

UV luminescence characterisation of organics in Mars-analogue substrates

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Abstract

Detection of organic matter is one of the core objectives of future Mars exploration. Detection of organic signatures are often hampered or modified by interaction with the host geological substrate. In that respect, UV excited Photoluminescence imaging offers a contactless, non-destructive and, through the addition of imaging, spatially resolved tool. We conducted UV induced photoluminescence analyses of (i) Mars analogue sediments and synthetic salts doped with polyaromatic hydrocarbons (PAHs), and (ii) CM carbonaceous chondrites and terrestrial kerogen. We show that that detection of PAHs in inorganic substrates is possible within gypsum and halite. Iron oxide, ubiquitously present on Mars' surface, hampers but does not completely quench the UV luminescence emission. Finally, the maturity of organic carbonaceous material influences the luminescence response.

1. Introduction

Delivery of exogenic organic matter is a daily process on Mars, up to $4 \times 10^{-4} \text{ g. m}^{-2} \text{ yr}^{-1}$ [1]. A fraction of this matter comprises PAHs, that are both ubiquitous in space and of astrobiological interest [2, 3]. The study of the fate of PAHs is the first step towards the detection of organic matter and putative organic biosignatures in situ on the martian surface. UV luminescence offers a new technique to achieve this [4, 5], whereby UV photon interactions cause electronic transitions to higher-energy states, followed by a quick relaxation and emission of a photon of longer wavelength – generally in the visible range. Compared to Raman, UV luminescence is several orders of magnitude more sensitive than Raman [6], while Raman provides more detailed structural information. Recently, the Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (“SHERLOC”) instrument was selected as part of the payload for the NASA Mars 2020 Rover mission. This instrument is a deep UV ($\lambda_{\text{ex}}=248.6 \text{ nm}$) Raman and Luminescence imaging spectrometer [7], and will be the first dedicated spectrometer with UV capability to

be deployed at the Martian surface. Here we test the potential of UV photoluminescence for detection of (i) low concentration PAHs embedded in Mars synthetic and natural analogues, and (ii) organic matter present in CM carbonaceous chondrites as a proxy for organics delivered to the Martian surface.

2. Methods and samples

Three Mars analogue sediments from Iceland were selected to represent the three broad mineral epochs of Mars: Mudstone (phyllosilicate), Gypsum (sulfate) and a Fe-oxyhydroxite “Oxide” sediment (iron oxide). These were spiked with either anthracene or pyrene (15 ppm, Sigma Aldrich PAHs solutions) and then pressed into pellets. Synthetic epsomite and halite crystals were prepared from $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and NaCl saturated solutions, including solutions spiked with either anthracene or Perylene (2 ppm), and solutions additionally spiked with iron oxide (hematite, 1 w. %). Finally, three CM chondrites were analysed, including the Meteorite Hills MET01072 meteorite (CM 2.3, 0.49 g) and the Alan Hills meteorite ALH84044 (CM2, 1.045 g), loaned from NASA JSC, USA, and Murchison (CM2.5, 1 g) loaned from the Natural History Museum, UK. A kerogen type IV sample was also included. UV luminescence analyses were performed both at room temperature, and at low temperature (30K) using the Hyperspectral Luminescence and Optical Spectroscopy (HeLIOS, Cross et al. 2013), with a number of excitation wavelengths (λ_{ex}) ranging from 225 – 375 nm.

3. Results and Discussion

Sediments-Differences in actual luminescence response are visible for Gypsum at $\lambda_{\text{ex}} = 280 \text{ nm}$ (figure 1-A, D) in the addition of perylene and anthracene, resulting in an increased luminescence at ~ 420 and 500 nm (Figure 1A). With $\lambda_{\text{ex}} = 365 \text{ nm}$, perylene does not produce such a large response when spiked onto gypsum. When spiked with PAHs, the Mudstone luminescence response shows only minimal changes with $\lambda_{\text{ex}} = 280 \text{ nm}$ excitation at ~420 nm and 580 nm (Figure 1B). PAHs on the Oxide matrix have little to no effect (Figure 1C and F). Thus, as previously observed for pure PAHs [8], the maximum

wavelength intensity for 2-5 rings PAHs is located at ~ 420 nm. **Salts**-The addition of PAHs influences the luminescence response only at $\lambda_{\text{ex}} = 365$ nm (figure 2 E-H). For all the samples, under $\lambda_{\text{ex}} = 365$ nm the addition of iron oxide also quenches the luminescence response, with an additional red emission peak at 720 nm. **Chondrites**-All meteorites and the Type IV kerogen exhibit a strong blue photoluminescence emission between 450 – 490 nm and an additional red emission luminescence peak centred at ~ 720 nm (Figure 3A), with a stronger response for CMs that have endured less thermal metamorphism. This is possibly the result of a higher maturity concentrating the chromophores (C=C and C=O bonds) and thus absorbs most of the luminescence [9].

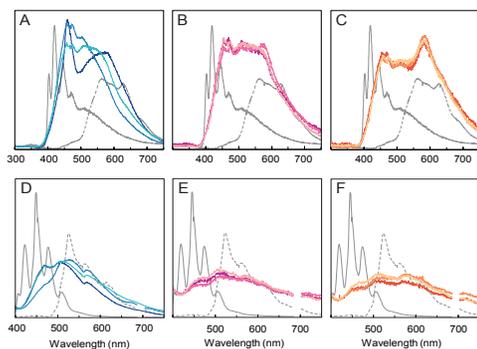


Figure 1: UV luminescence spectra of the pure Iceland sediment matrices (darkest colour) and those spiked with anthracene (mid-colour) and perylene (lightest colour) at $\lambda_{\text{ex}} = 280$ nm (A-C) and $\lambda_{\text{ex}} = 365$ nm (D-F) for Gypsum (Blue, A+D), Mudstone (Pink, B+E) and Oxide (Orange, C+F). Pure PAH luminescence spectra shown in grey (solid line = anthracene, dashed line = perylene).

For Murchison (face 2) and kerogen samples, the emission spectra become more resolved as excitation wavelength increases (figure 3B), as the number of resolvable peaks increases from 2 – 3 at the two shortest excitation wavelengths, to 5 resolvable peaks at the two longest excitation wavelengths.

4. Acknowledgements

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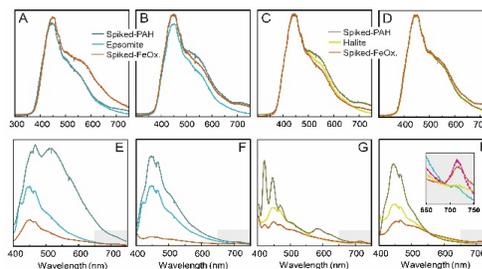


Figure 2: UV luminescence spectra of synthetic epsomite and halite at $\lambda_{\text{ex}} = 280$ nm (A -D) and $\lambda_{\text{ex}} = 365$ nm (E-H). Data are shown for crystals spiked with Anthracene (A, C, E, G) and Pyrene (B, D, F, H), and also with either PAH plus Fe oxyhydroxide (“Spiked-FeOx”).

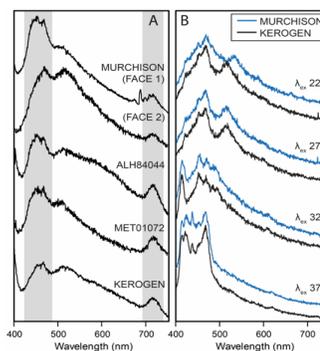


Figure 3: (A) UV luminescence spectra of carbonaceous chondrites and Type IV Kerogen, at $\lambda_{\text{ex}} = 365$ nm and room temperature. Two faces of Murchison are shown, one with a large visible chondrule (“Face 1”) and one face without any visible chondrules (“Face 2”); (B) UV luminescence spectra of Murchison (Face 2) and type IV Kerogen for $\lambda_{\text{ex}} = 225, 275, 325, 375$ nm.

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