

**QUANTIFICATION OF FLUORESCENCE EMISSION FROM EXTRATERRESTRIAL MATERIALS.** Jie Wei<sup>1</sup>, Alian Wang<sup>1</sup>, Walter Goetz<sup>2</sup>, and Kathryn Cornor<sup>1</sup>, <sup>1</sup>Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, St. Louis, MO, USA, <sup>2</sup>Max Planck Institute for Solar System Research (MPS), Germany, (jiewei@levee.wustl.edu).

**Introduction:** Fluorescence has long been used as an important tool in chemical and mineral analysis.[1] In organic compounds,  $\pi^*$  electronic states can be excited and lead to fluorescence emission with readily available light sources (>200 nm), while  $\sigma^*$  and  $n^*$  states are too high. Mineral fluorescence was found to vary with their sources and minor components. The presence of small traces of Rare-Earth-Elements (REE) in a mineral often generates sharp fluorescent peaks.

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.[2,3] No luminescent particles had been observed so far at the Phoenix landing site [2], and for the two rock targets at Gale Crater [4] on Mars. Furthermore, in earlier fluorescence imaging measurements of martian meteorites and returned Apollo lunar samples, no obvious fluorescence emissions were observed as well [5, 6]. 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* green Raman system without much fluorescence interferences [7-18].

Nevertheless, fluorescence emission has been a major interfering factor for the laser Raman spectroscopic measurements of some terrestrial geological samples, especially clays. Since some LRS systems are selected for definitive mineralogy and bio-signature detection for landed missions on Mars (ExoMars 2018 and Mars 2020), and LRS is anticipated to be used for many future missions, it has become necessary to **quantify** the fluorescence emission from extraterrestrial samples, in order to evaluate *if it is or isn't a treat*, to LRS for future planetary applications.

The evaluation and quantification of fluorescence emission from extraterrestrial materials is one of the tasks within the CIRS (Compact Integrated Raman Spectrometer) project selected by MATISSE program. Here, we report the preliminary results, on the fluorescence images of a series of Martian meteorites and carbonaceous chondrites. In comparison, an UV-fluorescence emitter standard (BAM) used for Phoenix-OM, some terrestrial samples including four clays standards from Clay Mineral Society and two soil sam-

ples from the Atacama Desert are measured under the same conditions, and quantified using the same methodology.

Table 1 Material list.

Category	No.	Description
Martian	1,2	MIL03346, 148/149
	3,4	EETA79001, 482/476
	5	Zagami
	6	Tissint
	7-10	NWA 3133/2788/5069/1839
Carbonaceous	11	Tagish lake (TL10a), C2
	12	Jilin, China, 1976 (fall), H5
	13	Bjurböle, Finland, 1899 (fall), LL4
	14	Independence, Jackson County, L6
	15	Dawn, H6
Terrestrial	16,17	Atacama Desert core area
	18	SWx-1
	19	KGA-2
	20	KGA-1
	21	SWy-1

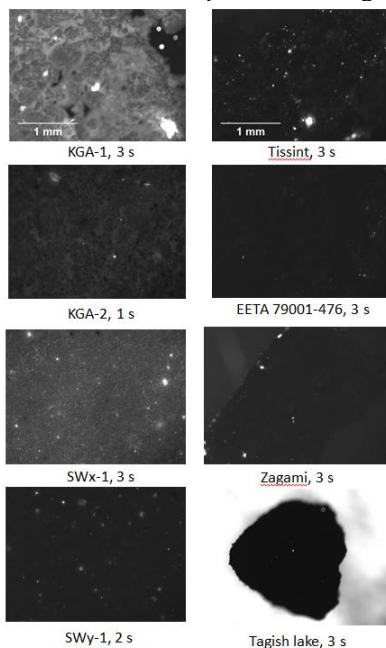
**Fluorescence microscopic measurements:** We selected to make first run of measurements using a fluorescence microscope (Nikon, E800), with a high detection sensitivity. The light source is a Xe arc lamp. Three Semrock filter sets were used to choose the excitation wavelength and the collecting fluorescence emission wavelength bands. They are:

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[11-12].

In order to quantitatively compare the fluorescence emission generated by different samples, all measurements using this microscope were carried out with the same objective (Nikon, x4/0.10) and camera gain. Exposure time was adjusted according to luminescence. Fluorethane was used as a relative standard. Luminescence intensities were normalized to the exposure time and to the fluorethane standard, for which imageJ was used.

**Fluorescent images of martian meteorites, carbonaceous meteorites, and terrestrial clays (380-396nm/412-480nm, exposure time is given):**



**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 (see the images above). In Fig. 1, the fluorescence intensity of Phoenix-OM standard BAM is also given, as a green star. Both the BAM and fluoranthene have the highest quantum yields with the UV/Blue excitation/emission bands.[2]

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 #20 (SWy-1) has the highest fluorescence levels among the samples. All the extraterrestrial samples have quantum efficiencies in  $10^{-5}$ - $10^{-4}$  region in the blue fluorescence range under UV excitation. The carbonaceous chondrites have similar quantum yields as the martian meteorites.

**Future work:** We are continue this measurement on many more extraterrestrials materials, and will report the full data set at the workshop. The use of 250 nm excitation for fluorescence emission of these samples will be carried our using our BUF imager, as the 2<sup>nd</sup> step of this investigation.

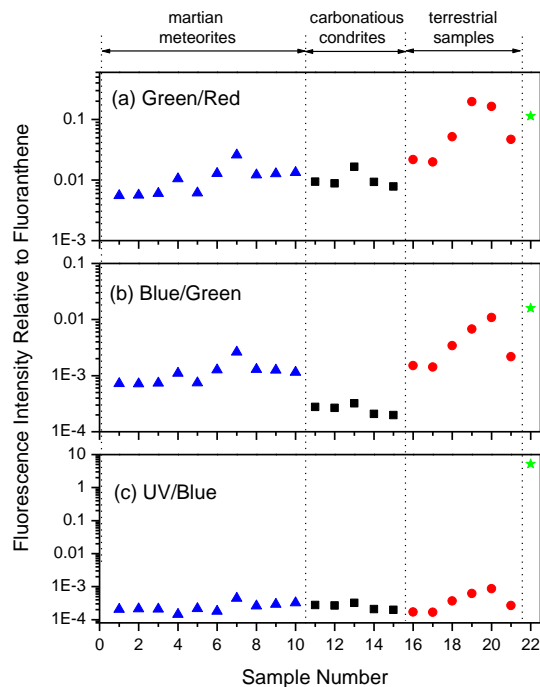


Fig. 1 Fluorescence intensities of differnent materials relative to fluoranthene, with the three excitation/collection bands. The green star represents values of BAM, the UV standard used in the Phoenix OM.

**References:** [1] Radley JA and Grant J (1939) Fluorescence analysis in ultra-violet light, Chapman & Hall Ltd. [2] Goetz W et al. (2012) Planetary and Space Sci., 70, 134. [3] Edgett K S et al. (2012) Space Sci. Rev., 170, 259. [4] Minitti et al., 2014 LPSC, abs# 2029; [5] Minitti et al., 2012 LPSC, abs# 2249; [6] Wang et al., 2003 LPSC, abs# 1753; [7] Wang et al., 1995, JGR, 100, 21189-21199; [8] Haskin et al., 1997, JGR, 102, 19293-19306; [9] Korotev et al., 1998, LPSC, abs#1797; [10] Wang et al., 1999, JGR, 104, 8509-8519; [11] Wang et al., 2004, JRS, 35, 504-514; [12]. Wang et al., 2004, Am. Minerals. 89, 665-680; [13] Kong et al., 2010, LPSC, abs# 2730; [14] Ling et al., 2011, ICARUS, 211, 101-113; [15] Takir et al., 2013, MPS, doi: 10.1111/maps.12171; [16] Haenecour et al., 2014, 11<sup>th</sup> GeoRaman, abs #5017; [17] Ling et al., 2014, 11<sup>th</sup> GeoRaman, abs#5089; [18] Wang et al., 2014, PSS.

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