

Activation of uranyl peroxides by ionizing radiation prior to uranyl carbonate formation

Zoe C. Emory,¹ Jay A. LaVerne,^{2,3} Peter C. Burns^{1,4*}

¹Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA

²Radiation Laboratory, University of Notre Dame, Notre Dame Indiana 46556, USA

³Department of Physics and Astronomy, University of Notre Dame, Notre Dame Indiana 46556, USA

⁴Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, USA

*pburns@nd.edu

Electrospray ionization mass spectrometry (ESI-MS)

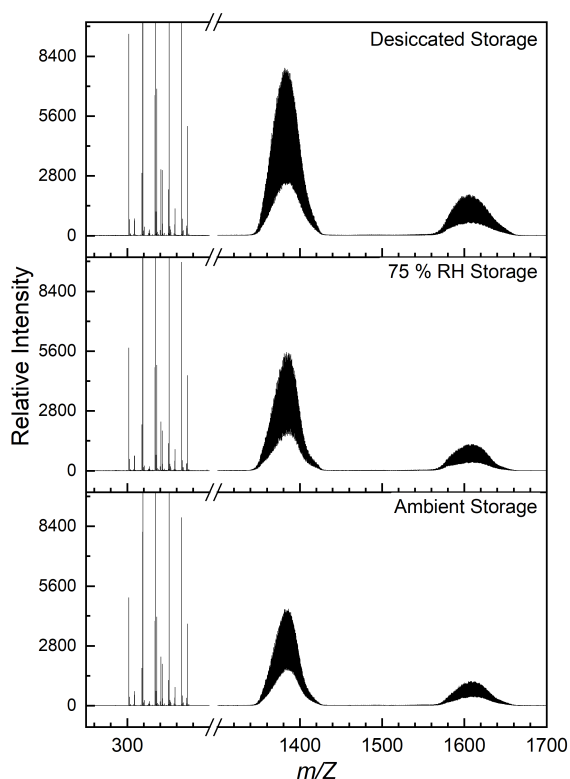


Figure S1. Electrospray ionization mass-spectrometry with ion filtering and collision induced dissociation. This figure highlights the unique fingerprint of the U_{28} cluster despite different storage environments.

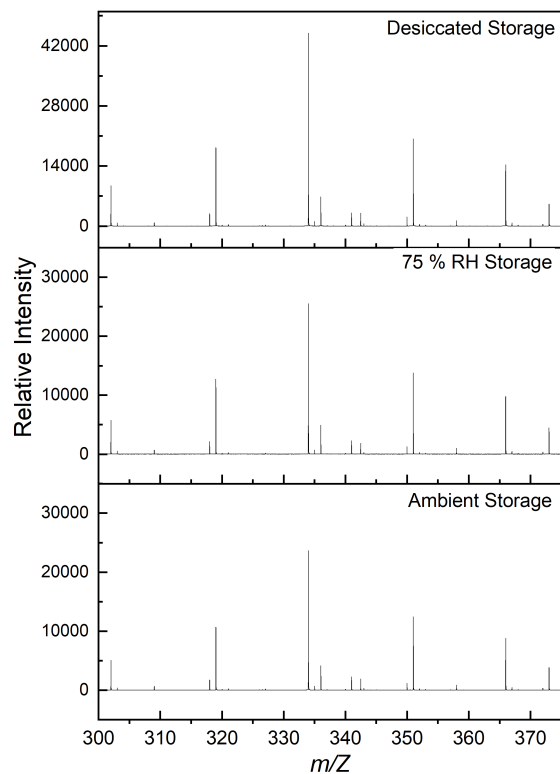


Figure S2. Electrospray ionization mass-spectrometry with ion filtering and collision induced dissociation. Zoomed in to lower m/z .

Figure S1 and Figure S2 show ESI-MS of dissolved Li-U_{28} salts (~ 200 ppm) after storage in ambient, 75 % relative humidity (RH), or desiccated conditions. The plots in Figures S1 and S2 result from tandem MS with collision induced dissociation (CID) following the methods developed by Rodriguez et al.¹ Ion filtering was done, selecting for ions at 1375 m/z with a window of ± 70 m/z . This corresponds to a mass of the U_{28} cluster anionic shell, affiliated Li^+ counter cations to give the associated charge state of -7 and -6 and additional water molecules associated with the cluster. Figure S2 highlights the low m/z region where anionic UO_x^- fragments are observed, where $x=4-8$, unique to U_{28} .

Single Crystal X-ray Diffraction

Table S1. Crystallographic Data for Li-U₂₈ Confirmation

<i>Crystal Data</i>	1
Formula	(Li ₂₈ [(UO ₂) ₂₈ (O ₂) ₄₂])
Formula Weight	2274.79
Crystal system	Tetragonal
Space Group	<i>P</i> -42 ₁ <i>c</i>
Temperature (K)	130
<i>a</i> (Å)	20.28178(17)
<i>c</i> (Å)	26.8954(3)
<i>V</i> (Å ³)	11063.4(2)
<i>Z</i>	8
ρ_{calc} (g cm ⁻³)	2.731
μ (mm ⁻¹)	20.482
<i>F</i> (000)	7560
Crystal Size (mm ³)	0.1 x 0.1 x 0.1
Crystal Color	Yellow
<hr/> <i>Data collection</i> <hr/>	
Diffractometer	Rigaku XtaLAB Synergy
λ (Å)	MoK α , 0.71073
μ (mm ⁻¹)	20.48
Data Range θ (°)	1.817 – 33.886
Limits <i>h</i> , <i>k</i> , <i>l</i>	-28 < <i>h</i> < 29 -26 < <i>k</i> < 20 -39 < <i>l</i> < 34
Measured reflections	69781
Total reflections(<i>N</i> ₂), observed (<i>N</i> ₁)	18884, 16607
Criterion for observed reflections	<i>I</i> > 2 \sqrt{I}
<i>R</i> _{int} (%)	0.0394
<hr/> <i>Refinement</i> <hr/>	
Refinement	Full-matrix least-squares on <i>F</i> ²
<i>R</i> ₁ , <i>wR</i> ₂ for <i>N</i> ₂	0.0513, 0.1215
<i>R</i> ₁ , <i>wR</i> ₂ for <i>N</i> ₁	0.0439, 0.1177
Goof (Goodness of fit)	1.114
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	2.971, -1.736

Gas Chromatography

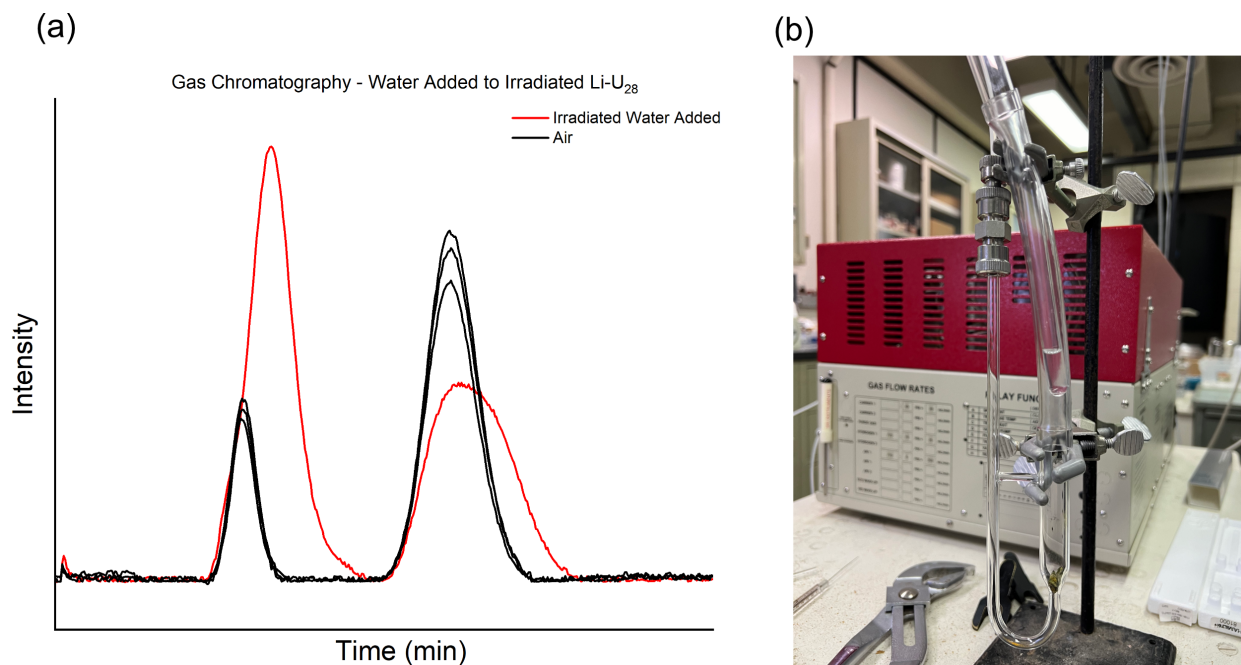


Figure S3. (a) Gas chromatography of air (black trace) and gas evolved from irradiated Li-U₂₈ material (red trace) immersed in water. The sample was irradiated to 42 MGy with under dry argon and stored in a desiccated environment. (b) 1 mL of helium flushed water was added to the material in a U-shaped tube.

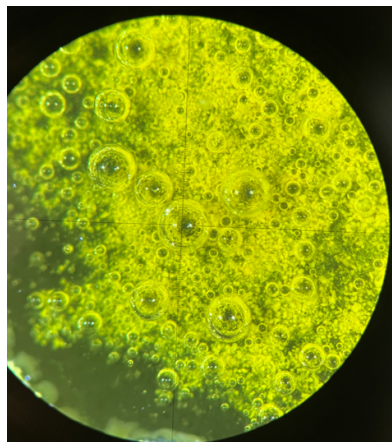


Figure S4. Water added to Li-U₂₈ irradiated to 42 MGy with He²⁺ ions under a dry Ar flow.

Gas chromatography (GC) was done to confirm the gas evolved from irradiated Li-U₂₈ is O₂. Li-U₂₈ irradiated in dry conditions evolved gas when water was added to the irradiated material, however, Li-U₂₈ irradiated under hydrated conditions did not. Samples irradiated in dry conditions contained an extraneous peak in the Raman spectra at 1553 cm⁻¹ that tentatively was assigned to O₂, based on published literature values.² This was confirmed by measuring the gas evolved from Li-U₂₈ irradiated and stored in dry conditions exposed to water.

1.0 mL of 18M Ω ultrapure water was purged with high purity helium gas in a glass ampule for 10 minutes and subsequently flame sealed, avoiding atmospheric exposure. The ampule was inserted into the GC above the irradiated material and the system was purged with helium. Once the baselines were collected, the glass ampule was crushed allowing the water to mix with the irradiated material below it. Gas production was observed, and data was collected.

X-ray Photoelectron Spectroscopy (XPS)

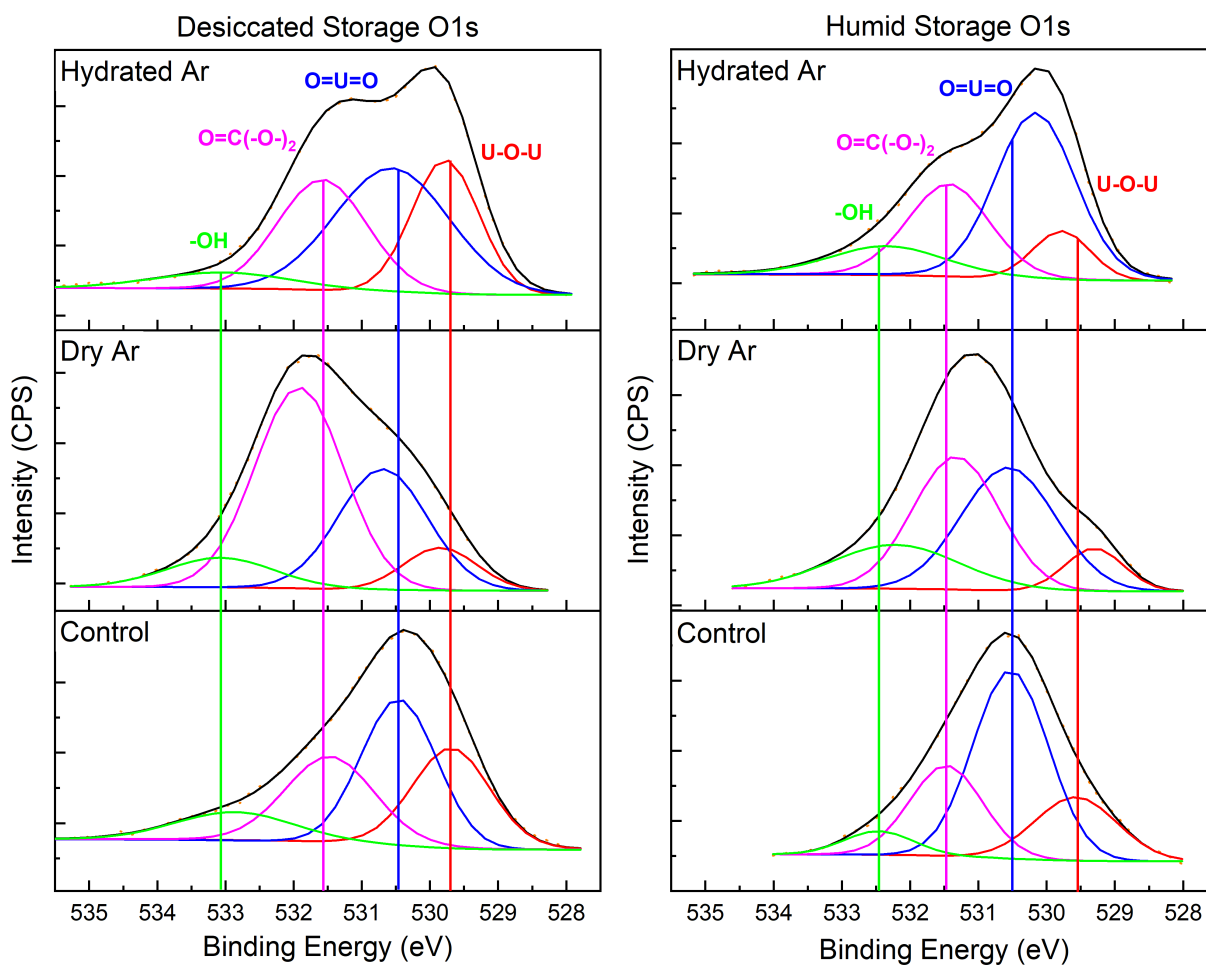


Figure S5. XPS of O1s envelopes for control and 42 MGy irradiated Li-U₂₈ kept in desiccated storage (left) 75 % RH storage (right) and hydrated or dry argon flow during He²⁺ ion irradiation (top, middle, respectively).

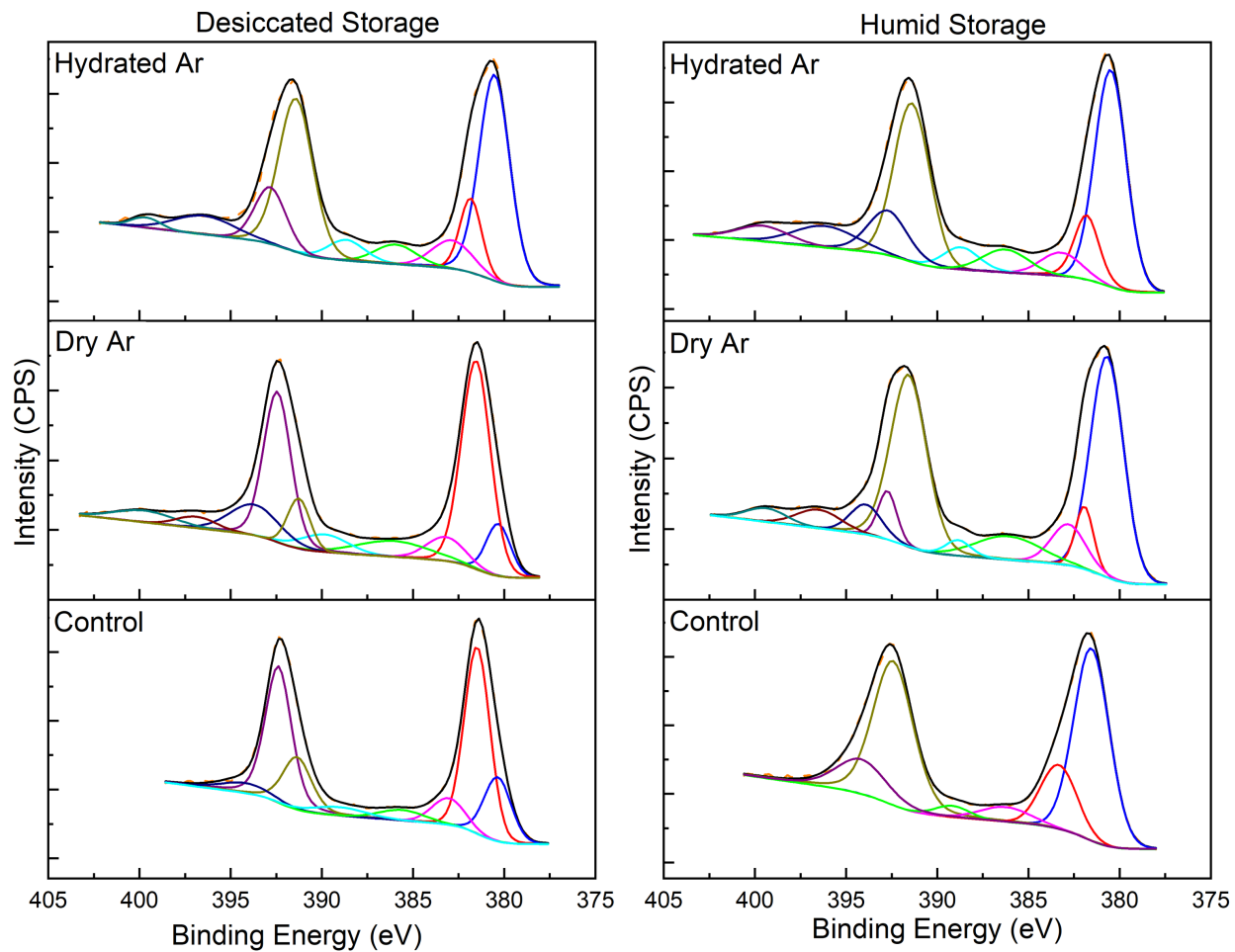


Figure S6. XPS of $U4f_{5/2}$ $U4f_{7/2}$ binding envelopes for 42 MGy irradiated $Li-U_{28}$ kept in desiccated storage (left) 75 % RH storage (right) and hydrated or dry argon flow during irradiation (top, middle, respectively).

EPR

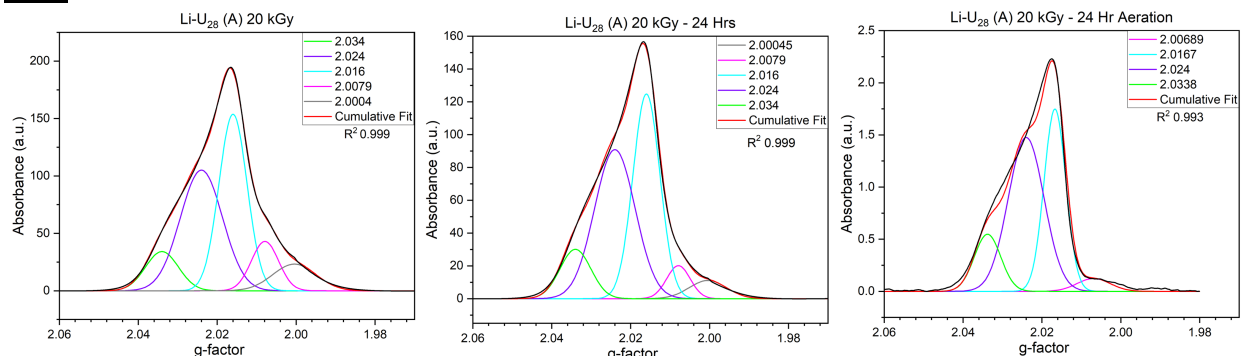


Figure S7. Left: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) from integrated EPR spectra, middle: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) and aged sealed for 24 hours from integrated EPR spectra, right: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) and aged sealed for 24 hours then aerated for an additional 24 hours from integrated EPR spectra. Take note of difference in peak intensities across graphs.

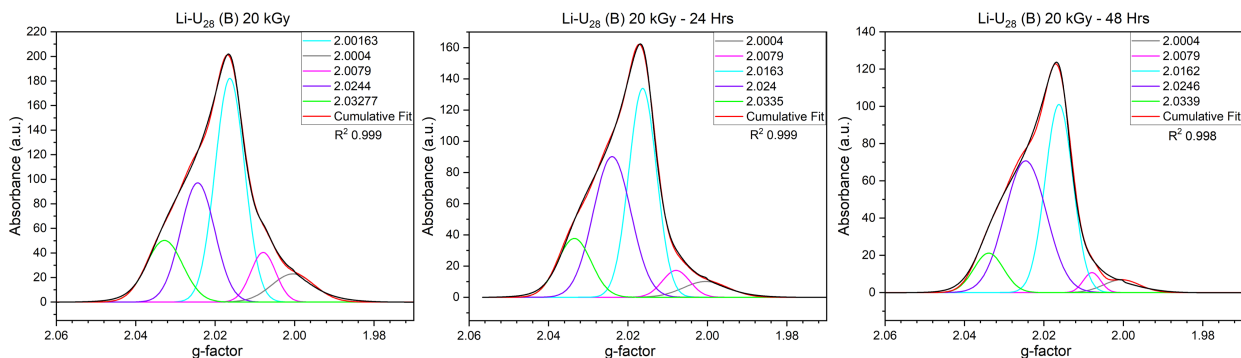


Figure S8. Left: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) from integrated EPR spectra, middle: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) and aged sealed for 24 hours from integrated EPR spectra, right: fit absorbance spectra of Li-U₂₈ γ -irradiated to 20 kGy (black) and aged sealed for 48 hours from integrated EPR spectra. Take note of difference in peak intensities across graphs.

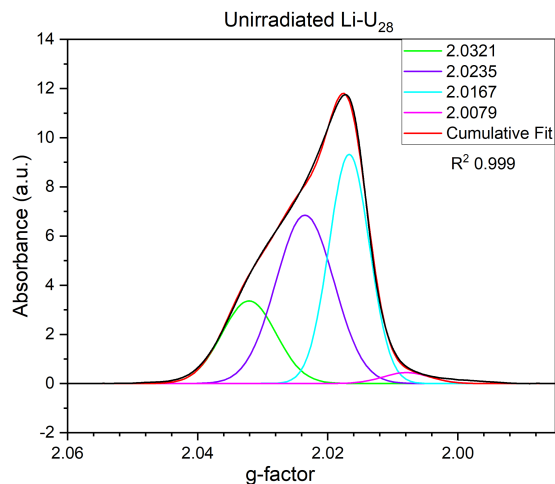


Figure S9. Fit absorbance of unirradiated Li-U₂₈ from integrated EPR spectra.

CO₃²⁻ ν₁ in Raman Spectra

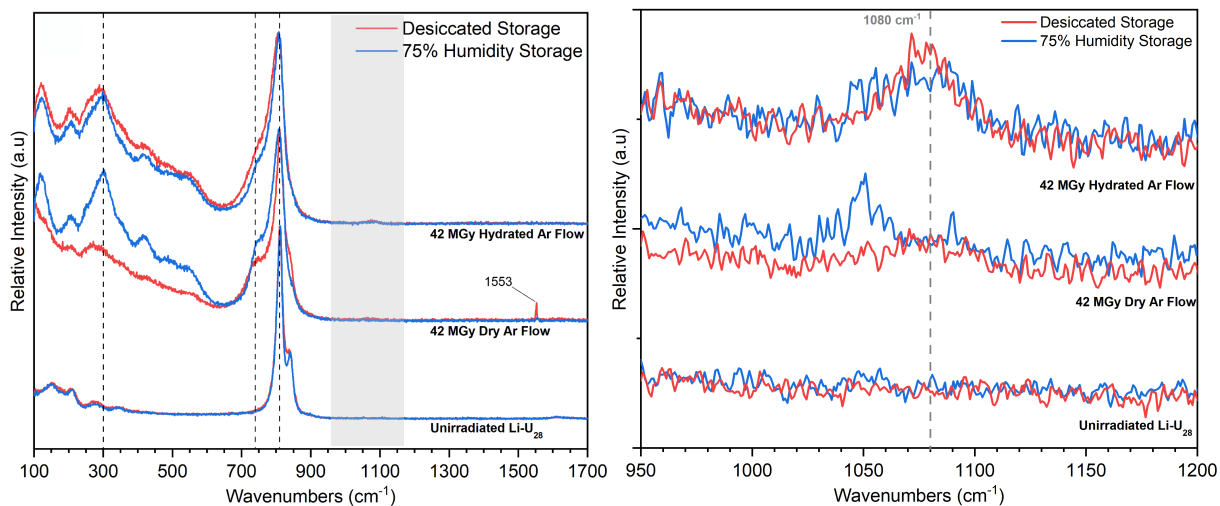


Figure S10. Raman spectra of He²⁺ ion irradiated Li-U₂₈ to 42 MGy. Stacked plots reference either dry or hydrated Ar flow over the surface of the sample during irradiation. Red traces are for samples stored in desiccated environments; blue traces are for samples stored in 75% relative humidity environments. The right plot is zoomed in centered at the small peak at 1080 cm⁻¹, assigned to the symmetric stretch (ν₁) of carbonate.

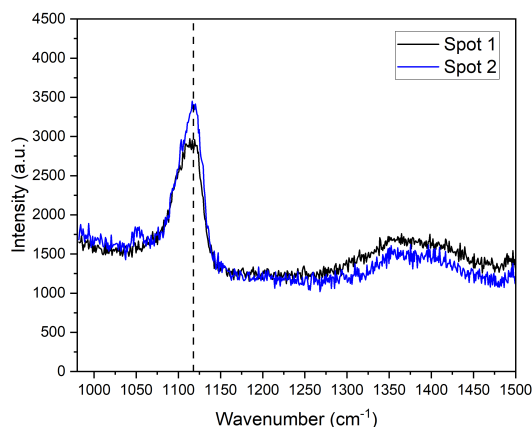


Figure S11. Raman spectra of He²⁺ irradiated Li-U₂₈ to 42 MGy. Raman spectra were collected as static scans (950-1500 cm⁻¹), 3s exposure, 5 accumulations, 0.5% laser power.

Figures S10 and S11 highlight the symmetric carbonate stretch present in the Raman spectra of He²⁺ irradiated Li-U₂₈. The extended scans presented in Figure S10 range from 100-2000 cm⁻¹ and include the very intense symmetric uranyl stretch, ultimately making the CO₃²⁻ ν₁ vibrational mode appear very small. The static scan narrowed to wavenumbers excluding the uranyl ν₁ stretch and including carbonate ν₁ mode confirms its presence.

References

- (1) Rodriguez, V. G.; Culbertson, H. J.; Sigmon, G. E.; Burns, P. C. Electrochemistry of Uranyl Peroxide Solutions during Electrospray Ionization. *Inorg. Chem.* **2023**. <https://doi.org/10.1021/acs.inorgchem.2c03904>.

- (2) Weber, A.; McGinnis, E. A. The Raman Spectrum of Gaseous Oxygen. *J. Mol. Spectrosc.* **1960**, *4* (1–6), 195–200. [https://doi.org/10.1016/0022-2852\(60\)90081-3](https://doi.org/10.1016/0022-2852(60)90081-3).