RAMAN SPECTROSCOPY FOR THE MOON: DEVELOPMENT OF A LUNAR-RELEVANT RAMAN SPECTRAL LIBRARY.

C. Caudill[1], E. Cloutis[1], S. Potin[1], S. Manigand[1]. [1]Centre for Terrestrial and Planetary Exploration (C-TAPE), University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada.

Introduction: Raman spectroscopy for planetary rover-based exploration is becoming a primary tool to investigate *in situ* geological materials. Following the incredible success of the ChemCam Raman instrument aboard the NASA Curiosity Mars Science Laboratory (MSL) rover, two Raman spectrometers were chosen for the recently-launched NASA Perseverance rover [1], and another is planned for the 2022 ESA-Roscosmos Rosalind Franklin rover [2]. The CNSA Chang'e-7 2024 lunar south pole lander and rover mission will also host a Raman spectrometer [3].

Although planned, future lunar landed missions will be equipped with Raman spectroscopy, to date, no Raman spectrometer has flown on a lunar mission. Therefore, we are developing a lunar-relevant Raman spectral library to support: (1) science and technology development and (2) implementation of flight-ready Raman spectral instruments suitable for future lunar rover missions.

Raman spectroscopy for lunar exploration: Raman spectroscopy provides non-destructive, remote analyses, making it desirable for rover-based exploration. Spectral and spatial resolution enables identification of mineralogy on a single-grain basis as well as characterization of complex multi-component grain assemblages [e.g., 4]. Raman spectra also do not exhibit the broad overlapping of features caused by overtones and combinations of modes observed in VIS-NIR and IR spectroscopy [e.g., 4], and thus, provides less ambiguous mineral phase identification.

Raman spectroscopy has been applied to the analysis of lunar samples for decades as an instrument that excelled at detecting minerals commonly found on the Moon, including olivine, pyroxene, feldspar, and silicate glasses [e.g., 6]. Raman analyses of lunar samples has further subcategorized these mineral phases depending on elemental geochemistry, delineating clinopyroxenes from orthopyroxenes and understanding the origins of lunar olivines through the Mg:Fe ratio, and the identification of several feldspar groupings [5]. Raman spectroscopy data has provided a more complex understanding of lunar materials and their origins, elucidating the effects of lunar surface modification processes such as weathering, physical-chemical processes [6], igneous petrology, origins and composition of lunar mare and highland rocks, and bombardment history of the Moon [e.g., 7].

Development of a lunar-relevant Raman spectral library:

Meteoritical analyses. Raman spectroscopy was performed on powered and whole rock sections of the Northwest Africa 11444 (NWA 11444) lunar highland melt breccia meteorite. Petrographic and geochemical analyses on NWA 11444 demonstrated chemically-variable pyroxenes (e.g., low and high-Ca), acicular plagioclase feldspar microlites and crystal fragments consistent with a breccia, and compositionally-complex olivine.

Our results confirmed earlier studies that Raman spectroscopy shows abundant diagnostic Raman peaks, without undue influence of induced broadband fluorescence. The small amount of observed broadband fluorescence is likely related to contamination by the terrestrial environment (Figure 1). Figure 2 demonstrates that Raman can distinguish chemical variants of pyroxene such as those present in NWA 11444; spectra of orthopyroxene and clinopyroxene are shown with respective diagnostic features present between 150 and 1000 cm-^{1} [8]. The peak positions of these features can be used to determine cation composition (Fe:Mg:Ca ratios), and thus allow inferences regarding the regional derivation of the meteorite, impact melt excavation and source material, and crustal evolution as represented in the materials [e.g., 9].

Additional lunar meteorites will be analyzed for the Raman lunar-relevant spectral library, including a number of lunar breccias, such as NWA 8277, NWA 11228, NWA 11303, and NWA 11788.

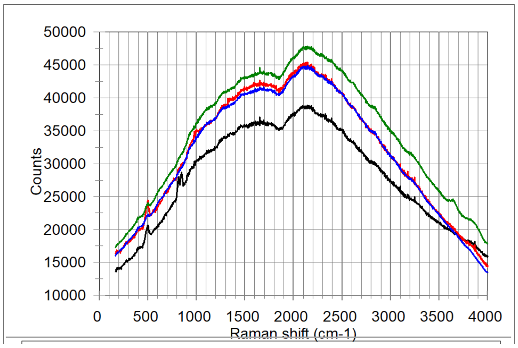

Figure 1. Raman spectra of lunar meteorite NWA 11444 collected in-house at C-TAPE.

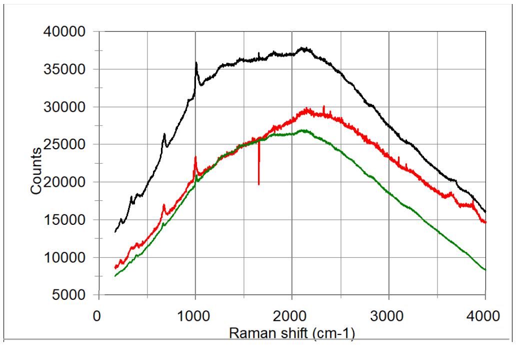

Figure 2. Raman spectra of low- and high-calcium pyroxenes measured at C-TAPE for the lunar-relevant spectral library.

Lunar analogues and lunar-relevant mineralogical analyses. To develop a robust lunar-relevant Raman spectral library, Raman spectra of lunar samples were measured as well as lunar-rock compositional analogues and mineralogical analogues. The main mineralogical constituents of the lunar surface that will be measured to build the library include olivine, plagioclase, ilmenite, and pyroxene. The detection and characterization of ices are also an important component to understand for lunar rover-based exploration, and our database will explore the capabilities of Raman spectroscopy for this objective.

Lunar olivines have a wide range of compositions [e.g., 10]. Raman spectra of low- and high-iron olivines demonstrate that they exhibit multiple diagnostic peaks (Figure 3). Peak positions can be used to determine composition; they vary by up to 20 cm^{-1} [11].

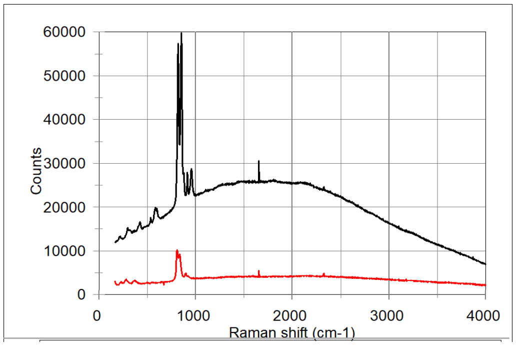

Figure 3. Raman spectra of a low- and high-iron olivine measured at C-TAPE for the lunar-relevant spectral library. Peak positions can be used to determine composition, in particular the strong peaks in the 800-900 cm-1 interval.

Lunar plagioclase is generally observed as a Ca-rich endmember (i.e., anorthite) [e.g., 13]. Plagioclase exhibits complex variation: transition between the Ca, Na, and K endmembers involves, exsolution, phase transitions, and structural changes. As a result, plagioclase Raman spectra are complex, but also highly diagnostic [12]. Plagioclase minerals within the Ca-rich plagioclase grouping exhibit rich geochemical variance that can be observed in Raman spectra (Figure 4).

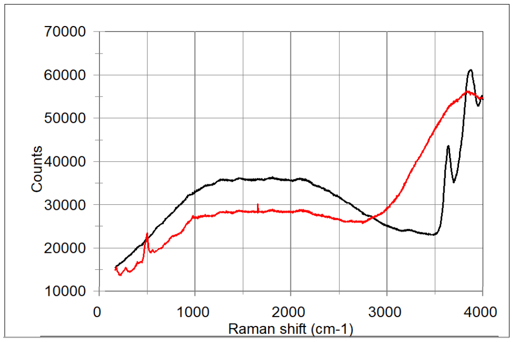

Figure 4. Raman spectra of two calcium-rich plagioclase feldspars measured at C-TAPE for the lunar-relevant spectral library. Structural and compositional variations lead to very different (and diagnostic) Raman spectra.

The Raman spectral database will be curated in parallel with the in-house development of LunaR – a baseline instrument study and build of a Raman spectrometer specifically for landed lunar missions, having a wide range of capabilities relevant to lunar science and exploration [13]. The robust Raman spectral library coupled with LunaR science and technology development will serve to address various lunar exploration objectives far beyond mineralogic assessments, including: the identification of trace elements; determine of oxidation states of mineral phases; detection and characterization of condensed volatiles and light organic molecules; identification of water and water ice; and, identification of hydrated materials and evidence of secondary alteration.

References: [1] Wiens et al, *Space Science Reviews*, 170, 167-227 (2012). [2] Rull et al., *Astrobiology, 17,* 627-654 (2017). [3] Zou et al., *LPSC, 51*, 1755 (2020). [4] Haskin et al., *JGR, 102(E8), 19293-19303* (1997).
[5] Ling et al., *Nature, 569,* 378-382 (2011). [6] Huidobro et al., *EPSC,* EPSC2018-883 (2018). [7] Righter et al., *40*(11), 1703-1722 (2005). [8] Huang, et al., *American Mineralogist, 85(3-4), 437*-479 (2000). [9] Li et al., *Nature, 569,* 378-382 (2019). [10] Papike et al., *Mineralogical Society of America, v36, ch. 5 (*1998). [11] (Mouri and Enami, *ournal of Mineralogical and Petrological Sciences, 103,* 100-104 (2008). [12] (Bersani et al., *Journal of Raman Spectroscopy,* 10.1002/jrs.5340 (2018). [13] Cloutis et al., *this conference.*