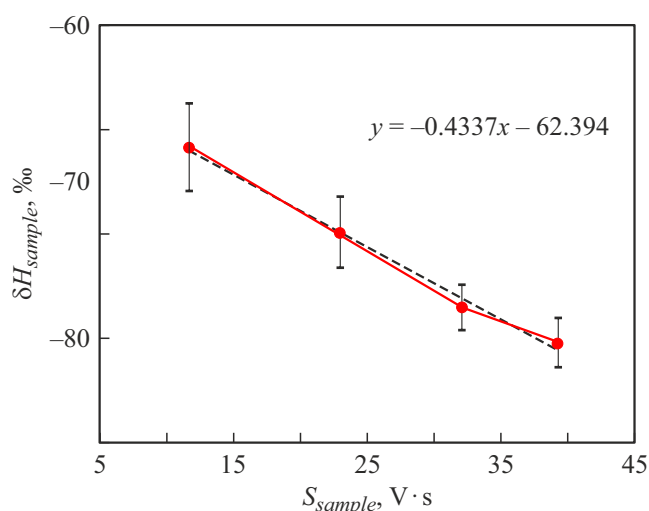


Figure 3. Isotopic composition of water vapor hydrogen versus the analytical peak area.

five-fold direct injection of an 0.1 μl water aliquot into the helium flow passing through the pyrolyzer, which provided an analytical peak 1 V in amplitude.

The results of the first two direct water injections were ignored because of the device memory effect leading to the $\delta^2\text{H}_{ref}$ distortion and decrease in the peak area. Fig. 3 shows the dependence of the water hydrogen isotopic composition on the analytical peak area.

Fig. 4 presents the dependence of the ratio of the target sample analytical peak area to the control sample area on the target sample actual volume.

To determine the true value of source sample $\delta^2\text{H}_{sample}$, setup TC/EA-IRMS was calibrated according to international standards SLAP (-428‰), OH4 (-109.4‰), OH3 (-61.3‰), and OH1 (-3.9‰).

The five-fold direct injection of the 0.1 μl source water sample into TC/EA prior to each experiment showed that the mean standard deviation index of the isotopic composition $\delta^2\text{H}_{ref}$ (σ_{ref}) in control samples (excluding the first two in each series) was less than 2 ‰. This index for the samples 0.1, 0.2, 0.3, and 0.4 μl in volume, which were injected into the reactor, was $\sigma_{0.1} = 5.3 \text{‰}$ ($n = 10$), $\sigma_{0.2} = 4.2 \text{‰}$ ($n = 9$), $\sigma_{0.3} = 2.7 \text{‰}$ ($n = 7$), and $\sigma_{0.4} = 3.0 \text{‰}$ ($n = 7$), respectively, where n is the number of experiments with the given volume of water injected into the reactor.

We have studied the dependence of variations in the source-water hydrogen isotopic composition on the injected source water volume during the sample motion from the sublimation reactor through the trap into the mass spectrometer; in the study, the path of water vapor motion under sublimation was simulated. This made it possible to estimate the loss and impact of side isotope effects on the final result, and also to determine the optimal volume for sample accumulation.

The analytical peak area and isotopic composition of each injected sample were automatically calculated in the Isodat program code using the built-in spectrum processing function. The analytical peak area depends linearly on the injected sample volume. By comparing the analytical peak areas S_{sample} of the sample under study and average analytical peak areas S_{ref}^{av} of control samples (excluding the first two samples in each series), the volume of water accumulated in the trap may be calculated using the obtained relationship $V = 0.1669(S_{sample}/S_{ref}^{av}) - 0.046$ (in μl).

Based on the data obtained, we have constructed a calibration curve reflecting the dependence of the measured isotopic composition on the sample's analytical peak area, which is linear in nature and may be represented as $\delta^2\text{H}_{sample} = -0.433S_{sample} - 62.394$. It is known that a shift in the isotopic composition depending on the sample volume is associated with the processes of water molecules adsorption on the walls of vacuum communications during their motion in the carrier gas flow. The isotopically heavy part of water molecules is stronger retained on the walls of communications, which leads to the isotopic composition heavying with decreasing injected sample volume.

Thus, if the sample volume is $0.22\mu\text{l}$, side isotopic effects not related to sublimation are minimal, and measured isotopic composition remains equal to the initial value (-72.6‰). Therefore, the time of sample accumulation under the water ice sublimation should be selected for each temperature taking into account the sublimation rate so as

to obtain the optimal sample accumulation volume in the trap, which best matches the sample's volume of $0.22\mu\text{l}$. The studied important feature of the technique will enable reliable measurements of isotope effects in unique processes occurring on the lunar surface.

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Conflict of interests

The authors declare that they have no conflict of interests.

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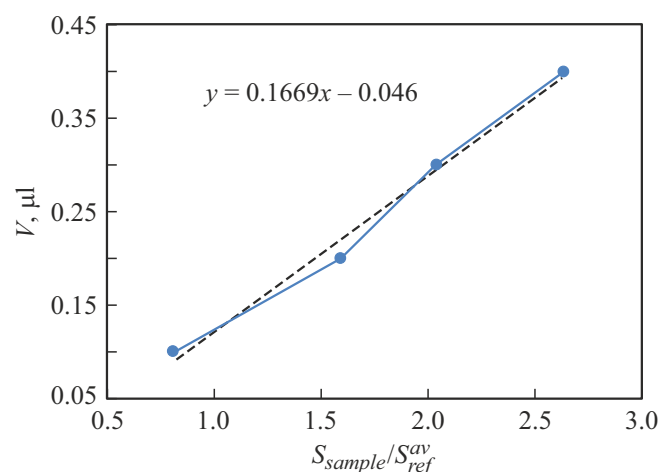


Figure 4. The ratio of the target sample analytical peak area to the control sample area versus the actual target sample volume.