

Lunar Integrating Cavity Raman Ultraviolet Spectrograph (Lunar ICARUS) Concept. K. D. Retherford^{1,2}, T. Z. Moore¹, U. Raut^{1,2}, C. M. Phillips-Lander¹, P. M. Molyneux¹, M. A. Miller¹, K. Nowicki³, S. P. Schwenzer⁴, R. C. Blase¹, M. W. Davis¹, T. J. Veach¹, G. J. Dirks¹, K. B. Persson¹, Y. D. Tyler¹, R. A. Klar¹, P. L. Karnes¹, M. A. Freeman¹, C. J. A. Howett³, A. Soto³, J. D. Mason⁵ and E. S. Fry⁵, ¹Southwest Research Institute, San Antonio, TX (kretherford@swri.edu), ²University of Texas at San Antonio, San Antonio, TX, ³Southwest Research Institute, Boulder, CO, ⁴The Open University, Milton Keynes, UK, ⁵Texas A&M University, College Park, TX.

Introduction: Assessments of lunar mineral trace species, hydration states, and related alterations of olivine and plagioclase feldspar provide key chronological markers for investigating the history of the lunar surface. The LCROSS mission's discovery of both water and hydrocarbon species in Cabeus crater highlights the potential role of the delivery of volatiles to the surface by comets and micrometeorites; subsequent modern day transport of such volatiles is of great interest for in situ resource utilization applications. Measurements of the D/H ratio of ices in Permanently Shaded Regions (PSRs) are also needed to understand the relative importance of key processes and sources.

Landed missions in the coming decade will employ a variety of techniques to assess the relative ages and compositions of individual rocks and full regions of interest in order to clarify the influence of the late heavy bombardment era, compared with ongoing impact processes as typified by soil properties. The Raman technique is well suited for these key mineralogical and volatile-isotope studies, and is rapidly advancing in readiness for planetary missions.

The first Raman systems flown into deep space are set for the next Mars rovers from both NASA and ESA. Our Integrating Cavity Raman Ultraviolet Spectrograph (ICARUS) instrument development program creates a new Deep-UV+VIS dual-laser Raman system capable of detecting complex molecular species, e.g., constraining their magnesite and calcite abundances, mineral hydrated states, and volatile-isotopes in PSRs. The instrument is suitable for lunar landers, rovers, and a gateway outpost.

Integrating Cavity Enhanced Raman Spectroscopy (iCERS) Technique: Many Raman instruments currently in development for planetary studies utilize a confocal technique where the excitation laser is focused to a small spot on the sample. Our integrating cavity technique enhances the Raman signal by up to six orders of magnitude relative to the confocal approach, enabling sensitive measurements of trace species and isotopes. Cavity enhanced fluorescence has already demonstrated femtomolar level measurement sensitivity for urobilin in liquid water, benzo[a]pyrene at 700 nanomole sensitivity (e.g., ~180 ppb wt. in 1 g water-ice), and for bulk pyrene down to 37 nanomole [1,2]. This recent technology advancement provides great promise for a wide range of applications, including numerous types of planetary science investigations requiring sensitive detections of trace composition.

Our new integrating cavity material is optimized for high total internal Deep-UV reflectance, based on the selection of high purity fumed silica for the cavity material. Incorporating two lasers and a UV LED with three different excitation-emission pathways is crucial for definitive interpretation of the spectral fingerprints that identify constituents within a sample – crucial data for studying mixed materials. Our fiber-fed multi-source measurement approach removes fluorescence-driven ambiguities from degenerate, non-unique signatures expected for the most interesting trace constituents, i.e., those best revealed by UV excitation.

Lunar ICARUS Concept: A TRL-4 cavity breadboard has been built and operated using internal SwRI funds (Figure 1), with demonstrated basic func-

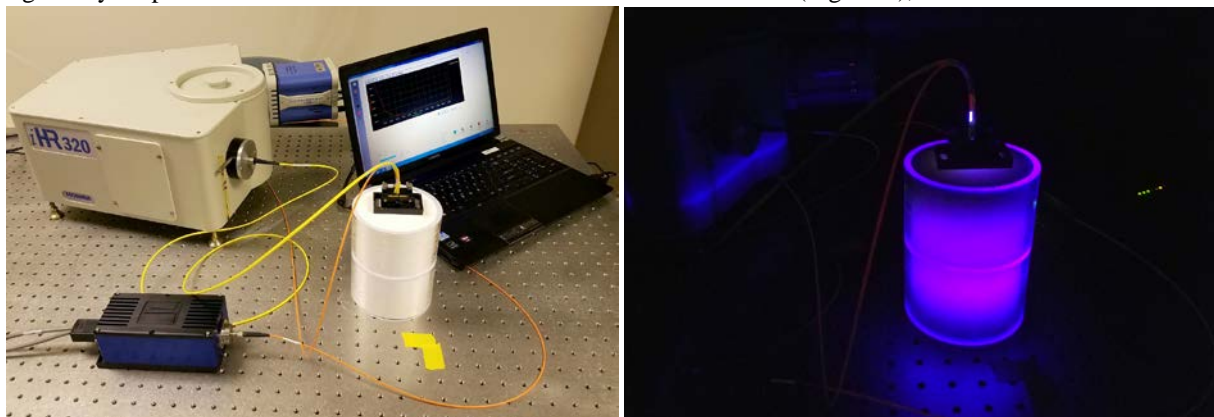


Figure 1. Functional prototype of an iCERS cavity operating at SwRI (TRL 4 demonstration).

tionality for key components and several example spectra [3,4].

Two spectrograph channels and one detector spanning Deep-UV/VIS wavelengths produce up to six separate spectral data products per sample. Samples of 1 mm to 1 cm scale are measured in bulk across their surface areas once placed inside the cavity, avoiding the need for contextual imaging and limitations of spot-targeting approaches used in stand-off Raman systems. Notch filters are included to obtain low-frequency phonon mode signatures of mineral hydration states.

Customization of the instrument concept for a landed lunar platform is ongoing. A fused-silica inner lining to the cavity is being developed to keep the cavity free from trace contamination while operating in situ. A variety of sample acquisition and handling systems may be accommodated in future studies. Next steps include mitigating the effects of dust while operating in the lunar environment and developing techniques to clean the cavity of any particulates accumulated after numerous sampling operations. The final instrument concept will be of sufficiently low mass, volume, and power to be compatible with inclusion on commercial lander systems.

Raman Spectral Reference Library: The prototype device is already capable of producing detailed laboratory Raman spectra of Apollo samples, icy mixtures, lunar simulants, and other materials relevant to in situ planetary surface studies (Figure 2). Next steps include conducting additional sensitivity demonstrations for a range of different materials relevant to lunar science; these Raman spectra will be contributed to the RRUFF spectral library [5]. Several research programs will be pursued in the next few years to leverage the

capabilities of this new enhanced Raman system while the ICARUS concept is further developed for flight missions.

References: [1] Bixler, J. N., et al. (2014) *PNAS*, 111.20, 7208-7211. [2] Bixler J. N. (2015) *Ph.D. Thesis*, Texas A&M University. [3] Retherford K. D., et al. (2017) *AAS/DPS Meeting* 49, Abstract #224.05, iPoster: <https://dps2017-aas.ipostersessions.com/default.aspx?s=22-35-18-50-3D-97-EE-6B-6B-87-E9-83-A6-CF-54-11&guestview=true>. [4] Moore, T. Z., et al. (2018) *Proc. of the SPIE*, 10657, doi:10.1117/12.2305180. [5] Lafuente B., et al. (2015) *Highlights in Mineralogical Crystallography*, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30.

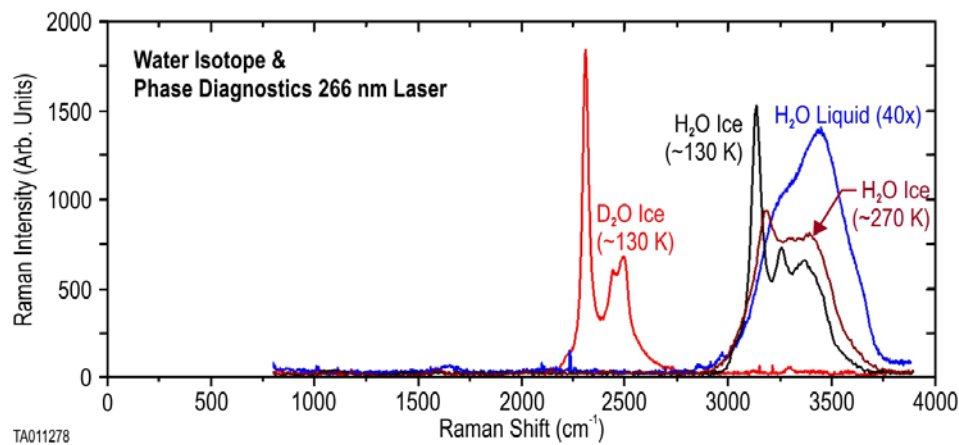


Figure 2. SwRI's TRL 4 cavity breadboard produced these spectra of water ice, deuterated water ice, and temperature/phase Raman signatures obtained with a Deep-UV 266 nm laser source. A collection time of 10 accumulations of 10 s was used with a 1200 grooves/cm grating system using the current spectrometer setup. Several improvements being applied to the optical couplings, detector, and laser sources will further improve quality.