PLANETARY LASER RAMAN SPECTROSCOPY FOR SURFACE EXPLORATION ON C/D-TYPE ASTEROIDS – **A CASE STUDY.** W. G. Kong^{1,2}, Alian Wang¹ Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (gavink@levee.wustl.edu), ² School of Space Science and Physics, Shandong University, Weihai, 264200, China.

Introduction: C/D-type asteroids occur in the outer part of main asteroid belt of our solar system. Some have been selected as the targets for planetary exploration missions because they were recognized to contain primitive materials from the early development stages of our solar system. Missions to investigate asteroids that have flown or will fly include the flybys (Voyager, Deep Space 1, Galileo by NASA, Rosetta by ESA), orbiters (NEAR Shoemaker and Dawn by NASA), lander (NEAR Shoemaker by NASA), and sample return (Hayabusa by JSA, Phobos Grunt by Russia, Marco Polo by ESA-JSA).

In situ characterization of surface and subsurface materials of asteroids are important to understand the evolution of the early solar system, the asteroids themselves, and their contributions to the planetary bodies of inner solar system[1]. This task can be achieved by Planetary Raman Spectroscopy in a landed mission.

Planetary Laser Raman spectroscopy: When irradiated by a laser beam, a molecule may absorb a photon and instantly emit a new photon with the same wavelength (Rayleigh scattering) or a different wavelength (Raman scattering). The wavelength of the radiation scattered by the Raman effect is a function of molecular structure and composition. With a laser excitation line in the visible spectral range, a Raman spectrometer (with optics and a detector optimized for visible λ) observes the vibrational and rotational transitions in a molecular system or crystal lattice, which are normally observed by NIR and Mid-IR spectroscopy.

Minerals and organic functional groups have unique Raman spectra enabling unambiguous phase identification[2,3,4]. Compared to VIS-NIR and mid-IR emission or reflectance spectra, Raman peaks are sharp, non-overlapping, and nearly free of overtones and combinations. Peak positions and widths are maintained for grain sizes down to tens of nanometers[5,6]. Minerals and organic species can be readily identified even in raw spectra of mixtures. Peak positions and patterns, not intensities, are used for identification. Organic species need not to be crystalline for detection.

The major Raman peaks of oxy-anionic species (silicates, phosphates, sulfates, carbonates, etc.) are determined by the chemical bonds with the highest covalence in their structures (i.e. Si_xO_y, PO₄, SO₄, CO₃, etc), modified by cations that link to them[7,8,9,10]. Rapid mineral classification and detailed structural and compositional information can be obtained through

laser Raman measurements in robotic surface exploration missions.

Raman signals can sometimes be covered by competing fluorescent photons. A "contact" Raman system uses a highly condensed excitation laser beam (10-20 µm diamter) and a short working distance (~cm) to ensure the highest efficiency for Raman signal excitation and collection, permitting a high sensitivity for many species[11]. In addition, a narrow excitation laser beam will provide the capability to detect minor or trace species whose signal would be obscured by major species if using a broad beam for excitation. In order to obtain the information on mineral modes and spatial relations, multiple Raman spectra will be required[12].

Application for the surface exploration of C/D-type asteroid: Because carbonaceous chondrites are thought to have a similar early solar system material origin as C/D-type asteroids, we conducted a Raman spectroscopic study of Murchison and Allende to demonstrate that Planetary Laser Raman Spectroscopy can address the major science questions of a surface exploration mission to C/D-type asteroids. The Murchison and Allende meteorites are two of the most studied carbonaceous meteorites due to their large mass. Murchison belongs to the CM2 group and was partially altered in its parent body [1]. Allende belongs to CV3 group and has experienced low temperature metamorphism in its parent body [13]. Raman spectroscopy has been used to study the carbonaceous matter in the Murchison meteorite [14,15].

Materials and measurements: Powdered samples and flat-cut rock chips from each of the Murchison and Allende meteorites were used for this study. A Holo-Lab5000-532 laser Raman spectrometer (Kaiser Optical Systems Inc.) was used to obtain Raman spectra of 4000 -100 cm⁻¹, that uses a 532 nm frequency-doubled Nd:YAG laser for excitation and a objective lens to condense a ~ 6 um diameter laser beam onto the sample. Automatic linear scans (99% time off-focus with known de-focusing distance) were made on both the powder and rock samples. Two sets of manual scans (100% time at-focus) were made for comparison reason.

Figure 1 and 2 show the typical Raman spectra obtained from major, minor, and trace species in the two meteorites.

Figure 1: Raman spectra of phases found in Murchison.

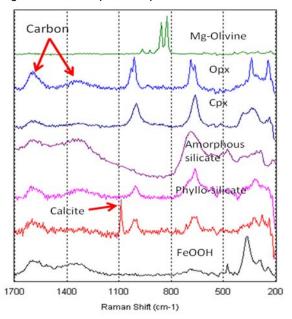
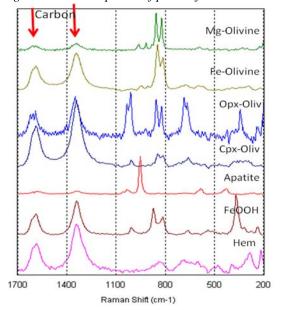


Figure 2: Raman spectra of phases found in Allende



<u>Information obtained:</u> 600 Raman spectra were obtained from six traverses of 100 points each, 91-97% of the spectra from each Murchison traverse are informative, and 70-98% of the spectra from each Allende traverse are informative. We found that the major challenge for obtaining an informative Raman spectrum from a measurement on those meteorite samples is not the off-focus distance (maximum ~ 0.1 mm for powder sample) but the fluorescence.

Previous Raman studies [13,14] have demonstrated that the structural disorder (revealed by Raman peak area ratios) of graphitic carbons can be used to estimate the metamorphic grade of the two meteorites. Figure 3 compares the compositional distributions of olivine spectra [8,16] in Murchison and Allende. Figure 4 compares the compositional distributions of pyroxene spectra [7] in these two meteorites.

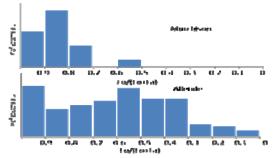


Figure 3: Fo/(Fo+Fa) molar ratio distribution for olivine in Murchison and Allende meteorites.

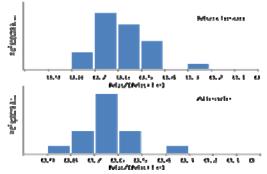


Figure 3: Mg/(Mg+Fe) molar ratio distribution for pyroxene in Murchison and Allende meteorites.

Summary: We have demonstrated the feasibility of using Planetary Laser Raman Spectroscopy for in situ characterization of the surface and subsurface materials of C/D-type asteroids.

Acknowledgment: We would thank K. E. Kuebler for her review. This study was supported by Chinese Scholarship Council to W. G. Kong.

References: [1] McSween H. Y. (1979) GCA 43, 1761-1770.

2] Nakamoto K. (2009) Infrared and Raman Spectra of Inorganic and Coordination Compounds, 6th edition. [3] Wang A. et al. (1994) Appl. Spectrosc. 48,959-968. [4] Nyquist R. et al. (1996) Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts. [7] Wang A. et al. (2001) Am. Mineral. 86, 790-806; [8] Kuebler et al. (2006) GCA 70,6201-6222 [9] Wang A. et al. (2004) Am. Mineral. 89, 665-680. [10] Freeman J.J. (2008) Can. Mineral. 46, 1477-1500. [11] Wang A. et al. (2003) JGR 108, E15005 [12] Haskin et al. (1997) JGR 102, 19293-19306 [13] Weinbruch S. (1994) GCA 58, 1019-1030. [14] Larsen K. L. and Nielsen O. F. (2006) J. Raman Spectrosc. 37, 217-222. [15] Chahrazade E. A. (2005) SPECTROCHIM ACTA A 61, 2049-2056. [16] Wang A. et al. (2004) J. Raman Spectrosc. 35, 504-514.