QUANTIFICATION OF FLUORESCENCE EMISSION FROM EXTRATERRESTRIAL MATERIALS AND INTERFERENCE TO MICRO-BEAM CW 532 NM RAMAN SPECTROSCOPY Jie Wei, Alian Wang, and Kathryn Connor, Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, St. Louis, MO, USA (jiewei@levee.wustl.edu).

Why meteorites? Meteorites and the samples returned by planetary missions supplied the extraterrestrial materials for human beings to study the solar system and beyond far away from Earth. They provide chemical and mineral compositions representing the planetary bodies in solar system, e.g., planets, satellites, asteroids, comets, and near-Earth objects. They can also serve for testing instruments for planetary exploration.

Three Raman systems have been selected for two landed missions on Mars (ExoMars 2018 and Mars 2020). Because of its capability of providing definitive molecular (organic and inorganic) identification and characterization, planetary Raman spectroscopy is anticipated to use for many more future missions to planets and small bodies.

In terrestrial geological applications of Raman spectroscopy, one of the major limitations comes from possible fluorescence interference from the analyzed samples. The fluorescence emission can be produced from bio-genetic species that were trapped in porous rocks or soils (e.g., clays). They can also be generated from the electronic transition modes of rare earth elements (e.g., REE–enriched minerals), or in some cases from transition metals.

Knowledge about fluorescence emission from extraterrestrial materials and how much it will interfere with planetary Raman spectroscopy in exploration will help in selecting the best Raman instrument configuration for a mission. For this study, we used a broad range of meteorites, with their categories cover 97% of all types of stony meteorites fallen on Earth, to mimic *the potential fluorescence threat* to a micro-beam cw 532 nm Raman system (MMRS/CIRS, with the simplest configuration and highest TRL) that we have been developing for planetary missions, supported by PIDDP, MIDP, ASTEP, and MatISSE programs.

Fluorescence observations on Mars and related: Fluorescence imaging has been applied in Mars exploration. Both the Optical Microscope (OM) on the Phoenix lander and the Mars Hand Lens Imager (MAHLI) on the Curiosity rover are equipped with longwave ultraviolet light sources (360 -390 nm and 365 nm, respectively), for luminescence detection.[1,2] No luminescent particles had been observed so far at the Phoenix landing site [1], and for the two rock targets at Gale Crater [3] on Mars. Furthermore, in earlier fluorescence imaging measurements of martian meteorites and returned Apollo lunar samples, no obvious fluorescence emissions were observed as well [4,5]. The low-fluorescent nature of Mars and lunar samples were also demonstrated by the fact that their full mineralogical characterization were reached by ordinary Laser Raman Spectroscopic (LRS) studies using an *in situ* cw green laser Raman system without much fluorescence interferences [6-17].

Extraterrestrial and terrestrial samples: Fluorescence emission from 15 achondrite (including martian and lunar) and chondrite (including carbonaceous) meteorites samples were measured. Six terrestrial samples including four clays standards from Clay Mineral Society and two soil samples from the Atacama Desert are measured under the same conditions, and quantified using the same methodology. Fluoranthene was used as a standard. A UV-fluorescence emitter (BAM) used for Phoenix-OM is used to double check the standard's emission with UV excitation.

Table 1 Material list. (Percent[a] is the percentage of the category in the ratio to the whole stony meteorite family.)

Category		Percent[a]	Sample No.	Description
Achondrites	Martian	~3%	1,2	MIL03346, 148/149
			3,4	EETA79001, 482/476
			5,6	Zagami, Tissint
	Angrite		18	NWA 2999
	Lunar		19	Dhofar 1627E
	Howardite		20	NWA6073
	Eucrite		21	DAG 647
Chondrites	Carbonaceous	3.4%	7	Tagish lake, C2
	Ordinary: LL	12.6%	8	Bjurbole, LL4
	Ordinary: L	36.6%	9	Independence, L6
	Ordinary: H	41.1%	10	Jilin, China, H5
			11	Dawn, H6
All types checked		**97%**		
Terrestrial			12,13	Soils from Atacama Desert core
			14-17	Clays: SWx-1, KGA-2, KGA-1, SWy-1

Fluorescence microscopic measurements: Fluorescence measurements used a fluorescence microscope (Nikon, E800) and three excitation/collection bands: UV/Blue (DAPI, 380-396 nm excitation and 412-480 nm fluo-collection); Blue/Green (FITC, 462-505 nm excitation and 510-560 nm fluo-collection); and Green/Red (TRITC, 530-555 nm excitation and 590-650 nm fluo-collection).

Deeper UV excitation below 300 nm cannot be carried out using this microscope, due to transparent limitation of the optics. The fluorescence properties of these extraterrestrial materials will be measured in next step using our own Bio-UV-Fluo (BUF) imager developed under ASTID and tested in Atacama under an ASTEP project [10-11]. Luminescence intensities were normalized and relative to the fluorethane standard.

Quantification of fluorescence emitting strength: Figure 1 gives luminescence intensities of all measured samples, relative to fluoranthene. The measurement uncertainty is about 20%. The values are averaged over well focused area in each fluorescent image.
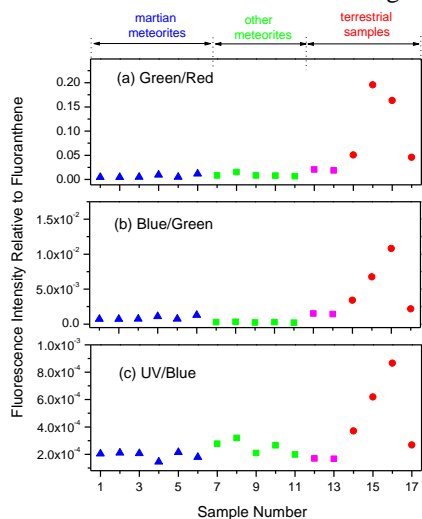

Fig. 1 Fluorescence intensities of different materials relative to fluoranthene.

With all three filter sets, terrestrial samples (clays and Atacama soils) show relatively higher fluorescence, which might be related to possible organic materials of bio-genetics with low electronic excited states. The terrestrial sample #16 (KGA-1) has the highest fluorescence level among the samples. All the exterritorial samples have quantum efficiencies in 10^{-5}-10^{-4} region in the blue fluorescence range under UV excitation. Other meteorites have similar quantum yields as the martian meteorites.

High % of informative Raman spectra from the meteorites: Figure 2 shows the percentage range (94-100%) of informative Raman spectra, using a micro-beam cw 532 nm (a Kaiser Hololab 5000) Raman spectrometer that has a similar performance to CIRS, from all extraterrestrial samples in this study. Figure 3 shows among 100-point Raman spectra acquired with auto scanning (without auto-focusing at each point), 98 spectra have clear Raman peaks that tell the chemical/mineral compositions of the species in measured meteorite. Such high % of informative spectra indicates

that fluorescence emission from those extraterrestrial samples has negligible effect in reducing Raman features from these materials. A few % of non-informative spectra can be caused by two reasons: (1) in rare cases, the fluorescence emission from minerals (REE-enriched); (2) from out-focusing Raman measurements during a multi-point auto scan without auto-focusing mechanism. Measurement with a laser distance sensor showed that the surface flatness of the Raman examined areas of that MIL 03346, 149 was within ±0.2 mm.
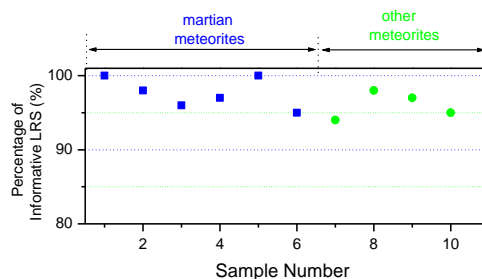

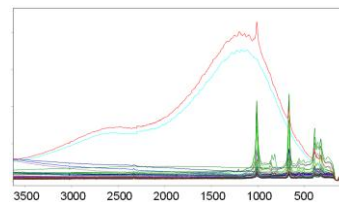Fig. 2 Micro-beam 532nm LRS informative percentages of extraterrestrial materials

Fig. 3 A set of Raman spectra acquired in one auto-scanning of MIL03346-149 without auto-focusing at each point

Conclusion: Quantification of fluorescence emission from 97% (in categories) of stony meteorites indicates that they have extremely low strength when compared with terrestrial clays. The line scans using the simplest Raman configuration, a micro-beam cw green Raman system, on those meteorites yield 94-100% informative spectra, that will be enough for the characterization of a rock sample.

References: [1] Goez W et al. (2012) *Planetary and Space Sci*., 70, 134. [2] Edgett K S et al. (2012) *Space Sci. Rev*., 170, 259. [3] Minitti et al., 2014 LPSC, abs# 2029; [4] Minitti et al., 2012 LPSC, abs# 2249; [5] Wang et al., 2003 LPSC, abs# 1753; [6] Wang et al., 1995, *JGR*, 100, 21189-21199; [7] Haskin et al., 1997, *JGR*, 102, 19293-19306; [8] Korotev et al., 1998, LPSC, abs#1797; [9] Wang et al., 1999, *JGR*, 104, 8509–8519; [10] Wang et al., 2004, *JRS*, 35, 504-514; [11] Wang et al., 2004, *Am. Minerals*. 89, 665-680; [12] Kong et al., 2010, LPSC, abs# 2730; [13] Ling et al., 2011, *ICARUS*, 211, 101-113; [14] Takir et al., 2013, MPS, doi: 10.1111/maps.12171; [15] Haenecour et al., 2014, 11th GeoRaman, abs #5017; [16] Ling et al., 2014, 11th GeoRaman, abs#5089; [17] Wang et al., 2014, PSS.