

## Testing tholins as analogs of the dark reddish material covering the Cthulhu region

**Marie Fayolle** (1,2), Eric Quirico (1), Bernard Schmitt (1), Lora Jovanovic (3), Thomas Gautier (3), Nathalie Carrasco (3), Will Grundy (4), Véronique Vuitton (1), Olivier Poch (1), L. Gabasova (1), Silvia protopapa (5), Leslie Young (5) and the New Horizons Surface Composition Science Theme Team.

(1) Université Grenoble Alpes/CNRS IPAG France, (2) TU Delft, The Netherlands, (3) LATMOS Guyancourt, France, (4) Lowell Observatory Flagstaff USA, (5) Southwest Research Institute Boulder USA.

### Abstract

Pluto's fly-by by the New Horizons spacecraft in July 2015 has revealed a dark reddish equatorial region (informally named Cthulhu). The non-icy material constituting the terrains of this region may have been formed from the sedimentation of aerosols [1,2]. Here, we investigate this hypothesis through the interpretation of the data collected by the visible imager (MVIC) and the near-infrared spectrometer (LEISA). Analogs (tholins) of Pluto's aerosols were synthesized in conditions that mimic Pluto's high atmosphere, and their optical properties were determined and used in Hapke models. We show that some of these tholins fit the reflectance level fairly well in the near-infrared, but don't match the shape of the red visible slope. In addition, several tholin bands are absent in LEISA observations, which might be due to a highly porous crust (formed from ice/tholin sublimation or microgravity), or to GCR irradiation. The first is our preferred interpretation.

### 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 ~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.

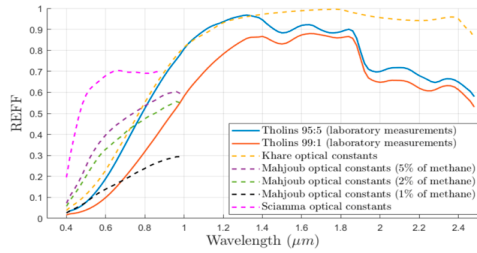
### 1. Experimental

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 ~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 ~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.

### 2. 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].

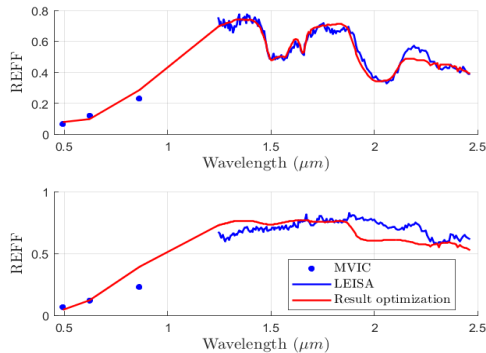
Tholin reflectance spectra were collected for incidence angles of 0, 30 and 60°, and emission angles between -70 and 70° (every 10°). Their single scattering albedo (SSA) and phase function were determined through a least-squares inversion of a simplified Hapke reflectance model fitting the experimental data.



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

### 3. 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  $\text{CH}_4$  ice and the second as a mixture of  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{OH}$  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  $\text{H}_2\text{O}$ -rich region and the other one to the  $\text{H}_2\text{O}$ -poor region.



**Figure 2:** Best optimization results for the  $\text{H}_2\text{O}$ -rich (upper panel) and  $\text{H}_2\text{O}$ -poor (lower panel) regions.

The best match (Fig. 2) between the numerical model and MVIC/LEISA data has been obtained with the

$\text{N}_2:\text{CH}_4=99:1$  tholins. Once mixed with hydrocarbon ices, they account fairly well for the Cthulhu photometric level, but not for the visible spectral slope in the  $\text{H}_2\text{O}$ -poor terrains, and they still display weak overtone/combination bands that are not present in LEISA observations.

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.: The Pluto system : Initial results from its exploration by New Horizons. *Science*, 350, aad1815, 2015.
- [2] Grundy, W., et al.: Pluto's haze as a surface material. *Icarus*, 314, pp 232-245, 2018.
- [3] Potin, S., et al.: Shadows: A spectro-gonio radiometer for bidirectional reflectance studies of dark meteorites and terrestrial analogues. Design, calibrations and performances on challenging surfaces. *Applied optics*, 57(28), pp.8279-8296., 2018.
- [4] Cruikshank, D., Allamandola, L., Hartmann, W., Tholen, D., Brown, R., Matthews, C., and Bell, J.: Solid CN bearing material on outer solar system bodies. *Icarus* 94, pp 345-353, 1991.
- [5] Cook, J., et al.: The distribution of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  and hydrocarbon-ices on Pluto: analysis of New Horizons spectral images. *Icarus*, 2018.
- [6] Poch, O., et al.: Sublimation of water ice mixed with silicates and tholins: evolution of surface texture and reflectance spectra, with implications for comets, *Icarus* 267, pp 154-173, 2016.