Haze and Cosmic Ray Influences on Pluto's Compositional Environments. W.M. Grundy[1], R.P. Binzel[2], M.W. Buie[3], A.F. Cheng[4], J.C. Cook[5], D.P. Cruikshank[6], C.M. Dalle Ore[6,7], A.M. Earle[2], K. Ennico[6], D.E. Jennings[8], C.J.A. Howett[3], I.E. Linscott[9], A.W. Lunsford[8], W.B. McKinnon[10], C.B. Olkin[3], A.H. Parker[3], S.Protopapa[11], D.C. Reuter[8], K.N. Singer[3], J.R. Spencer[3], S.A. Stern[3], H.A. Weaver[4], and L.A. Young[3]. [1]Lowell Observatory, Flagstaff AZ (w.-grundy@lowell.edu); [2]Massachusetts Institute of Technology, Cambridge MA; [3]Southwest Research Institute, Boulder, CO; [4]Johns Hopkins University Applied Physics Laboratory, Columbia MD; [5]Unaffiliated, Westminster CO; [6]NASA Ames Research Center, Moffett Field CA; [7]SETI Institute, Mountain View CA; [8]NASA Goddard Space Flight Center, Greenbelt MD; [9]Stanford University, Stanford CA; [10]Washington University of St. Louis, St. Louis MO; [11]University of Maryland, College Park MD.

Pluto surface context: The 2015 exploration of Pluto by NASA's New Horizons spacecraft revealed a spectacular diversity of landscapes across the planet, ranging from ancient, heavily cratered terrains to youthful regions being rapidly resurfaced by sublimation, condensation, glaciation, and convection [1,2]. Near-infrared spectral maps show strikingly varied compositions [3], including volatile ices of N_2, CO, and CH_4, along with ices of H_2O and heavier hydrocarbons that are inert at Pluto surface temperatures (30 to 60 K). Energy inputs to Pluto's surface environment from insolation and radioisotope decay are minuscule compared with terrestrial values. Yet abundant volatile compounds enable geological activity that reshapes Pluto's surface through diverse geological processes acting over a range of timescales, as attested to by the complex and highly heterogeneous spatial distribution of these materials and the features they form. As on Earth, the presence and activity of volatiles enables modification and mobilization even of inert materials, creating an especially rich geological tapestry.

Drivers of chemical evolution: Pluto's surface and atmosphere are exposed to space radiation with energies sufficient to break chemical bonds. Solar ultraviolet light is one key source. Much of the UV is Ly α (1216 Å, 10.2 eV), with a flux at Pluto's 39 AU mean heliocentric distance of $\sim 2 \times 10^{12}$ photons $m^{-2}\ s^{-1}$. Ly α photons have insufficient energy to break the N≡N triple bond in N_2 (though scarcer, shorter wavelength UV photons can do so), but they readily break the C−H bond in methane. Ly α is thus strongly absorbed by CH_4 in Pluto's upper atmosphere [4]. UV light leads to photochemical production of heavier hydrocarbons, primarily C_2H_2, C_2H_4, and C_2H_6, although nitriles such as HCN and HC_3N are also produced [5].

Another contributor to atmospheric chemistry is the plasma of solar wind protons and electrons with typical energies in the keV range. Upstream of Pluto's atmosphere, fluxes of these particles are of the order of 10^9 to 10^{10} particles $m^{-2}\ s^{-1}$, albeit highly time-variable [6]. Details of the plasma interaction with the atmosphere are uncertain, but it is likely an important additional driver of radiolytic chemistry, with each particle having ~100 × the energy of a Ly α photon.

Photolysis and radiolysis cause formation of haze particles in Pluto's upper atmosphere, hundreds of km above the surface [4,7,8]. These settle out relatively rapidly, on timescales of order days to months. On descent, they grow through accretion of additional material. At a few 10s of km altitude the atmospheric temperature reaches 110 K [4], above the melting points of C_2H_4 and C_2H_6. Initially fractal, fluffy haze particles could partly melt there and collapse to spherical shapes due to surface tension, hastening their descent. The mass flux of haze particles to Pluto's surface is estimated as 5×10^{-7} kg $m^{-2}\ yr^{-1}$ [5] with a composition consisting of 91% hydrocarbons and 9% nitriles by mass. Stoichoimetrically, H:C:N are 35:24:1.

Absorption by Pluto's atmosphere prevents EUV photons ($\lambda \leq$ Ly α) and solar wind particles from reaching the surface, at least during present-day atmospheric conditions. But if/when the atmosphere seasonally collapses [9,10], surface ices would be directly affected by these radiation sources, though haze already on the surface would only be processed in zones where the frozen-out atmosphere did not cover it.

Cosmic rays penetrate Pluto's atmosphere, with energies in the MeV through GeV range. When such a highly energetic particle impacts the surface, it triggers a cascade of lower energy secondary and tertiary particles that penetrate further into the surface, creating a substantial swath of damage: broken chemical bonds and excited radicals that react to create new chemical species. At lower energies, this cascade is dominated by the component nuclei and electrons of the target atoms (elastic collisions), while at higher energies, atomic nuclei themselves can be disrupted, producing a shower of more exotic particles (inelastic collisions). Estimates of cosmic ray penetration into the heliosphere suggest that Pluto receives relatively low fluxes of 100 keV to 10 MeV protons compared with objects orbiting closer to the heliopause [11], but above 100 MeV, the fluxes are similar. Cosmic rays are sparse, but the energies delivered by individual particles are enormous, and over time they can modify surface chemistry, too.

Three distinct chemical environments: The combined compositional influence of settling haze particles and cosmic rays on Pluto's surface is explored here for 3 distinct provinces: (1) ancient, volatile-free regions, (2) intermediate age CH_4 ice deposits, and (3) youthful, convecting N_2 ice glaciers. Knowing neither the long-term evolution of Pluto's atmospheric structure and haze production nor cosmic ray exposure history, our null hypothesis is that present-day conditions apply throughout the planet's history.

Pluto's **volatile-free equatorial belt** is exemplified on the encounter hemisphere by eastern Cthulhu Regio[1], much of it heavily cratered and presumably ancient. Similar-looking maculae girdle the planet, dark and red at visible wavelengths with higher near-infrared albedos between 1.25 and 2.5 µm [12]. From estimated haze production rates [5], 500 g settles onto each m^2 of otherwise inert surface every Myr, producing an optically thick ~5 mm coating if its bulk density is 1000 kg m^{-3}. Estimates of cosmic ray radiolysis at 40 AU [11] suggest that depths down to only ~10^{-5} mm receive chemically significant doses in a Myr, so cosmic rays cannot process the accumulating material fast enough to keep up with the fallout. Those calculations ignore effects of secondary particles from higher energy inelastic collisions, and are thus only a lower limit. But it looks difficult to explain the dark reddish coloration of the equatorial maculae if Pluto's surface was perpetually shielded from other sources of energetic radiation by the atmosphere, since the hydrocarbons in the haze would be neither red nor dark without radiolytic processing. Episodes of atmospheric freeze out would enable much more radiation to reach the ground and redden the accumulating hydrocarbon material in those zones, but the atmospheric freeze-out would need to occur at non-equatorial latitudes.

Pluto has various **regions rich in CH_4 ice** [3], with some admixture of N_2 and CO ices [13]. These include Lowell Regio (the north polar zone), the bladed terrain of Tartarus Dorsa, bright mid-latitude crater rims and scarps, and mountain ridges. Many of these areas show morphological evidence for km-thick mantling of underlying topography. Such thick CH_4 ice deposits would require many Pluto seasons to accumulate and so could be related to the ~3 Myr cycle of mega-seasons [14], or perhaps something even longer. If such a deposit takes 1 Myr to form, it would incorporate 0.5 cm of haze, or 5 parts per million of its bulk volume. That sounds paltry, but if it arrives as 1 µm spheres [8], there would be ~5000 haze particles per cm^3 of CH_4 ice. They could significantly alter the rheological behavior by pinning grain boundaries, unless they dissolve into the CH_4 ice (solubilities in CH_4 of many of the relevant hydrocarbons and nitriles are unknown). If the CH_4 ice accumulates slower, the fraction of haze incorporated would be greater still. These deposits appear pale in color, consistent with deposition too fast for appreciable radiolysis even during times of atmospheric collapse. But uplands in Lowell Regio feature a distinctive golden hue, suggesting they could be more ancient deposits, or had received additional radiation during airless seasons. Perhaps this is where the atmosphere was sequestered and irradiated during seasonal atmospheric collapse.

Finally, consider the **N_2 ice in Sputnik Planitia** [15]. Convective overturn timescales are of the order of 10^5 years and the thickness of the glacier is likely in the range of 1 to a few km. Haze particles deposited on the glacier surface would collect until they reach a subduction zone after ~10^5 years and 0.5 mm of accumulation, possibly along with CH_4 ice that had seasonally condensed onto the surface of the glacier. If that material is subducted, it would be convectively mixed into (and possibly dissolved in) the N_2 ice. If Sputnik is 2 km thick and has been churning for 4 Gyr, then accumulated haze could account for ~1% of its bulk. Whether that amount of heavier hydrocarbons and nitriles would significantly alter the rheology of the N_2 ice is unclear, but even smaller fractional quantities of C dramatically affect the mechanical properties of Fe.

Conclusion: Extrapolating Pluto's present-day atmospheric haze production over geological history, suggests hydrocarbon haze particles could be the main constituent of volatile-free regions on Pluto. The accumulation rate is too great for only the radiation that penetrates through Pluto's atmosphere to account for their dark red coloration, calling for airless episodes. Haze particles could be a mechanically significant contributor to thick CH_4 ice mantles in many regions and even to the glacial ice in Sputnik Planitia. Cosmic ray damage accumulates slowly. It could play a role in Pluto's most ancient regions, but times of atmospheric collapse are likely required to account for observed levels of radiolytic processing of surface materials.

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[1] All place names in this abstract are informal.