

**TESTING THOLINS AS ANALOGS OF THE DARK REDDISH MATERIAL COVERING THE CTHULHU REGION.** M. Fayolle<sup>1,2</sup>, E. Quirico<sup>1</sup>, B. Schmitt<sup>1</sup>, L. Jovanovic<sup>3</sup>, T. Gautier<sup>3</sup>, N. Carrasco<sup>3</sup>, W. Grundy<sup>4</sup>, V. Vuitton<sup>1</sup>, O. Poch<sup>1</sup>, L. Gabasova<sup>1</sup>, S. protopapa<sup>5</sup>, L. Young<sup>5</sup> and the New Horizons Surface Composition Science Theme Team.

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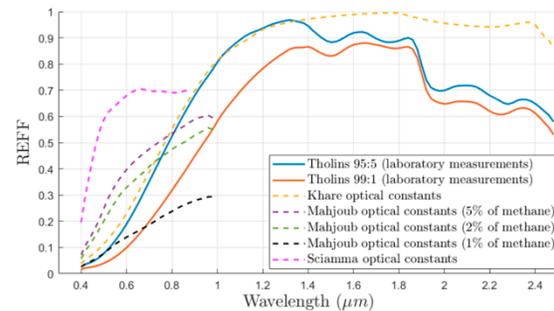
**Introduction:** Pluto's flyby by the New Horizons spacecraft in July, 2015 has brought many insights into the chemical composition of Pluto's surface. Of particular interest is the equatorial Cthulhu region, whose terrains seem to contain a dark, reddish and non-icy surface material. This material has not yet been firmly identified, and might result from the sedimentation of aerosols formed in Pluto's tenuous atmosphere, from a chemistry triggered by the dissociation of  $N_2$ ,  $CH_4$  and  $CO$  gases [2]. Complex macromolecular organic materials sharing similarities with those forming Titan's haze may then coat Cthulhu's terrains as a  $\sim 5$  m layer (assuming the present deposition rate has been the same since the formation of Pluto). Here, we question this scenario through the interpretation of MVIC/LEISA data based on laboratory experiments. The optical properties of analogs of Pluto's aerosols (tholins) were determined by spectro-gonio-radiometry, and were used to fit the reflectance spectra collected by the MVIC and LEISA instruments.

**Experimental:** Tholin samples were synthesized in a cold plasma reactor at LATMOS and recovered as a dusty material composed of spherical grains, with a size distribution peaking at  $\sim 210$  nm in radius (estimated from Scanning Electron Microscopy). Two gas compositions were used,  $N_2:CH_4=99:1$  and  $95:5$  (with 500 ppm of  $CO$  for each), relevant to atmospheric compositions at  $\sim 400$  km and  $600$  km, respectively. The tholin reflectance spectra were collected with a spectro-gonio-radiometer at IPAG operating in the range  $0.4-4 \mu m$ , covering the full spectral range of MVIC/LEISA observations ( $0.4-2.5 \mu m$ ). The absolute photometric accuracy was of 1 %, and measurements could be done under various illumination and observation geometries [3]. Measurements were carried out under vacuum and with gentle heating in order to remove adsorbed water.

**Reflectance measurements:** The reflectance spectra collected in the laboratory are displayed in Figure 1, along with spectra calculated from optical constants published in the literature. They reveal absorption bands at  $1.5$ ,  $1.75$ ,  $1.9$  and  $2.3 \mu m$ , due to overtones and combinations of N-H, C-H and CN [4].

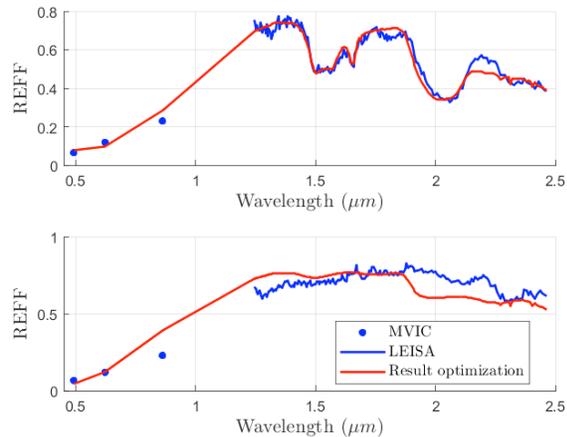
Tholin reflectance spectra were collected for incidence angles of  $0$ ,  $30$  and  $60^\circ$ , and emission angles between  $-70$  and  $70^\circ$  (every  $10^\circ$ ). Their single scattering albedo

(SSA) and phase function were determined through a least-squares inversion of a simplified Hapke reflectance model fitting the experimental data.



**Figure 1:** Tholin reflectance spectra compared to spectra calculated with optical constants from literature.

**Comparison with MVIC/LEISA:** A direct comparison of tholin spectra and MVIC/LEISA spectra (for similar illumination and observation geometries) reveals a clear mismatch: (1) tholins have a higher reflectance factor in the near-infrared; (2) the tholin absorption bands are not observed in Pluto spectra. To get a quantitative assessment, MVIC/LEISA spectra of the Cthulhu region were fitted with a Hapke reflectance model, using the inverted tholin SSA. The surface was modelled as a spatial mixing of two units: one covered with  $CH_4$  ice and the second as a mixture of  $H_2O$ ,  $C_2H_6$ ,  $CH_3OH$  ices and tholins, following [5]. An optimization algorithm has been applied to solve for the mass ratios of these compounds. This process has been conducted for two different Cthulhu spectral data, the first one corresponding to the  $H_2O$ -rich region and the other one to the  $H_2O$ -poor region. The best match (Fig. 2) between the numerical model and MVIC/LEISA data has been obtained with the  $N_2:CH_4=99:1$  tholins. Once mixed with hydrocarbon ices, they account fairly well for the Cthulhu photometric level, but not for the visible spectral slope in the  $H_2O$ -poor terrains, and they still display weak overtone/combination bands that are not present in LEISA observations.



**Figure 2:** Best optimization results for the H<sub>2</sub>O-rich (upper panel) and H<sub>2</sub>O-poor (lower panel) regions.

Three explanations, at least, are possible to account for this misfit. (1) The terrains may be contaminated by interplanetary dust impacting, bringing dark materials into the aerosols layer. However, additional experiments on tholins mixed with pyrrhotite (an opaque mineral as analog of dark interplanetary dust) and subsequent modelling led to a drop of the reflectance in the near-infrared. (2) Galactic Cosmic Rays (GCR) irradiation is known to promote dehydrogenation reactions, carbonization and perhaps amorphization. This scenario needs to be tested through experimental simulations. Nevertheless, if the dark materials of the Cthulhu terrains result from aerosol sedimentation, the effective exposure duration would not last over  $\sim 50000$  years, which corresponds to a low irradiation dose. (3) A high porosity of the dark terrains is the third explanation. Laboratory experiments have shown that a highly porous tholin crust, formed from sublimation experiments, does not display combination/overtone bands in the near-infrared [6]. On Pluto, ice/tholin sublimation, or simply low gravity deposition, may promote the formation of highly porous materials, which do not show bands in the near-infrared.

**References:** [1] Stern, A., et al. (2015) *Science*, 350, aad1815. [2] Grundy, W., et al. (2018) *Icarus*, 314, 232-245. [3] Potin, S., et al. (2018) *Applied optics*, 57(28), 8279-8296. [4] Cruikshank, D., et al. (1991) *Icarus* 94, 345-353. [5] Cook, J., et al. (2018) *Icarus*, In press. [6] Poch, O., et al. (2016) *Icarus*, 267, 154-173.