THE COLORS OF 486958 2014 MU_{69} ("ULTIMA THULE"): THE ROLE OF SYNTHETIC ORGANIC SOLIDS (THOLINS).

D. P. Cruikshank[1], W. M. Grundy[2], D. T. Britt[3], E. Quirico[4], B. Schmitt[4], F. Scipioni[5], C. M. Dalle Ore[5], J. C. Cook[6], L. Gabasova[4], S. Protopapa[7], S. A. Stern[7], H. A. Weaver[8], A. J. Verbiscer[9], J. R. Spencer[7], C. J. A. Howett[7], R. P. Binzel[10], A. H. Parker[7], New Horizons Composition Team. [1]NASA Ames Research Center, MS 245-6, Moffett Field, CA (Dale.P.Cruikshank@NASA.gov), [2]Lowell Observatory, Flagstaff, AZ (w.grundy@lowell.edu), [3]University of Central Florida, [4]Université Grenoble Alpes, [5]SETI Institute, Mountain View, CA, [6]Pinhead Institute, Telluride, CO, [7]Southwest Research Inst., Boulder, CO, [8]Applied Physics Lab., Laurel, MD, [9]Univ. Virginia, Charlottesville, VA, [10]MIT, Cambridge, MA

Tholins as coloring agents on planetary surfaces: Many Solar System bodies exhibit colors in the visible spectral region that range from yellow to red to brown. From color alone, and in the absence of diagnostic spectral bands, the composition of the chromophore(s) cannot be unequivocally determined, and many candidate materials have no strong absorption bands at $\lambda<3\mu m$ wavelength. Some minerals are naturally colored, and others acquire color by space weathering processes that abstract iron from Fe- and Ni-bearing minerals and deposit nanometer-size blebs on regolith grains [1]. In cases of icy surfaces, the red or brown colors are interpreted as refractory complex organic solids synthesized by the photolysis or radiolysis of carbon-bearing components, particularly CH_4 ice [2,3]. In laboratory simulations of astrophysical settings, these complex organics are called *refractory residues* [4,5], while those synthesized in simulations of planetary environments are called *tholins*. In terms of composition, chemical structure, and origin, the definition of tholins is broadly encompassing . The colors of the Kuiper Belt object Ultima Thule (UT) emerging from a preliminary analysis of data returned from the New Horizons spacecraft within a few days of the flyby event of January 1, 2019, are described in [6,7] and compared with comets. Both of these investigations note that when all the data are available for analysis, the explanation for the red color UT will probably require a coloring agent in the form of a tholin made in simulated planetary conditions in the laboratory (see [8]).

Tholins are relevant both to atmospheres and surfaces of planetary bodies. They are created in the laboratory and are broadly characterized as relatively refractory (i.e., stable at T>100 K) organic complexes produced by energetic processing of simpler carbon-bearing and other molecules in the gas or solid phase. Tholins are disordered polymer-like materials made of repeating chains of linked subunits and complex combinations of functional groups. Khare *et al.*, [9,10] showed that colored particles are made by UV photolysis of gaseous CH_4 and N_2 in simulated Titan atmosphere conditions. While the complex refractive indices of this "Titan tholin" published by Khare *et al.* [11] have been used in modeling spectra of the surfaces of many planetary bodies, the analytical techniques available in the laboratory at the time the tholin was synthesized were insufficient to reveal the full details of its complex structure (e.g., [9]). A more complete structural analysis of Titan tholins made over a range of gas pressures relevant to Titan's atmosphere showed that the quantity and size of aromatic ring compounds increases with decreasing pressure, and the abundance of saturated C-H bonds is less at low pressures, with a concomitant increase in N-H bonds [12,8]. Additionally, the C/N ratio is greater at high pressure because N is incorporated into the tholin less efficiently. Tholins formed at low gas pressures have clusters of N-substituted polycyclic aromatic compounds connected by C- and N- branched networks. The pressure also affects the degree of N-substitution in both aromatic and aliphatic structures. In terms of color, tholin films formed at low pressure show stronger UV/Vis absorptions and are reddish-brown, in contrast to yellow-colored tholins formed at higher pressure. The efficacy of using gas-phase tholins to model solid surfaces can be questioned, but the absence of optical constants for tholins made in conditions considered more appropriate has resulted in their use as the best available data. In addition, complex organics occurring as a component (together with minerals and ices) of the bulk composition of Kuiper Belt objects may reflect formation in a gas-rich environment in the nascent solar nebula. In terms of modeling planetary surfaces, we note that the particular radiative transfer model in which the optical constants of tholins are used can be a major factor in the interpretation of the results, because values for the derived relative concentrations, particle sizes and other parameters vary significantly [13].

Tholins that appear to be more directly related to the surfaces of planetary bodies that are mostly or entirely ice-covered and have extremely tenuous atmospheres (e.g., Pluto) or no atmosphere (e.g., Charon) can be synthesized in the laboratory by the energetic processing of ices of various compositions. Early ice experiments [3] produced tholins containing carboxylic acids, urea, HCN and other nitriles, alcohols, ketones, aldehydes, and amines, with other unidentified materials of high molecular weight (several hundred Da). Corresponding experiments related to Pluto used UV and kilovolt electron irradiation to produce refractory residues in an ice mix of N_2, CH_4, and CO [14,15]. Those experiments showed that the degree of N substitution in both aromatic and aliphatic structures was significantly greater in the e^- radiolysis runs than those photolyzed by UV, because the electrons were more efficient in breaking the N≡N bond. The color, composition, and molecular structural properties of the radiolytic tholin in [15] were expanded upon in [16] (Fig. 1)

Preliminary results suggest that both the albedo and the color of UT are relatively uniform across the surfaces of the two near-spherical components, with the notable exception of the neck region where they are in contact. In that zone the albedo is higher and the color is less red than elsewhere, possibly as a consequence of small particle size and downhill movement of material. Although the bulk composition of UT is expected to include fine-grained mineral material, it is likely that the dominant components are ices, with H_2O being the most abundant. Additional native ices are expected to include CH_4, NH_3, and possibly the more volatile CO, and N_2, all of which are likely components of the early solar nebula. CH_4 and other hydrocarbons are most amenable to photolytic and radiolytic alteration to refractory complex organics, and in most laboratory tholin synthesis experiments is the principal C-bearing component.

The observed composition of comets may reflect the bulk composition of UT, although with much of the comets' volatile inventories evaporated away by passage(s) through the inner Solar System (see [17]). New insight into the composition of refractory organic complexes that occur in comets comes from the Rosetta investigation of comet 67P/Churyumov-Gerasimenko, both from remote sensing observations of the nucleus from close range [18] and from the in situ analysis of solid particles ejected from the nucleus and collected by the spacecraft [20]. The low albedo of the nucleus of 67P results from a mixture of a dark refractory polyaromatic carbonaceous component (consistent with the broad definition of tholin) and opaque minerals thought to be iron sulfides and Fe-Ni alloys [18]. Particles ejected from the nucleus and analyzed on the spacecraft are consistent with the remote sensing data with nearly equal fractions by weight of organic matter and anhydrous mineral phases [19]. While the low albedo of the comet's nucleus is accounted for in this mixture, the ultra red color in the visible spectral region is not.

The color of UT will be fully evaluated when the complete data set is available, and detailed comparisons can be made with other Kuiper Belt objects, planetary satellites, and comets, and the role of tholins can be modeled. See Fig. 2.

References:[1] Hapke, B. (2001) *JGR Planets* 106 (E5), 10039-10074. [2] McDonald G. D. et al. (1996) *Icarus* 122, 107-117. [3] Thompson, W. R. et al. (1987) *JGR* 92, 14,933-14,947. [4] Bernstein, M. P. et al. (1995) *Astrophys. J.* 454, 327-344. [5] Greenberg, J. M. et al. (2000) *Astrophys. J. Lett.* 531, L71-L73. [6] Quirico, E. et al. (2019) This conference. [7] Protopapa, S. et al. (2019) This conference. [8] Cruikshank, D. P. et al. (2005) *Adv., Space Res*. 36, 178-183. [9] Khare, B. N. et al. (1981) *Icarus* 48, 290-297. [10] Khare. B. N. et al. (1984) *Adv. Space Res.* 4, 59-68. [11] Khare, B. N. (1984) *Icarus* 60, 127-137. [12] Imanaka, H. et al. (2004) *Icarus* 168, 344-366. [13] Poulet, F. et al. (2002) *Icarus* 160, 3313-324. [14] Materese, C. K. et al. (2014) *Astrophys. J.* 788, 111 (11pp), June 20. [15] Materese, C. K. et al. (2015) *Astrophys. J.* 812, 150 (9pp), October 20. [16] Cruikshank, D. P. et al. (2016) *47th LPSC* abstract 1700. [17] Poch, O. et al. (2016) *Icarus* 266, 288-305. [18] Quirico, E. et al. (2016) *Icarus* 272, 32-47. [19] Bardyn, A. et al. (2017) *MNRAS* 469, 571-5722.

Acknowledgements: This work was funded by NASA. We thank NASA, the Deep Space Network, JPL, KinetX Aerospace, the entire present and past New Horizons team, and the Gaia and HST missions for making the flyby of MU69 successful.

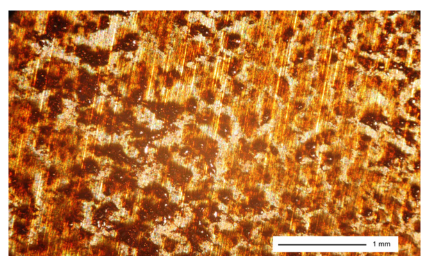

Figure 1. Natural color and texture of Pluto ice tholin from [15], made by electron radiolysis of an ice mixture of N_2:CH_4:CO (100:1:1). Striations are scratches in Al foil substrate on which the ice was deposited. Scale bar 1 mm.

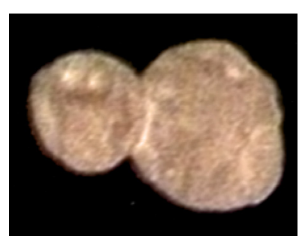

Figure 2. Ultima Thule from New Horizons. The color from a lower resolution Multispectral Visible Imaging Camera (MVIC) image was overlaid on a Long Range Reconnaissance Imager (LORRI) image taken on 1 Jan 2019, 05:01:47 UTC.