Introduction: The surface of Pluto displays an array of colors ranging from yellow to red to brown, while the surface of Charon is largely gray with a north polar zone of red color similar to regions on Pluto[1,2]. Pluto's surface shows layers of intensely colored material in tilted and transported blocks, and fractured geographical units. This arrangement suggests episodes of formation or deposition of that material interspersed with episodes of emplacement of ices having little or no color. The ices identified on the surfaces of these two bodies (N₂, CH₄, CO, C₂H₆, H₂O on Pluto, and H₂O and NH₃ on Charon)[3,4] are colorless, as are nearly all ices in a powdery state. The colors on Pluto probably arise from the in situ formation of a macromolecular carbonaceous material generated by energetic processing of the ices on the surface[5]. Laboratory experiments producing refractory tholins particularly relevant to Pluto explored the chemistry of both UV and low-energy electron bombardment of a mix of Pluto ices $(N_2:CH_4:CO = 100:1:1)[6,7]$. We can term this Pluto ice tholin PIT.

Water ice in the crystalline state characterizes Charon's surface, and while most of Charon's surface is neutral in color, with geometric albedo ~0.38 [2,3], the polar zone and a light cover of fainter but similar reddish color over some surface regions suggest a common origin with the colored material on Pluto. NH₃ or NH₃•*n*H₂O was identified from disk-integrated Earth-based spectra[e.g.,8,9], and a few concentrated NH₃ exposures have been found in the New Horizons spectral images [10].

Open Questions: In terms of the composition and evolution of the surfaces of Pluto and Charon, a number of puzzles present themselves. Why does H_2O ice dominate the surface of Charon? What is the origin of the NH₃ or NH₃ hydrate found in low abundance over most of the surface, with a few isolated outcrops of higher concentration? How can NH₃ persist on Charon when it is readily destroyed by UV radiation? Why is the overall albedo of Charon rather low and the color mostly neutral, except for the north polar region, which displays a color similar to many regions on Pluto? Why is NH₃ or its hydrate not identified on Pluto, while a number of other molecules are?

Toward an Understanding: Turning first to recent laboratory studies of the refractory residues left from the UV or electron irradiation of the Pluto ice mix (PIT) noted above, chemical analysis shows the presence of a number of small molecules, including NH₃, plus complex macromolecular carbonaceous material. Mass spectra of organic molecules desorbed from the residue show a high degree of aromatization, while UV fluorescence imaging shows an overall high concentration of organics. The yellow-to-brown colors of the residue are consistent the presence of conjugated carbon-carbon chains. Material of comparable complexity characterizes the insoluble organic matter (IOM) in carbonaceous meteorites[11]. IOM is found to contain small molecules and radicals trapped in the carbonaceous complex for astronomical time scales. The PIT also contains small molecules, notably NH₃, and probably radicals that are stable on long timescales.

The low albedo and neutrally colored regions of Charon may be caused by the presence of tholin, possibly PIT, that has largely been radiation processed to the point where most of the hydrogen is lost and the color has consequently vanished. This overprocessing, or carbonization of tholins is known from early work[e.g., 12]. Such over-processing would be expected for an old surface that is not refreshed with PIT, which might either be excavated from depth, where it was made in a previous epoch of this body's history, or made currently or recently from an inventory of N₂ and CH₄ ices. In this view, the surface underlying the gray material bears orange PIT that has been protected from overprocessing, or possibly a mix of CH₄ and N₂ ices in which PIT has been made relatively recently through the same or similar processes as are currently active on Pluto itself. The visible surface ice layer(s) of Charon are dominantly composed of the very refractory crystalline H₂O ice, as noted above, and its low albedo is a consequence of intermixing or light blanketing by carbon-dominated, over-processed tholin.

Concerning the current presence of NH₃ or NH₃•H₂O exposed over most of Charon, NH₃ synthesized in the tholin-making process and trapped for a long time can slowly diffuse out of the complex tholin matrix, diffuse through the overlayer of H₂O ice, and appear in small concentration on the optical surface, as detected spectroscopically. The destruction by UV and replenishment by upward diffusion would, in principle, reach some balance, and that balance could be different in different epochs of the evolution of the Pluto-Charon system. It is also noteworthy that NH₃ diffusing through H₂O results in the hydration of the ammonia, thus producing NH₃•*n*H₂O[13,14]. Other small molecules may also diffuse out of the tholin,, but either fail to emerge on the surface with the H₂O ice, or go undetected because of low concentration or spectroscopic insensitivity. Other such molecules could include H_2CO , HCOOH, and N-bearing species. There has been no detection of NH_3 or its hydrate(s) on Pluto to date, but they may be present and undetectable because of low concentration and the interference of other, stronger absorption bands of the known constituents.

In order for tholin to be made on Charon's surface, the necessary ingredients must be present, at least for some period of time. A nitrogen-bearing molecule is clearly needed to produce the NH₃ now seen. PIT is N-rich (N/C~0.9 for the electron-generated tholin[6]), so the very volatile N₂ is needed, in addition to CH₄, which is significantly less volatile. The presence of colored PIT or similar material on Charon is indicated by the coloration of the north polar region. Thus, while a primordial inventory of NH₃ could be native to Charon, it appears more likely that N₂ was an initial component of the body, as it apparently was for Pluto. If, then, Pluto and Charon shared a common inventory of primordial ices, there could have been an epoch in Charon's history when a PIT-like material would form there before all the N₂ was lost. Remaining CH₄ ice would be radiation processed to the point of the loss (or near loss) of the CH₄ spectral signature and its conversion to elemental carbon, which now appears as a neutral, albedo-lowering component of the H₂O ice surface.

This view of the chemical evolution of Charon's surface appears to require that some amount of N_2 and CH_4 survived the event of its formation so that the raw materials for tholin formation were available for the synthesis of the colored and neutral components. Pluto's volatile inventory somehow survived the moonforming event, as well as tidal heating that must have occurred after Charon was formed and as the two bodies became locked in rotation-revolution. Similarly, some fraction of Charon's volatiles must have survived the tidal heating.

Summary and Conclusions: A hypothesis is presented to link the color and chemical characteristics of Pluto and Charon to the histories of their volatile inventories and to recent laboratory experiments. Pluto's surface and atmosphere are chemically active in that photolysis and radiolysis of N_2 , CH_4 , and CO found in both the gaseous and solid states is in progress, producing refractory materials that color the landscape to varying degrees, most likely dependent on the ages of surface units, and the level of atmospheric density over time.

 NH_3 found on Charon may be explained as a product of the radiation processing of the same simple molecules as now found on Pluto and sequestered in the resulting complex organic material that is referenced here as Pluto ice tholin (PIT). While the modern surface of Charon is denuded of N_2 and (possibly) CH_4 ices, the PIT generated in an earlier epoch underlies the H_2O ice surface. NH_3 diffuses out of the PIT and through the H_2O to emerge on the surface, where it soon is lost by dissociation. Some or all of the NH_3 is hydrated by the process of diffusion through H_2O ice.

The colored region at Charon's north pole results from the excavation of PIT formed in an earlier epoch by the removal of the H₂O-ice-dominated overlayer. The region around the crater informally called Organa[10] is enriched in NH₃ by some aspect of the impact process that produced it, perhaps by reducing the overburden of H₂O ice, thus exposing a layer in which NH₃ diffusing out of tholin had accumulated.

The hypothesis presented here challenges scenarios of the formation of the Pluto-Charon binary and concepts of volatile retention by both components in the face of the energetics of formation and tidal locking. It further invites a closer look at the formation and evolution of the coloring components of the surfaces of both bodies.

References:

- [1] NASA press release of Oct. 1, 2015.
- [2] Stern, S. A. et al. (2015) *Science* Issue 6258, id.aad1815
- [3] Cruikshank, D. P. et al. (2015) Icarus, 246, 82-92
- [4] NASA press release of Oct. 8, 2015.
- [5] Cruikshank, D. P. et al. (2016) LPSC abst.
- [6] Materese, C. K. et al. (2014) *Ap.J.*, 788, 111 (11 pp) June 20.
- [7] Materese, C. K. et al. (2015) *Ap.J.*, *812*, 150 (9 pp) October 20.
- [8] Cook, J. C. et al. (2007) *Ap.J.* 663, 1406-1419.
- [9] Merlin, F. et al. (2010) Icarus 210, 930-943.
- [10] NASA press release of Oct. 29, 2015.
- [11] Delpoux, O. et al. (2011) *Geochim. Cosmochim Acta*, 75, 326-336.
- [12] Thompson, W. R. et al. (1987) J. Geophys. Res. 92, 14,933-14,947.
- [13] Uras, N. and Devlin, J. P. (2000) J. Phys. Chem A 104, 5770-5777.
- [14] Livingston, F. E., et al. (2002) J. Phys Chem A 106, 6309-6318.