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PLUTO'S SPUTNIK PLANITIA: COMPOSITION OF GEOLOGICAL UNITS FROM INFRARED SPECTROSCOPY

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Abstract

We have compared spectroscopic data of Sputnik Planitia on Pluto, as acquired by New Horizons' Linear Etalon Imaging Spectral Array (LEISA) instrument, to the geomorphology as mapped by White et al. (2017) using visible and panchromatic imaging acquired by the Long-Range Reconnaissance Imager (LORRI) and the Multi-spectral Visible Imaging Camera (MVIC). We have focused on 13 of the geologic units identified by White et al. (2017), which include the plains and mountain units contained within the Sputnik basin. We divided the map of Sputnik Planitia into 15 provinces, each containing one or more geologic units, and we use LEISA to calculate the average spectra of the units inside the 15 provinces. Hapke-based modeling was then applied to the average spectra of the units to infer their surface composition, and to determine if the composition resulting from the modeling of LEISA spectra reflects the geomorphologic analyses of LORRI data, and if areas classified as being the same geologically, but which are geographically separated, share a similar composition. We investigated the spatial distribution of the most abundant ices on Pluto's surface - CH₄, N₂, CO, H₂O, and a non-ice component presumed to be a macromolecular carbon-rich material, termed a tholin, that imparts a positive spectral slope in the visible spectral region and a negative spectral slope longward of ~1.1 μm. Because the exact nature of the non-ice component is still debated and because the negative spectral slope of the available tholins in the near infrared does not perfectly match the Pluto data, for spectral modeling purposes we reference it generically as the negative spectral slope endmember (NSS endmember). We created maps of variations in the integrated band depth (from LEISA data) and areal mass fraction (from the modeling) of the components. The analysis of correlations between the occurrences of the endmembers in the geologic units led to the observation of an anomalous suppression of the strong CH₄ absorption bands in units with compositions that are dominated by H₂O ice and the NSS endmember. Exploring the mutual variation of the CH₄ and N₂ integrated band depths with the abundance of crystalline H₂O and NSS

endmember revealed that the NSS endmember is primarily responsible for the suppression of CH₄ absorptions in mountainous units located along the western edge of Sputnik Planitia. Our spectroscopic analyses have provided additional insight into the geological processes that have shaped Sputnik Planitia. A general increase in volatile abundance from the north to the south of Sputnik Planitia is observed. Such an increase first observed and interpreted by Protopapa et al. 2017 and later confirmed by climate modeling (Bertrand et al., 2018) is expressed geomorphologically in the form of preferential deposition of N₂ ice in the upland and mountainous regions bordering the plains of southern Sputnik Planitia. Relatively high amounts of pure CH₄ are seen at the southern Tenzing Montes, which are a natural site for CH₄ deposition owing to their great elevation and the lower insolation they are presently receiving. The NSS endmember correlates the existence of tholins within certain units, mostly those coating the low-latitude mountain ranges that are co-latitudinal with the tholin-covered Cthulhu Macula. The spectral analysis has also revealed compositional differences between the handful of occurrences of northern non-cellular plains and the surrounding cellular plains, all of which are located within the portion of Sputnik Planitia that is presently experiencing net sublimation of volatiles, and which do not therefore exhibit a surface layer of bright, freshly-deposited N₂ ice. The compositional differences between the cellular and non-cellular plains here hint at the effectiveness of convection in entraining and trapping tholins within the body of the cellular plains, while preventing the spread of such tholins to abutting non-cellular plains.

1. Introduction

In 2015 the New Horizons spacecraft encountered dwarf planet Pluto, unveiling a complex and diverse icy world (Stern et al., 2015). Prior to New Horizons' flyby, Pluto had been extensively studied from ground-based and space telescopes. Observations in the visible (VIS; e.g., Lorenzi et al., 2016) and infrared range (IR; e.g. Cruikshank et al., 1976; Grundy et al., 2013; 2014; Merlin, 2015, Olkin et al., 2007; Protopapa et al., 2008), determined that Pluto's

uppermost surface layer is mostly composed of frozen N₂, CH₄, CO, C₂H₆, along with additional non-ice, organic components (Cruikshank et al., 2015). This surficial coating overlies bedrock made of H₂O ice.

The surface of Pluto exhibits distinct terrain types, the most conspicuous being Sputnik Planitia*, a 1000 km by 1300 km wide impact basin that is interpreted to have formed $\gtrsim 4$ Gya (Moore et al., 2016; McKinnon et al., 2016; Johnson et al., 2016; Keane et al., 2016; Nimmo et al., 2016; Schenk et al., 2018). The deep basin represents a powerful cold trap and a natural setting for the accumulation of volatile ices spread across Pluto's surface, principally N₂ and CO ice (Bertrand & Forget, 2016; Hamilton et al., 2016; Earle et al., 2017). Modeling of volatile behavior in response to topography has shown that infilling of the basin with the majority of surface N₂-CO ice would be complete by tens of millions of years after its formation (Bertrand et al., 2018). Most of the surface of Sputnik Planitia today is depressed by 2.5-3.5 km relative to the basin rim, and by 2 km relative to Pluto's mean radius (Schenk et al., 2018). No impact craters are seen within Sputnik Planitia in contiguous 315 m/pixel mapping coverage (Robbins et al., 2017; White et al., 2017; Singer et al., 2019), indicating very recent resurfacing of its plains. The central and northern portions of Sputnik Planitia are marked by a reticulate pattern of troughs a few km wide that divide the plains into ovoid cells (Stern et al., 2015; Moore et al., 2016). The cells likely originated due to solid-state convection of the N₂-CO ice, with a surface renewal timescale of < 1 Myr (McKinnon et al., 2016; Trowbridge et al., 2016; Buhler & Ingersoll, 2018). Cells are absent within the southern and eastern parts of Sputnik Planitia, which instead display featureless plains or dense concentrations of sublimation pits reaching a few km across (Stern et al., 2015; Moore et al., 2016; White et al., 2017). A discontinuous chain of mountain ranges, consisting of discrete angular blocks with apparently random orientations, extends for hundreds

* Some feature names mentioned in this paper are now formalized while others are informal

of kilometers along the western margin of Sputnik Planitia (Moore et al., 2016; Skjetne et al., 2020). These are interpreted to be fragments of Pluto's tectonized and brecciated H₂O ice crust that were intruded by glacial N₂-CO ice covering the uplands and flowing into the Sputnik basin in the aftermath of the impact, and subsequently dislodged, transported and rotated by the glacial ice to form the ranges (Moore et al., 2016; Stern et al., 2015; Howard et al., 2017; O'Hara & Dombard, 2020).

We report here a compelling analysis of the Sputnik Planitia region, performed by comparing the data acquired by the LOng-Range Reconnaissance Imager (LORRI) (Cheng et al., 2008) with the spectroscopic observations returned by the Linear Etalon Imaging Spectral Array (LEISA) (Reuter et al., 2009). Our investigation has the goal to understand if the terrain units identified by White et al. (2017) on the basis of geologic analysis, display distinct spectral characteristics in addition to their geomorphology and albedo.

2. Geologic and spectral mapping

A geological map of Sputnik Planitia was produced by White et al. (2017), using a mosaic of 12 LORRI images as the base map. The base map covers the plains themselves and the surrounding uplands. The mapping defined 15 geologic units, based primarily on the surface texture and albedo that they present at the 386 m/pixel scale of the base map; topographic relief as expressed in the global stereo digital elevation model (Schenk et al., 2018) was generally not useful for unit definition due to the extreme flatness of the plains. In this work we focus on 13 of the 15 units presented in White et al. (2017), excluding the Impact Crater (ic) and Bright, Pitted Uplands (bpu) units because they are exterior to Sputnik Planitia. Figure 1 - which corresponds to Figure 5 in White et al. (2017) - shows the Sputnik Planitia geological map, and Table 1

describes the diagnostic characteristics and interpretations of these units as presented in White et al. (2017).

Cellular plains occupy the core of Sputnik Planitia, with cell boundaries consisting of trough and ridge morphology. The cellular plains are brighter in the central-south area (bcp), and darker in the central-northern part (dcp). The northern margin of Sputnik Planitia shows very low-albedo plains (tbp), but within which cell boundaries can still be discerned. The western rim of Sputnik Planitia is occupied by chains of randomly oriented blocky mountains (abm) - embayed by inter-block material (ibm) - and by dark-pitted, marginal plains (dmp), and dark, ridged terrain (drt). A few isolated mountain blocks of unit abm are seen within the plains of unit dcp, separated from the main ranges. The spatially largest abm area inside the cellular plains of Sputnik Planitia is Coleda de Dados Colles. To the east and south, Sputnik Planitia shows four types of pitted plains. The lightly pitted plains (lpp) bound the cellular plains along their eastern margin, the sparsely (spp) and deeply pitted plains (dpp) dominate the southernmost region of Sputnik Planitia, and the patchy, pitted, marginal plains (pmp) separate the interior plains from the surrounding highlands along the eastern and southwestern boundaries of Sputnik Planitia. These pitted plains units are concentrated within the eastern and southern regions of Sputnik Planitia, but small expanses of the units are identified on the northern and western edges as well, where they are embayed by the cellular plains and mountain units. Conglomerations of blocks reaching a few km across are seen within the cellular and pitted plains in the eastern portion of Sputnik Planitia, forming the scattered hills unit (sh).

The 13 units that form Sputnik Planitia and its mountain ranges do not commonly concentrate in a single, spatially coherent region, and often occur in several localities across the mapping area that are isolated from each other. To gauge geographical variation in the spectral properties

of these units, we have divided the Sputnik Planitia map into 15 provinces* (Figure 2). These provinces typically display contiguous geomorphological characteristics across their expanse, specifically cellular plains for the “Cellular plains” province, non-cellular plains for the “south pitted plains” and “east pitted plains”, “southwest buffer”, “west pitted plains” and “north pitted plains” provinces, and mountainous and hilly terrain for the ten “Montes” and “Colles” provinces. This strategy allows us to define the bulk spectral characteristics of each of the 13 units across the entire mapping area, and also the spectral characteristics for isolated occurrences of each unit within these separate provinces. This in turn will allow us to assess the degree to which spatially distant occurrences of a particular unit are spectrally similar, and if their spectra do vary with location, then what factors contribute to such variation.

The scientific payload onboard NH designed to investigate the spectral characteristics of Pluto’s surface is Ralph, a multispectral imager composed by two different instrument sub-systems covering the visible (VIS) and near infrared (NIR) regions of the spectrum with two independent spectrometers. The first component is MVIC, the Multi-spectral Visible Imaging Camera, with its three VIS and NIR channels, blue (400–550 nm), red (540–700 nm), and NIR (780–975 nm), and a narrow CH₄ band filter (860–910 nm). The second instrument sub-system is the Linear Etalon Imaging Spectral Array (LEISA). LEISA has two filter segments, the first covering the 1.25–2.5 μm short wave infrared (SWIR) spectral region (spectral power $\lambda/\Delta\lambda = 240$) to produce spectral maps, the second covering the 2.1–2.25 μm range ($\lambda/\Delta\lambda = 560$) to investigate the solid-N₂ absorption feature centered at 2.15 μm . LEISA scans the 0.9°x0.9° FOV in a push broom fashion (Reuter et al., 2009). In this work we used the data from the LEISA SWIR segment only.

* Some feature names mentioned in this paper are now formalized while others are informal

We considered three high spatial resolution (ranging between ~ 6 and ~ 9 km/pixel) LEISA spectral image cubes to produce a mosaic of Sputnik Planitia with the Integrated Software for Imagers and Spectrometers (ISIS) routines. The image cubes were first projected on a common simple cylindrical map, centered at 180°E and 0°N , with a pixel resolution to 2 km/px (smaller than the original resolution of the three LEISA scans). We then converted the I/F radiance (as defined in Hapke, 2012) into a reflectance factor (*REFF*) to minimize the effect of solar incidence on the reflected radiance and maximize the absorbing and scattering properties of the surface materials (Schmitt et al., 2017). The *REFF* is calculated, for each pixel, by dividing the I/F radiance by the cosine of the incidence angle (Hapke, 2012), assuming isotropic scattering of the surface (Lambertian photometry). The I/F values have been corrected by the scaling factor in the LEISA radiometric calibration of 0.74 ± 0.05 reported by Protopapa et al. 2020. The three projected cubes were then averaged together to create the final spectral mosaic. LORRI basemap used by White et al. (2017) for the geologic classification, was projected and sampled at the same scale of the LEISA mosaic, so to precisely compare them. We selected regions of interest on the LEISA mosaic corresponding to the Sputnik Planitia geologic units identified in White et al. (2017) by using the ENVI image analysis software.

Figure 1: Geologic units identified in Sputnik Planitia by White et al. (2017) through analysis of New Horizons LORRI images. The original 15 units initially identified were reduced to 13 here, to include only the geologic units within and around Sputnik Planitia. The basemap mosaic is a combination of 12 LORRI images, with a spatial resolution of 386 m/px.

Table 1. Descriptions and interpretations of 13 geologic units within Sputnik Planitia mapped by White et al. (2017).

Unit	Description	Interpretation
Bright, Cellular plains (bcp)	High albedo plains divided into ovoid cells by a network of troughs. Cell interiors typically display a pitted	Plains of $\text{N}_2\text{-CO}$ ice undergoing continuous resurfacing by solid-state convection. High albedo is caused by

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	texture at a scale of a few hundred meters towards their edges. Concentrates in central Sputnik Planitia.	condensation of atmospheric N ₂ -CO onto the Dark, Cellular plains to form a thin mantle of pure N ₂ -CO ice.
Dark, Cellular plains (dcp)	Similar to the Bright, Cellular plains, but with a lower albedo. Concentrates in northern and western Sputnik Planitia, but also appears as enclaves within the Bright, Cellular plains near the main contact between the two units.	Unit is deficient in N ₂ -CO relative to the Bright, Cellular plains and represents the exposed portion of the convecting N ₂ -CO ice mass, which displays a high content of entrained tholin accumulated.
Dark, Trough-Bounding Plains (tbp)	Low albedo plains at the northern edge of Sputnik Planitia that surround cell margins, which appear as narrow, dark lines. Exhibit flow patterns around obstacles at the margin with the surrounding uplands.	N ₂ -CO ice with an especially high concentration of entrained tholins at the edges of the cells and in the bounding troughs. Flow patterns indicate recent mobility of the N ₂ -CO ice.
Lightly Pitted Plains (lpp)	High albedo plains displaying a shallow, densely pitted texture at a scale of a few hundred meters.	Sublimation of N ₂ -CO ice across the surface of the plains.
Deeply Pitted Plains (dpp)	High albedo plains featuring dense concentrations of dark-floored pits reaching a few km across. Pits can be single or merge to form doublets and chains of elongate, aligned pits. Pit swarms sometimes form wavelike patterns.	Sublimation pits that may be widening existing fractures formed by ice shearing in the N ₂ -CO ice plains. Floors are covered by dark tholins. Wavelike patterns may reveal stress fields associated with flow paths.
Sparsely Pitted Plains (spp)	Smooth, high albedo plains featuring scattered pits with subdued and softened relief.	Plains that have been resurfaced by flow of N ₂ -CO ice, and/or blanketing by atmospheric N ₂ -CO condensation, which acts to relax/infill pit topography.
Patchy, Pitted, Marginal Plains (pmp)	High albedo, often-hummocky plains on the margins of Sputnik Planitia. Generally, it displays a patchy texture of close-spaced shallow pits interspersed with smooth, featureless zones. Dark flow lines are often seen where the unit occurs along the border with the Bright, Pitted Uplands.	Shallow N ₂ -CO ice draped over underlying topography, which may contribute to the heterogeneous texture of the unit. Glacial flow of the unit is occurring from valleys in the Bright, Pitted Uplands to the open plains of Sputnik Planitia.
Dark-Pitted, Marginal Plains (dmp)	High albedo plains displaying chains of elongate, dark-floored pits interspersed with smooth, lightly pitted zones. Unit occurs on the western edge of Sputnik Planitia.	Shallow N ₂ -CO ice draped over underlying topography. The ice may be residual and relatively immobile compared to that of the Patchy, Pitted, Marginal Plains. Dark pit floors represent Cthulhu Macula, which this unit overlies.
Chaotic, Angular, Blocky Mountains (abm)	Discontinuous chain of mountain ranges, consisting of angular blocks with random orientations. Ranges	Fragments of the H ₂ O ice crust that have been detached by tectonism and intruded, transported, and rotated by glacial N ₂ -CO

	extend along the western margin of Sputnik Planitia, with a few isolated blocks occurring within its interior.	ice. The mountain blocks are now grounded within shallow N ₂ -CO ice of Sputnik Planitia.
Chaotic, Inter-Block Material (ibm)	Chaotically oriented, close-packed blocks, reaching several km across, that are interstitial to and embay the Chaotic, Angular, Blocky Mountains.	Like the Chaotic, Angular, Blocky Mountains, but finer texture may indicate breaking up of mountain blocks into smaller fragments and/or size filtering thereafter.
Scattered Hills (sh)	Hills scattered across east Sputnik Planitia that reach a few km across and tend to collect into densely packed clusters. Chains of aligned hills occur proximal to the Bright, Pitted Uplands. In the Bright, Cellular plains, the hills are always coincident with the cell boundaries.	CH ₄ ice fragments eroded from the Bright, Pitted Uplands that have rafted into Sputnik Planitia on valley glaciers of denser N ₂ -CO ice. In the Bright, Cellular plains, convective motions corral them into clusters at cell boundaries.
Dark, Ridged Terrain (drt)	Situated between the Chaotic, Angular, Blocky Mountains of western Sputnik Planitia and uplands to the west. Aligned ridges are oriented parallel to the edge of Sputnik Planitia, and display wavelengths from several hundred meters to a few km.	Possibly Chaotic, Inter-Block Material covered by dark mantling material. Compression of this unit by pressure exerted from westward motion of the Chaotic, Angular, Blocky Mountains may produce the ridges.
Bright, Chaotic Terrain (bct)	High albedo plains interspersed with darker blocks reaching several km across, on the northwest margin of Sputnik Planitia. E-W oriented troughs and scarps cross the unit. Parts of the unit are depressed by several hundred meters below the bordering Chaotic Inter-Block Material.	Unit represents uplands material that is experiencing extensional tectonism and subsidence, and possible intrusion by N ₂ -CO ice of Sputnik Planitia. High albedo of the plains indicates a surface covering of N ₂ -CO ice, possibly 'overflowed' from Sputnik Planitia. Unit may represent an incipient stage of formation of the Chaotic, Angular, Blocky Mountains.

Figure 2: The 15 provinces that we have divided the Sputnik Planitia geologic map into, with each province containing one or more geologic unit. Indeed, some geologic unit covers areas that are spatially distant and surrounded by very diverse terrain types. For example, spp unit can be found in 5 different provinces: in the northernmost part of Sputnik Planitia (North Pitted Plains), embedded in the cellular plains; in the West Pitted Plains, again close to the cellular plains, but also to the blocky mountains; in the Hillary Montes region, surrounded by inter-blocky material; in the Southwest Buffer and the South-East Pitted Plains, where the other types of pitted plains dominate.

3. Methodology

The LEISA mosaic allows us to calculate the average spectrum of each geologic unit inside each province, giving a total of 48 spectra. The average spectra of the 13 geologic units are shown in Figure 3. In the spectral region covered by LEISA's low-spectral-resolution segment

(1.25–2.5 μm), the spectrum of Sputnik Planitia is dominated, on average, by CH_4 , N_2 , and CO ice absorptions (e.g. Grundy et al., 2016). Some regions also show the presence of H_2O ice. CH_4 has four series of broad absorptions in the region between 1.30–1.43 μm (Range 1), 1.59–1.83 μm (Range 2), 1.90–2.00 μm (Range 3), and 2.09–2.48 μm (Range 4), and a single band centered at 1.48 μm (Schmitt et al., 2017). CO and N_2 absorption bands are centered at 1.58 μm and 2.15 μm , respectively.

Figure 3: Average spectra of the 13 geologic units identified by White et al. (2017). The boxes indicate the location of the main absorption bands of CH_4 , CO and N_2 .

3.1 Absorption bands analysis

We calculated the integrated band depth of the main CH_4 , N_2 , CO , and H_2O ice absorptions in LEISA spectra by following the method of Schmitt et al. (2017):

$$BD_{\lambda_1\lambda_2} = 1 - \frac{\int_{\lambda_1}^{\lambda_2} REFF(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} Cont(\lambda)d\lambda} \quad (1)$$

λ_1 and λ_2 are the positions of the right and left shoulders of the absorption bands, listed in Table 2. To limit the effect of random noise, we calculated the shoulder's continuum value by averaging the reflectance of five points around λ_1 and λ_2 . $REFF(\lambda)$ is the reflectance at the bottom of the band, integrated over the wavelength range between λ_1 and λ_2 , and $Cont(\lambda)$ is the continuum, calculated as a best fit line between the two shoulders.

Table 2: List of absorption bands, with the range of wavelengths used to evaluate the positions of the right and left shoulders for each of them.

Ice	Nominal minimum position	Right shoulder	Left shoulder
CH_4	Range 1 1.30–1.43 μm	1.2929 - 1.3116 μm	1.4205 - 1.4417 μm

	Range 2 1.59–1.83 μm	1.5777 - 1.6004 μm	1.8202 - 1.8466 μm
	Range 3 1.90–2.00 μm	1.8871 - 1.9147 μm	1.9857 - 2.0149 μm
	Range 4 2.09–2.48 μm	2.0747 - 2.1053 μm	2.4723 - 2.4892 μm
	1.48 μm	1.4681 - 1.4734 μm	1.4895 - 1.5003 μm
CO	1.58 μm	1.5552 - 1.5777 μm	1.5777 - 1.6004 μm
N ₂	2.15 μm	2.1207 - 2.1519 μm	2.1441 - 2.1756 μm
H ₂ O	2.02 μm	1.8371 - 1.8638 μm	2.1647 - 2.1965 μm

3.2 CH₄ band shifts

Solid nitrogen (N₂) can appear in two different, temperature-dependent states: cubic, or α -, and hexagonal, or β - (e.g., Grundy et al., 1993). N₂ absorption on Pluto is consistent with the β -phase, stable at $T > 35.6$ K (Quirico & Schmitt, 1997; Grundy et al., 2013).

CH₄ and N₂ form complex mixtures on the surface of Pluto since these two ices attract each other at the molecular level. Prokhvatilov and Yantsevich (1983) demonstrated that at Pluto's average surface temperature (40 K), CH₄ and N₂ ice are partly soluble and can form two mixing phases: a CH₄-rich component that is CH₄ saturated with N₂ (CH₄:N₂), and a N₂-rich component that is N₂ saturated with CH₄ (N₂:CH₄). When a small concentration of CH₄ is dissolved within N₂, CH₄ absorption bands show a shift towards shorter wavelengths (Schmitt & Quirico, 1992; Quirico & Schmitt, 1997), with the shift decreasing with increasing amount of CH₄ dissolved in the N₂ (Protopapa et al., 2015). This means that smaller values of the observed CH₄ band shift correspond to higher fraction of pure CH₄ ice.

To quantify the amount of CH₄ dissolved in the N₂ matrix for each geologic unit across Sputnik Planitia, we used the following method to estimate the average shift of the CH₄ absorptions. We take a pure CH₄ ice spectrum model, with a grain size of 0.5 mm, as reference.

The following procedure is applied to both LEISA and the reference pure CH₄ spectrum. We consider the left and right shoulders of each CH₄ absorption band listed in Table 3 (for the triplets, we considered each local minimum), and we calculated a straight-line continuum between the two shoulders. For each absorption feature (and local minimum), we divided the spectrum by the straight-line continuum. The continuum-removed bands are fit with a cubic spline with an increment of 100 steps, and we assumed the absolute minimum of the spline curve as the band's minimum position. The shift for each minimum is defined as the difference between the pure CH₄ ice and the LEISA spline estimated minima. We have, at the end of this process, eight different band shifts values. From our calculations, and from Schmitt et al. (2017), each individual CH₄ absorption shows a different band's minimum shift. We calculated the average CH₄ band shift parameter by averaging the eight shift values together. The shift towards shorter wavelengths (increasing N₂-rich ice) is indicated by an increasing positive value of the shift index.

Table 3: List of CH₄ absorption bands in the wavelength range covered by LEISA, with the range of wavelengths used to evaluate the positions of the right and left shoulders for each of them.

CH ₄ range	Nominal minimum position	Right shoulder	Left shoulder
Range 1 - triplet 1.30–1.43 μm	1.33 μm	1.3093 μm	1.3453 μm
	1.36 μm	1.3453 μm	1.3827 μm
	1.40 μm	1.3827 μm	1.4200 μm
Single band	1.48 μm	1.4681 μm	1.4949 μm
Range 2 - triplet 1.59–1.83 μm	1.66 μm	1.6271 μm	1.6948 μm
	1.72 μm	1.6948 μm	1.7419 μm
	1.79 μm	1.7419 μm	1.8128 μm
Range 3 - broad band 1.90–2.00 μm	2.20 μm	2.1762 μm	2.2365 μm

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3.3 Radiative transfer model

The spectra of the geologic units inside each province have been modeled by using a modified version of the Hapke theory (i.e. Hapke et al., 1993; 2012). The Hapke parameters used here are from Verbiscer et al. (2019): the Henyey-Greenstein single particle phase function asymmetry parameter $g = -0.36$, and the amplitude and width of the opposition surge due to shadow hiding, $B_0=0.307$ and $h=0.206$ respectively. Coherent backscatter was not considered in the model. For a full and complete description of the Hapke methodology we employed here, we refer to Cook et al., (2019).

The models consider several endmember components, combined into two spatially separate units by considering an areal mixture. In Tables 4 and 5, the two units are labeled with the letters A and B. Each unit can have one or more endmembers. When more than one endmember is considered, they are intimately mixed together.

As proven by previous work (e.g. Protopapa et al., 2017; Schmitt et al., 2017), CH_4 is ubiquitous within Sputnik Planitia. It can either be diluted within N_2 -rich ice, or it can be a pure endmember (Douté et al., 1999; Young et al., 2018). We considered optical constants of CH_4 ice diluted in N_2 ice from Protopapa et al. (2015), and pure CH_4 ice optical constants from Grundy et al. (2002). Pure CH_4 is used here as a substitute for the CH_4 -rich component ($\text{CH}_4:\text{N}_2$), since previous studies have shown that the wavelength shifts are very small in that phase (Protopapa et al., 2017). N_2 can also appear on the surface as pure ice. We used optical constants from Grundy et al. (1993).

The spectra of several geologic units have a marked negative spectral slope in the wavelength range covered by LEISA. After several attempts to model the negative spectral slope with a wide range of components, we concluded that the optical constants of the clay mineral kaolinite fit this

spectral feature the best. Figure 4 shows the spectrum of unit drt in Baret montes - the region with the strongest negative spectral slope - compared with seven Hapke models, calculated by considering the optical constants of seven different materials selected to account for the observed negative spectral slope: amorphous carbon, kaolinite, montmorillonite, Pluto tholin, serpentine, Titan tholin, and Triton tholin. Kaolinite returned the best result.

Figure 4: LEISA spectra of unit drt in Baret overlapped by seven Hapke theory-based best fit models, calculated by considering the optical constants of seven different materials to account for the observed negative spectral slope. The spectra are offset for clarity.

This does not mean that kaolinite is present on Pluto's surface, because small structures will scatter greater at shorter wavelengths. For this paper, however, we assume that the negative spectral slope is due to a separate endmember and adopt kaolinite as representative of the negative spectral slope endmember (NSS endmember).

A negative spectral slope can be explained also by physical properties of the surface material, such as a surface coating of ultra-fine grains (Stephan et al., 2017, Protopapa et al. 2020). We do not consider ultra-fine grains in this work, as it is outside the scope of this work.

The NSS endmember is presumed to be a relatively refractory non-ice macromolecular carbon-rich organic material formed by energetic processing of Pluto's atmosphere of CH₄, N₂, CO, and other minor gaseous components, as well as the solid forms of these molecules in the surface ices. Both ultraviolet radiation and charged particles readily transform these simple molecules into disordered macromolecular complexes generally termed tholins. Tholins exhibit a range of yellow-to-red color in the visible spectral region and are thought to account for the red colors of numerous Solar System bodies (e.g., Cruikshank et al. 2005). Materese et al. (2014, 2015) determined the compositions and structures of tholins produced by UV photolysis and low-voltage electron radiolysis of an ice mixture of N₂, CH₄, and CO (100:1:1) relevant to

Pluto's surface. The radiolytic produced tholin was further analyzed by Cruikshank et al. (2016), demonstrating its negative spectral slope at $\lambda > 1.1 \mu\text{m}$.

Tholins synthesized in gas phase experiments appropriate for modeling the spectra of the atmospheres of Titan or Triton have positive rather than a negative spectral slope (Khare et al., 1984; 1993; 1994), and do not introduce a sufficiently negative spectral slope in models of LEISA spectra of Pluto's surface units (Figure 4) unless accounting for fine grains. Indeed, Protopapa et al. 2020 reproduces successfully Pluto's MVIC+LEISA observations using Titan tholin like material with ultra-fine grains. As we explained before, we will not explore the contribution of fine grain in this paper. At the same time, there is very little published information on the optical constants for tholins synthesized in ices. Cruikshank et al. (2016) published a reflectance spectrum of the tholin produced by electron radiolysis of the $\text{CH}_4:\text{N}_2:\text{CO}$ ice mixture in the experiments of Materese et al. (2015) considered to be relevant to Pluto's surface. Optical constants were derived from that reflectance spectrum by assuming a grain size of $10 \mu\text{m}$ (Protopapa et al. 2021). While the derived optical constants for that Plutonian tholin show a subtle negative spectral slope trend, it is insufficient to account for the negative spectral slope found in LEISA spectra (Cook et al., 2019). To test the optical constants of Plutonian tholins, and to compare them to the results obtained with the NSS endmember, we selected four spectra to be modeled with the inclusion of the Plutonian tholin. The results are discussed in detail in Section 4.4. Three of these spectra were taken from unit drt within the Baret, Hillary, and Al-Idrisi Montes provinces, located on the western rim of Sputnik Planitia, as they show particularly negative spectral slope spectra. The last spectrum was taken from unit sh in the Columbia Colles province. This was selected because, even though this unit is located on the eastern perimeter of Sputnik Planitia and was classified as the “scattered hills” unit by White et

al. (2017), it does show spectral and geomorphological characteristics that are more similar to those of unit drt than to those of other occurrences of unit sh (see Section 5 for further details).

The mountain ranges that line the western perimeter of Sputnik Planitia are **composed** of H₂O ice (Grundy et al., 2016; Protopapa et al., 2017; Schmitt et al., 2017; Cook et al., 2019). We consider both crystalline and amorphous H₂O ice, with optical constants from Grundy & Schmitt (1998) and Mastrapa et al. (2008) respectively.

The optical constants for CH₄:N₂ mixtures, pure β -N₂ and H₂O-ices are known at specific temperature values. The optical constants at intermediate values of temperature are calculated in our models by linearly interpolating the optical constants at measured temperatures, and by searching for the temperature which minimizes the χ^2 . However, the changes in χ^2 due to temperature variation are typically small and can confidently constrain the temperature **only** between 40 and 60 K. The temperatures reported in this paper are the best-fit values only.

The endmembers used for each geologic unit in the 15 provinces are listed in Table 4. The first areal mixture (unit 0 in Table 4) includes higher-volatility materials, namely CH₄ (pure or diluted in N₂-rich ice) and pure β -N₂. The second unit (unit 1) includes lower-volatility materials, namely crystalline or amorphous H₂O ice, and NSS endmember.

Figure 5 shows the average LEISA spectra of the geologic units for each province, superimposed on the corresponding model. It must be noted that the model never considers the CO 1.58 μ m spectral region because of lack of reliable optical constants (Protopapa et al., 2017). This band corresponds to the (3-0) overtone, which is weaker than the (2-0) band centered at 2.35 μ m (seen in ground-based, disk-integrated observations). Even though reliable optical constants are available for the CO spectral region around 2.35 μ m, it lies in a gap in our knowledge of the optical constants for CH₄:N₂. Furthermore, the CH₄ bands appear saturated in

the data, and any attempt to accommodate for the diluted CH₄ optical constants without proper understanding of the bands would likely yield large uncertainties in our fit for the CO band at 2.35 μm .

To understand the areal abundance of the endmembers in each unit, we calculated the areal mass fraction as the product of the endmember's mass fraction with its corresponding fractional area. This parameter represents the surface percentage of each geologic unit covered by each endmember, and it will be used in the compositional maps to indicate the abundance of each endmember in the geologic units (see section 4 for further details).

Table 4: Parameters used to model the LEISA spectra with a modified version of the Hapke theory (i.e. Hapke 1993, 2012).

Province *	T (K)	CH ₄ fraction (%)	Component	Unit	Mass fraction	Grain diameter (mm)	Fractional Area	Areal mass fraction (%)
ABM								
Baret Montes	44	1.20	N ₂ :CH ₄	A	1.000	297.9	0.214	21.4
			NSS endmember	B	0.467	0.004	0.786	36.7
			Crystalline H ₂ O		0.533	0.20		41.9
Cellular plains	45	1.80	Pure CH ₄	A	0.003	0.18	0.664	0.2
			N ₂ :CH ₄		0.997	70.0		66.2
			Crystalline H ₂ O	B	0.871	5.66	0.336	29.3
			Amorphous H ₂ O		0.129	0.03		4.3
Hillary Montes	43	0.25	N ₂ :CH ₄	A	0.007	86.0	0.348	0.2
			β-N ₂		0.993	120,453.0		34.5
			NSS endmember	B	0.426	0.01	0.652	27.8
			Crystalline H ₂ O		0.574	0.331		37.5
Southwest buffer	48	1.00	Pure CH ₄	A	0.005	0.62	0.817	0.4
			N ₂ :CH ₄		0.995	595.7		81.3
			Crystalline H ₂ O	B	1.0	0.01	0.183	18.3
Tenzing Montes	50	0.05	Pure CH ₄	A	0.015	1.68	0.907	1.4
			N ₂ :CH ₄		0.985	58.4		89.3
			Crystalline H ₂ O	B	1.0	0.30	0.093	9.3
Zheng He Montes	55	2.90	N ₂ :CH ₄	A	1.0	29.63	0.333	33.3
			Crystalline H ₂ O	B	0.376	4.8E-03	0.667	25.1
			NSS endmember		0.624	0.43		41.6
Al-Idrisi Montes	44	0.70	N ₂ :CH ₄	A	1.0	120.3	0.646	64.6
			Crystalline H ₂ O	B	1.0	0.01	0.354	35.4
BCP								

* Some feature names mentioned in this paper are now formalized while others are informal

Cellular plains	46	0.60	Pure CH ₄ N ₂ :CH ₄	A	2.44•10 ⁻⁵ 1.00	0.004 155.1	1.0	0.002 99.998
BCT								
Al-Idrisi Montes	44	0.80	N ₂ :CH ₄	A	0.095	19.719	0.605	5.7
			β-N ₂		0.905	336.1		54.8
			NSS endmember	B	0.353	0.004	0.395	14.0
			Crystalline H ₂ O		0.647	0.153		25.5
DCP								
Cellular plains	44	1.70	Pure CH ₄		9.38•10 ⁻⁵	0.33		6.86•10⁻³
			N ₂ :CH ₄	A	0.07	26.0	0.731	4.9
			β-N ₂		0.93			68.2
			NSS endmember	B	1.0	0.01	0.269	26.9
Al-Idrisi Montes	44	2.30	N ₂ :CH ₄	A	0.033	9.208	0.557	1.9
			β-N ₂		0.967	512.3		53.9
			NSS endmember	B	0.467	0.006	0.443	20.7
			Crystalline H ₂ O		0.533	0.071		23.6
DMP								
Baret Montes	47	2.20	Pure CH ₄		0.001	0.332		0.1
			N ₂ :CH ₄	A	0.114	44.9	0.611	7.0
			β-N ₂		0.885	1597.9		54.1
			NSS endmember	B	1.000	0.007	0.389	38.9
Hillary Montes	48	1.2	N ₂ :CH ₄	A	1.000	88.000	0.614	61.4
			NSS endmember	B	1.000	0.006	0.386	38.6
DPP								
Hillary Montes	48	0.60	Pure CH ₄	A	0.001	0.109	1.0	0.1
			N ₂ :CH ₄		0.999	662.8		99.9
North pitted plains	45	0.45	Pure CH ₄	A	0.0002	0.021	1.0	0.02
			N ₂ :CH ₄		0.999	224.6		99.98
Cellular plains	47	0.66	Pure CH ₄	A	0.001	0.087	1.0	0.1
			N ₂ :CH ₄		0.999	288.3		99.9
East pitted plains	48	4.50	N ₂ :CH ₄	A	0.020	12.7	0.712	1.4
			β-N ₂		0.980	1868.6		69.8
			NSS endmember	B	1.000	0.022	0.288	28.8
South pitted plains	54	7.50	Pure CH ₄		3.4•10 ⁻⁴	0.492		0.03
			N ₂ :CH ₄	A	0.018	12.2	0.793	1.4
			β-N ₂		0.982	1572.7		77.9
			NSS endmember	B	1.000	0.025	0.207	20.7
West pitted plains	45	0.30	Pure CH ₄	A	0.009	1.949	1.0	0.9
			N ₂ :CH ₄		0.991	37.8		99.1
DRT								
Baret Montes	42	0.80	N ₂ :CH ₄	A	1.0	1040.0	0.285	28.5
			NSS endmember	B	0.747	0.003	0.715	53.4
			Crystalline H ₂ O		0.252	0.019		18.1
Hillary Montes	45	0.60	Pure CH ₄	A	0.003	1.52	0.389	0.1
			N ₂ :CH ₄		0.997	296.6		38.7
			NSS endmember	B	0.630	0.005	0.611	38.5
			Crystalline H ₂ O		0.370	0.072		22.6
Al-Idrisi Montes	42	0.50	Pure CH ₄	A	0.001	0.87	0.215	2.3•10⁻²
			N ₂ :CH ₄		0.999	1277.3	0.215	21.5
			NSS endmember	B	0.637	0.003	0.785	50.0

* Some feature names mentioned in this paper are now formalized while others are informal

Tenzing Montes	58	5.00	Pure CH ₄		0.001	0.416		0.04
			N ₂ :CH ₄	A	0.014	14.83	0.792	1.1
			β-N ₂		0.985	2326.5		78.1
			NSS endmember	B	1.0	0.017	0.208	20.8
SH								
Astrid Colles	48	4.80	Pure CH ₄		2.4•10 ⁻⁵	23.65		0.002
			N ₂ :CH ₄	A	0.020	10.26	0.676	1.3
			β-N ₂		0.980	1258.8		66.3
			NSS endmember	B	1.0	0.022	0.324	32.4
Challenger Colles	48	1.40	Pure CH ₄		1.87•10 ⁻⁴	0.644		0.01
			N ₂ :CH ₄	A	0.053	39.9	0.680	3.6
			β-N ₂		0.947	3397.6		64.4
			NSS endmember	B	1.0	0.006	0.320	32.0
Columbia Colles	52	4.60	Pure CH ₄		2.94•10 ⁻⁵	0.337		0.001
			N ₂ :CH ₄	A	0.001	11.849	0.456	0.05
			β-N ₂		0.999	124,708.0		45.5
			NSS endmember	B	0.398	0.005	0.544	21.7
Crystalline H ₂ O		0.602	0.200		32.8			
Soyuz Colles	47	4.30	Pure CH ₄		4.92•10 ⁻⁵	1.044		0.004
			N ₂ :CH ₄	A	0.016	13.221	0.803	1.3
			β-N ₂		0.984	2518.6		79.0
			NSS endmember	B	1.0	0.007	0.197	19.7
East pitted plains	48	3.50	Pure CH ₄		1.20•10 ⁻⁴	0.448		0.01
			N ₂ :CH ₄	A	0.026	16.927	0.796	2.0
			β-N ₂		0.974	2041.8		77.5
			NSS endmember	B	1.0	0.013	0.204	20.4
SPP								
Hillary Montes	52	3.60	Pure CH ₄		4.87•10 ⁻⁴	0.319		0.03
			N ₂ :CH ₄	A	0.070	23.20	0.700	4.9
			β-N ₂		0.929	652.4		65.1
			NSS endmember	B	1.0	0.018	0.300	30.0
East pitted plains	50	1.4	N ₂ :CH ₄	A	0.127	70.4	1.000	12.7
			β-N ₂		0.873	198.6		87.3
South pitted plains	44	0.50	Pure CH ₄	A	2.9•10 ⁻⁴	0.09	1.000	0.03
			N ₂ :CH ₄		0.990	322.1		99.0
North pitted plains	48	0.80	Pure CH ₄		2.5•10 ⁻⁵	0.002		2.5•10⁻³
			N ₂ :CH ₄	A	1.000	136.6	1.000	99.998
Cellular plains	48	3.20	Pure CH ₄		2.67•10 ⁻¹⁰	1.227		1.9•10⁻⁸
			N ₂ :CH ₄	A	0.038	11.86	0.731	2.8
			β-N ₂		0.962	1124.0		70.3
			NSS endmember	B	1.0	0.011	0.269	26.9
Southwest buffer	54	5.00	Pure CH ₄		3.86•10 ⁻⁴	0.409		0.03
			N ₂ :CH ₄	A	0.031	16.473	0.815	2.5
			β-N ₂		0.968	1010.4		78.9
			NSS endmember	B	1.0	0.026	0.185	18.5
West pitted plains	44	0.25	Pure CH ₄		4.0•10 ⁻³	1.6		0.4
			N ₂ :CH ₄	A	0.996	57.9	1.000	99.6
TBP								
Cellular	45	1.30	Pure CH ₄	A	7.48•10 ⁻¹⁰	0.252	0.616	4.6•10⁻⁸

plains	N ₂ :CH ₄		0.124	18.62		7.6
	β-N ₂		0.876	2399.3		53.9
	NSS endmember	B	1.0	0.010	0.384	38.4

Figure 5: Comparison between LEISA spectra, averaged for each geologic unit in the 15 provinces, and the models calculated by applying the Hapke theory. Each panel also reports the components used in the models, with their fractional area.

4. Spectroscopic Analysis

The spectral indicators obtained from the methodology in Section 3, and the areal mass fraction and grain size of the models' components, are presented as grayscale variation maps. Dark grays are associated with suppressed band depths, or lower areal mass fraction and smaller grain size, and light grays with stronger absorptions and higher areal mass fraction and grain size values.

4.1 CH₄ and N₂

4.1.1 CH₄ band shifts

CH₄ and N₂ are the two most abundant ices on Pluto's surface. Many studies (eg. Prokhvatilov and Yantsevich, 1983; Lunine & Stevenson, 1985; Protopapa et al., 2015) have showed that the phase of the two ices, pure or diluted in each other, depends on the surface temperature. On average, they are most likely to be found in two distinct phases on Pluto's surface (for an average temperature of 44 K): CH₄ saturated in N₂ ice (CH₄:N₂) and N₂ saturated in CH₄ ice (N₂:CH₄). The N₂:CH₄ binary phase diagram, generated from X-ray diffraction experiments by Prokhvatilov & Yantsevich (1983), shows that at Pluto's surface temperature, the solubility limits for the two phases are 3% (of N₂:CH₄) and 5% (of CH₄:N₂). The dilution of CH₄ in the N₂ matrix produces a shift in the minima of the CH₄ absorptions: the smaller the shift, the higher the CH₄ abundance (Protopapa et al., 2015).

* Some feature names mentioned in this paper are now formalized while others are informal

To understand how, and in which ice phase, CH₄ and N₂ are distributed within the geologic units of Sputnik Planitia, we calculated the shift in the LEISA spectra following the method described in Section 3.4, and we show the result in Figure 6.

The highest values of the band shift index in the map refer to areas characterized by N₂-rich ice, while the lowest values indicate CH₄-rich ice. The units with the highest index value are bct in Al-Idrisi Montes and bcp in the Cellular plains. As a general trend, the geologic units in the north and center of the mapping area, especially those within Al-Idrisi Montes and the Cellular plains, have higher values of the shift index than units in the southwest: unit abm in Hillary Montes and Zheng He Montes shows the lowest index values. The central cellular plains of Sputnik Planitia (unit bcp) and unit bct in the northern part of Al-Idrisi Montes are the regions richest in N₂-rich ice. The amount of N₂ slightly decreases from unit bcp to the northern areas of the Cellular plains (units dcp and tbp), and to the lpp unit of the South and East pitted plains. The shift index decreases - and consequently so does the N₂-rich ice abundance – to the west, incorporating units ibm and dmp in Hillary Montes, pmp and abm in Southwest buffer, and abm, ibm and pmp in Tenzing Montes. The units covering the southernmost and easternmost areas of the South and East pitted plains (dpp, pmp, and spp) have index values around 0.004, the transition point between the N₂-rich and CH₄-rich ices. This north-to-south trend of increasing N₂ abundance has previously been noted by Schmitt et al., (2017), and Protopapa et al. (2017).

Figure 6: Variation of the CH₄ band shift index across the geologic units of Sputnik Planitia. The highest values of the band shift index in the map (light grey) indicate areas characterized by N₂-rich ice, while the lowest values (dark grey) indicate CH₄-rich ice.

4.1.2 CH₄ from LEISA spectra

CH₄ ice displays a large number of absorption bands in Pluto's spectra, organized in triplets or in single broad bands (Figure 3 and Tables 2 and 3). We used equation 1 to calculate the integrated band depths of each CH₄ signature listed in Table 2, and we present them in Figure 7.

The areas with the most suppressed absorptions in almost all CH₄ ranges considered - Range 1, Range 2, Range 4, and 1.48 μ m (Fig. 7 a,b,d,e) - are units drt and bct in Al-Idrisi Montes, and units drt and abm in Baret Montes. Hillary and Tenzing Montes, on the other hand, show deeper CH₄ absorptions, with values similar to units bct and dcp. At 1.48 μ m, units bcp and dcp of the Cellular plains and unit lpp of the South and East pitted plains have similar band depth values. In CH₄ Range 1, Range 2, and Range 4 this similarity also extends to units lpp and pmp of the South and East pitted plains.

In many **aspects**, the CH₄ Range 3 map (Fig. 7c) appears to be the inverse of the other four panels: the absorption bands are more suppressed in units bcp, dcp, and tbp of the Cellular plains, where the intensities are similar to Al-Idrisi and Baret Montes, and in unit bct of Al-Idrisi Montes. Furthermore, the CH₄ absorption is deeper in the Southwest buffer and Tenzing Montes provinces.

Schmitt et al. (2017) found the same trend observed here for the four ranges of CH₄ triplets: the intensity of the CH₄ bands is high inside units bcp and dcp of the Cellular plains in Ranges 1, 2, and 4, whereas the strength of the band in Range 3 decreases in the very same areas, but not in the southwestern territories corresponding to the Southwest buffer and Tenzing Montes provinces.

Fig. 7: Maps of variation of the integrated band depths of the main CH₄ absorptions: *Range 1 (1.30-1.43 μ m; A), Range 2 (1.59-1.83 μ m; B), Range 3 (1.90-2.00 μ m; C), Range 4 (2.09-2.48 μ m; D), and the single band at 1.48 μ m (E). The Range 3 map (C) shows opposite trends compared to the other four spectral ranges, a behavior that was previously observed in other studies (e.g. Schmitt et al, 2017).*

4.1.3 CH₄ from model spectra

Figure 8 displays the amount of CH₄ diluted in the N₂-rich phase (panel a) and the temperatures (panel b) estimated by the models. The maps in Figure 8a and 8b show that the amount of CH₄ diluted in N₂ and the temperature are both very low in the northern, western, and central regions of Sputnik Planitia, and increase in the south and west. A similar trend was already found by Protopapa et al. 2017 (see their figure 5 panel C). The highest temperature and CH₄ content are found in unit lpp of Hillary Montes. Here the concentration of CH₄ reaches 9.1%, with an estimated temperature of 53 K. Units dpp in South pitted plains, lpp in East pitted plains, ibm in Hillary Montes, pmp and spp in Southwest buffer, and pmp and ibm in Tenzing Montes have CH₄ content between 5% and 7%, and high temperatures, between 52 and 58 K. The remaining provinces across the mapping area show CH₄ content below 5%, reaching a minimum in unit lpp of South pitted plains (0.4%), dpp of West pitted plains (0.3%) and abm of Tenzing Montes (0.05%). CH₄ in unit dcp in the Cellular plains accounts for 0.06%, which increases to 1.3% and 1.7% in units tbp and dcp respectively.

Units abm in Zheng He Montes and pmp in Tenzing Montes, Baret Montes, and Southwest buffer have the highest temperatures, ranging between 55K and 58K. Units drt, bct and dcp, on the other hand, show temperatures ranging between 43 and 45 K.

The fraction of CH₄ diluted in N₂ estimated in the models, and the corresponding predicted temperatures are consistent with the results from Protopapa et al. (2017), which showed a dilution content of CH₄ in N₂ in the Sputnik Planitia region ranging between 0.1% and 5%.

Pure CH₄ can also be found in Sputnik Planitia but always in very small amounts, below 1.5% (Figure 9a and b). The grain size ranges between 0.004 and 2 mm. Only one unit shows a larger grain size, sh in Astrid Colles (23.6 mm).

Fig. 8: Maps of percentage variation of CH₄ diluted in N₂-rich ice (A) and temperatures (B) estimated by the spectral modeling.

Fig. 9: Maps of variation of pure CH₄ areal mass fraction (A) and grain size (A) estimated by the spectral modeling. Pure CH₄ covers almost all geologic units in Sputnik Planitia, but its percentage is very low, below 1.5%.

4.1.4 N₂ from LEISA spectra

N₂ was discovered on the surface of Pluto through the detection of its absorption band at 2.15 μ m (Owen et al., 1993), located in a spectral region dominated by the CH₄ Range 4 absorption (Figure 3). This band is relatively weak, and the fact that it is clearly observed in almost all Pluto's spectra means that the N₂ layer is thick enough to allow the light to travel for a significant path length (on the order of centimeters) before being absorbed or reflected (Grundy et al., 1993; Cruikshank et al., 2015). The strong absorptions of CH₄, on the other hand, only need a layer some microns thick to be clearly observable in a spectrum. N₂ is, therefore, the most abundant ice on Pluto's surface, and it is contaminated by smaller amounts of CH₄, CO and other minor constituents (Cruikshank et al., 1984).

The 2.15 μ m integrated band depth variation map is shown in Figure 10.

The deepest N₂ absorptions are localized in small areas, namely in unit bct at the northern end of Al-Idrisi Montes, and in spp of the West pitted plains. Unit bcp of the Cellular plains, and units lpp and spp in the South pitted plains, also show deep N₂ absorptions. The band intensity decreases northwards, in units dcp and tdp of the Cellular plains, eastward, in units lpp, dpp and pmp of the E pitted plains, and southwards, in units dpp and pmp of the S pitted plains. The western areas have, on average, weaker or even null N₂ absorption. In fact, unit abm in Hillary and Tenzing Montes shows negligible amounts of N₂. Low N₂ content is also observed in units abm and drt of Al-Idrisi Montes, abm of Zheng He Montes, and all the units of Baret Montes, Southwest buffer and Tenzing Montes. In the east, Challenger Montes show similar, suppressed intensities, standing out from its surroundings. A comparison with Figure 6, shows that the very

same provinces with weak N₂ absorptions also have small values of the shift parameter, confirming the prevalence of CH₄-rich ice.

Fig 10: Map of variation of the integrated band depth of N₂ at 2.15μm.

4.1.5 N₂ from model spectra

For the temperature values estimated by the models, the phase diagram suggests that most N₂ within Sputnik Planitia is in the form of N₂:CH₄ ice. The N₂-rich phase can coexist with increasing amounts of pure N₂ in the β-form if the temperature rises.

Figure 11 and Figure 12 show the areal mass fraction, in the “A” panels, and the grain size, in the “B” panels, of N₂:CH₄ ice and of pure β-N₂ respectively.

From Figure 11a, we can observe high amounts of N₂:CH₄ covering the very central regions of Sputnik Planitia, corresponding to units bcp in the Cellular plains and lpp and spp of the South pitted plains. In the West, units abm of Al-Idrisi Montes, dpp of West pitted plains and Hillary Montes, abm of Southwest buffer and Tenzing Montes also show high abundance of N₂. In the remaining territories, the areal mass fraction of N₂-rich ice decreases sharply, dropping below 10%. A similar trend was observed in Protopapa et al. (2017). However, the difference in the absolute numbers of abundance are to be attributed to differences in the modeling (e.g., Hapke parameters, areal versus intimate mixture). The geologic units where N₂:CH₄ abundance is low, though, correspond to areas where pure β-N₂ has high concentrations (Figure 12a). Units dcp and tbp in the northern part of the Cellular plains, bct and ibm in Al-Idrisi Montes, abm, ibm and spp in Hillary Montes, pmp and spp in Southwest buffer, ibm and pmp in Tenzing Montes, and lpp, dpp, spp, and pmp of East and South pitted plains have pure β-N₂ areal mass fraction ranging between 35.4% and 98.6%.

The grain size of the N₂:CH₄ ice is below 200 mm in most provinces. Some units in the west show, on the other hand, coarser grain sizes, reaching 800 mm. For pure β-N₂, the grain size is always very large, on average above 350 mm.

Fig. 11 Maps of variation of N₂:CH₄ areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

Fig. 12 Maps of variation of pure β-N₂ areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

4.1.6 Distribution of CH₄-rich and N₂-rich ices

The distribution of CH₄-rich and N₂-rich ices can be inferred by integrating the abundance maps shown previously with correlation plots between the CH₄-band shift index and the CH₄ and N₂ integrated band depths.

Figure 13a shows the scatter plots of the CH₄ integrated band depths in Ranges 1 (top panel), 2 (middle panel), and 4 (bottom panel) versus the CH₄ shift index. We grouped these spectral indices together because they show similar trends with the band position index. The points are organized in two groups, separated in the plots by a dotted line. The first group (G1), above the line, shows increasing band strength with increasing values of the shift parameter. The second group (G2), below the dotted line, also shows a positive trend, but the points are more dispersed. Furthermore, the values of the CH₄ integrated band depths in G2 are lower than the units in G1. The Pearson correlation coefficient calculated for the data belonging to G1 and G2 confirm the positive correlations. For G1, CH₄ Range 1 has a moderate correlation with the CH₄ shift ($\rho = 0.44$), while for Range 2 ($\rho = 0.78$) and Range 4 ($\rho = 0.82$) the correlation coefficient has higher values. The points belonging to G2 appear more dispersed, but a positive trend is still visible. The correlation coefficient is $\rho = 0.24$ for the Range 1, $\rho = 0.62$ for the Range 2, and $\rho = 0.74$ for the Range 4.

The units included in G1 show increasing shift index with integrated band depths associated with a west-east trend. The units covering the western provinces show the most suppressed CH₄ absorptions in Ranges 1, 2, and 4, and smaller values of the shift index. Moving toward the central and eastern territories, the two spectral parameters increase in value.

Group G2 includes **the following** units, in order of increasing values of the shift index and integrated band depths: drt, ibm, abm of Baret Montes, drt of Al-Idrisi Montes, sh of Columbia Colles, drt of Hillary Montes, abm of Al-Idrisi Montes, tbp of the Cellular plains, and lpp, ibm, bct, and dcp of Al-Idrisi Montes. All these units, excepting sh and tbp, are located on the western edge of Sputnik Planitia.

The depth of an absorption band **is controlled by several physical parameter**, primarily the amount of ice, grain diameter, and the single particle phase function. Generally, the greater the amount of ice, or the larger the grain size, or the more a grain scatters incident sunlight preferentially in the forward direction (Verbiscer et al., 2006), the deeper the absorptions.

To examine the influence of the scattering on the best fit models, we examined the H-band (1.59-1.82 μm) range of the spectrum from spp unit of North Pitted Plains. We used this spectrum because the surface is mostly smooth (i.e. no mountains slopes) and likely minimizes changes in the spectrum due to phase, emission or incidence angles. **We find that changes in the Henyey-Greenstein g -value affects best-fit parameters like temperature and dilution.** Because we adopt the global value for the Henyey-Greenstein g -value from Verbiscer et al (2019) which is based on a fit to visible, not near-infrared, data at 0.55 μm , our best-fit values for temperature and dilution should be considered preliminary, as additional analysis would be required to understand the local g -values in the H-band in each region we examined. For the

scope of this paper, we will focus on abundance and grain size variation as the main parameters **controlling** the spectra shape and the bands depth.

Based on the abundance relationship alone, we might be led to conclude from Figure 13a that the increase in CH₄ band strength with the CH₄-shift index is due to an increase in CH₄ abundance. When the shift index was presented in section 3.2, though, we specified that higher index values correspond to lower amounts of CH₄-rich ice. Therefore, a trend in abundance, opposite of what observed in Figure 13a, is expected if grain scattering properties are not taken into account: the CH₄ integrated band depth should be less intense - or, the abundance of CH₄ should decrease - with increasing values of the shift index. This trend, then, can be explained by a difference in the scattering properties of particles within spectral Ranges 1, 2, and 4.

Figure 13b displays the integrated band depths of CH₄ Range 3 (top panel), 1.48 μ m band (middle panel), and N₂ absorption band at 2.15 μ m (bottom panel). In contrast to the three plots in Figure 13a, these spectral parameters show a clear and single trend with the CH₄ shift index.

As we observed in Figure 7, the CH₄ Range 3 absorption shows a very different abundance distribution across Sputnik Planitia compared to the other CH₄ absorptions. This discrepancy is also reflected in the plots showed in Figure 13b, where the intensity of the band shows a decrease in strength with increasing band shift, consistent with the definition of the CH₄ shift index. The Pearson correlation coefficient between Range 3 and the shift index is equal to -0.67, proving that an anti-correlation exists. We also observe that the band intensity decreases from the western to the central and eastern units, indicating a higher abundance of CH₄-rich ice in the western mountain ranges. Some exceptions are observed: units abm, ibm, and lpp of Al-Idrisi Montes have CH₄ absorption values in Range 3 similar to the Cellular plains, South and East pitted plains, and the four Colles provinces, while units bct and dcp have the most suppressed band

values. The **scatter plot of the CH₄ band at 1.48 μm as a function of the CH₄ band shift results in an elongated cloud, without any measurable slope**, but rather a flat trend. The correlation coefficient is indeed $\rho = -0.12$. Finally, the bottom panel of Figure 13b shows a positive correlation ($\rho = 0.68$) between the intensity of the N₂ band at 2.15 μm and the CH₄ band shift: the abundance of N₂-rich ice increases where the CH₄-shift index has higher values.

The unexpected behavior of the strongest CH₄ absorptions (Ranges 1, 2, 4) has been previously observed, mainly in Schmitt et al. (2017). The authors compared the strength of the CH₄ main absorptions with a CH₄-band shift parameter and observed that the data relative to Sputnik Planitia were offset with respect to the rest of Pluto's surface.

The absorptions plotted in Figure 13A do not increase, or decrease, in depth linearly with a variation of abundance of CH₄, grain size or forward scattering, but they anyway tend to saturate quickly with increasing abundance of CH₄, or with increasing grain size or forward scattering. Therefore, these three ranges cannot reliably be used to infer the CH₄ abundance and, in turn, to understand if abundance or grain size can in fact explain the unexpected trend. The absorption in Range 3 and the band centered at 1.48 μm are weaker, and a larger quantity of CH₄ would be necessary to make them saturated. Therefore, the plots in Figure 13B are more reliable for understanding how CH₄-rich and N₂-rich ices distribute across Sputnik Planitia. Furthermore, the trends in Figure 13B are consistent with the results from the models shown in Figures 8, 11 and 12. The geologic units with the lowest value of the shift index are mostly located in the southwestern mountain ranges, mainly Hillary and Zheng He Montes. Indeed, the models for units abm and ibm of these areas show **the highest** concentration of CH₄-rich ice. The central part of the Cellular plains and the East and South pitted plains show high abundance of N₂:CH₄ ice or of pure β-N₂, as well as high values of CH₄-shift index and of N₂ integrated band depth.

The hypothesis we can formulate to understand the trends of Figure 13A, based on the data shown thus far, is that N₂ and CH₄ are mixed with, or in close contact with patches of, some contaminants, or that there are differences in the single particle phase functions. The effect of these materials or surface particles that are more backscattering would be to suppress the CH₄ band depths - leaving the band shift unaltered - on the western regions where they may be more exposed and, therefore, more abundant. The CH₄ band at 1.48 μm is minimally affected by contaminants since its trend represents a transition between the absorptions in Figure 13A and the CH₄ absorption in Range 3 of Figure 13b. This last feature doesn't seem to be sensitive to contaminants, but rather to a variation in the abundance of CH₄ or N₂ ices.

To support this idea, we plotted the CH₄ integrated band depths in Ranges 1, 2, and 4 against the CH₄ integrated band depth in Range 3 (Figure 14). The three plots clearly show a lack of correlation between the represented parameters, the Pearson coefficients being $\rho = 0.34$ (Range 1), $\rho = 0.11$ (Range 2), and $\rho = 0.01$ (Range 4). The low or null correlations suggest that the **physical property controlling** the depth of the CH₄ absorptions in Ranges 1, 2, and 4 is not affecting the absorption in Range 3. Because of the different sensitivity of the four ranges to the variation in CH₄ ice abundance and grain size, we can exclude these two **physical** parameters as the main reason for the trend observed in Figure 13a.

It is worth noticing from Figure 14 that units bct and dcp in Al-Idrisi Montes have the most suppressed absorptions in Range 3, but quite intense values in Ranges 1, 2, and 4. Indeed, these two units show the deepest bands among the units belonging to group G2 (Figure 13A). Unit drt in Baret and Al-Idrisi Montes has very suppressed bands in all CH₄ ranges, while in Hillary Montes the same unit has quite deep absorption in Range 3, but weak intensities in the other CH₄ ranges.

Fig 13: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the CH₄ shift index. The data are split into two groups, separated by a dotted curve. The points belonging to group G1, above the curve, show increasing band strength with increasing values of the shift parameter. The second group (G2), below the dotted line, also shows a positive trend, but the points are more dispersed. Furthermore, the values of the CH₄ integrated band depths in G2 are lower than the units in G1. The positive trends in both groups contradicts the definition of the CH₄ shift index, i.e. higher index values correspond to lower of CH₄-rich ice amount. Therefore, a trend opposite of what observed in panel A is expected: the CH₄ integrated band depth should be less intense - or, the abundance of methane should decrease - with increasing values of the shift index. (B) Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μ m (middle), and the N₂ integrated band depth at 2.15 μ m (bottom) with the CH₄ shift index. As opposite to the three plots in panel A, these spectral parameters show a clear and single trend with the CH₄ shift index, in agreement with the definition of the CH₄ shift index.

Fig 14: Scatter plot showing the correlation between the CH₄ integrated band depths in Ranges 1 (top), 2 (middle), and 4 (bottom) versus the CH₄ integrated band depth in Range 3. The plots clearly show a lack of correlation between the represented parameters, indicating that the factor influencing the depth of the CH₄ absorptions in Ranges 1, 2, and 4 doesn't have any (or it has negligible) effect on the absorption in Range 3.

4.2 CO

Figure 15 displays the spatial distribution of the **CO absorption** across Sputnik Planitia, centered at 1.58 μ m. The **CO absorption is generally weak; the deepest ones** occur in units abm in Southwest buffer and units lpp and spp on the eastern perimeter of the Cellular plains. Unit bcp in the Cellular plains, units ibm and pmp in Tenzing Montes, and units lpp and spp in the South and East pitted plains, also show high CO content. The band intensity decreases in the northern portion of Sputnik Planitia, in units dcp and tbp, and in the eastern and southern units of the South and East pitted plains, dpp and pmp. The regions mostly depleted in CO (where the integrated band depth is close to 0) are units abm in Zheng He and Hillary Montes, and drt in Baret Montes. CO content in Al-Idrisi Montes is low and quite constant in all its geologic units, excepting bct, where the band intensity decreases even more. The CO distribution in the Cellular plains, South and East pitted plains, Hillary Montes, and Baret Montes closely resembles the N₂ trend observed in Figure 11. Other areas, on the other hand, show an anti-correlation with the N₂ distribution. The most remarkable differences are observed for units bct and ibm in Al-Idrisi Montes, in the North and West pitted plains, and in the abm units of the Cellular plains, Southwest buffer and Tenzing Montes.

More complex is the comparison with the CH₄ integrated band depth maps of Figure 7. As we described before, CH₄ absorptions are deeper in Ranges 1, 2, 4 and in the 1.48 μm band in the Cellular plains and South and East pitted plains provinces, and in some units of Hillary Montes and Southwest buffer. Units abm and drt of Al-Idrisi and Baret Montes instead show the weakest CH₄ absorptions. The CO integrated band depth map shows the same trend in the very same provinces. CH₄ Range 3, on the other hand, shows the opposite results, the band being more intense where the other CH₄ and the CO absorptions are shallower.

We investigated the correlation between CH₄ and N₂ absorptions with CO in Figure 16. The scatter plot of CH₄ in Ranges 1, 2, and 4 versus the CO integrated band depth is displayed in Figure 16a. On average, CO correlates well to the three CH₄ absorptions, the Pearson linear correlation coefficient being 0.64 for Range 1, 2, and 4. We notice, though, that the units do not distribute in the same way, but they can be split into two groups, separated in the three panels of Figure 16a by a vertical dotted line. The units on the left side have a sparse distribution and no apparent trend. They are all located on the western edge of Sputnik Planitia, excepting unit tbp in the Cellular plains and unit sh in Columbia Colles. The points on the right portion of the plots belong to units in the central and eastern parts of Sputnik Planitia, excepting the Southwest buffer and Tenzing Montes. For these units, the correlation between the integrated band depths of CO and CH₄ is also not evident, having a flat distribution.

Figure 16b shows the CO integrated band depth plotted against the integrated band depth of CH₄ in Range 3 and at 1.48 μm , and of N₂. The only clear correlation occurs between CO and the band at 1.48 μm , with $\rho=0.53$, while the correlation coefficient for CH₄ band in Range 3 and N₂ are negligible, being 0.09 and 0.12 respectively.

If we compare these results with Figure 13, we can notice some similarities. CH₄ in Ranges 1, 2, and 4 showed an unexpected trend in Figure 13a, the absorptions becoming deeper with increasing values of the CH₄ shift parameter. The abundance of CH₄ or its grain size cannot explain the discrepancy, since they weakly influence the depth of those bands. CH₄ in Range 3 and N₂, on the other hand, have a trend consistent with the definition of the CH₄ shift index: low values of the index indicate dominance of CH₄-rich ice, while high values of the index imply high abundances of N₂-rich ice.

Comparing Figure 13a with Figure 16a, we observe that geologic units showing deeper CH₄ absorptions and higher values of the CH₄ shift index also have strong CO bands. Similarly, units having a random distribution in Figure 13a (group G2) also have a sparse distribution and low CO values in Figure 16a (on the left side of the dotted line). **The top and bottom panels of Figure 16b are not useful for any definitive interpretation, since the CO integrated band depth doesn't have any clear correlation with either integrated band depth of CH₄ in Range 3 or N₂.**

Grundy et al. (2013, 2014), and Schmitt et al. (2017) noticed that CO is almost absent in areas dominated by CH₄-rich ice, but it is abundant in N₂-rich areas. The comparison of the CH₄ shift index map in Figure 6 with the CO map in Figure 15 leads to the **confirm** of the authors' conclusion for almost all geologic units in Sputnik Planitia, with a few exceptions. Units bct in Al-Idrisi Montes, drt in Baret and Hillary Montes, and dpp and spp in the West pitted plains are the most evident: CO absorption is suppressed where the shift indicates dominance of N₂-rich ice.

The correlation between CO and N₂ is also evident when comparing Figure 15 with the N₂:CH₄ (Figure 11a) and pure β -N₂ (Figure 12a) maps. Units with high amounts of N₂-rich ices,

like bcp and dcp in the Cellular plains, and spp in South pitted plains, or with considerable presence of pure β -N₂, such as lpp in East pitted plains, have strong CO intensities. We also notice that the CO band is weaker where no pure β -N₂ is observed, like Zheng He Montes, and drt in Baret Montes.

Fig. 15: Map of variation of CO integrated band depth at 1.58 μ m.

Fig 16: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the CO integrated band depth. Because the data shows to different trends, we split them into two groups, separated by a vertical dotted line. The units on the left side have a positive trend but a sparse distribution, the points on the right portion of the plots show a flat distribution. (B) Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μ m (middle), and the N₂ integrated band depth at 2.15 μ m (bottom) with the CO integrated band depth. The only clear correlation occurs between CO and the band at 1.48 μ m, while the correlation coefficient for CH₄ band in Range 3 and N₂ are negligible.

4.3 H₂O

The presence of crystalline H₂O ice on Pluto's surface was investigated and proved by numerous works, e.g. Grundy et al. (2016), Protopapa et al. (2017); Cook et al. (2019), and Cruikshank et al. (2020).

In our models we consider H₂O ice in two forms, crystalline and amorphous.

The spatial variation of the crystalline H₂O ice as predicted in the models is presented in Figure 17. The left panel (Figure 17a) depicts the areal mass fraction, the right panel (Figure 17b) the grain size. The mountain ranges extending along the western boundary of Sputnik Planitia are the only provinces hosting crystalline H₂O ice, excepting Columbia Colles in the east. The H₂O ice abundance ranges between 2% and 42%.

Unit abm in the mountain ranges of Baret and Hillary Montes show the highest percentage of crystalline H₂O ice (37% to 42%). Al-Idrisi Montes displays a lower percentage, ranging between ~25% and ~35% across its constituent units. The units in Southwest buffer and Tenzing Montes, and the drt unit in Baret Montes, show a decrease in crystalline H₂O ice, being between ~9% and ~18%. The grain size in all the units is smaller than 6 mm. The largest grains are found

in the Southwest buffer, followed by Hillary and Tenzing Montes. In all the other units, the crystalline H₂O ice grain size is estimated to be smaller than 0.2 mm.

The estimate of the amount of H₂O ice from LEISA data is not a trivial task. Indeed, the main H₂O ice absorptions occur at 1.5 μ m, the location of the gap in the CH₄:N₂ optical constants, and at 2.02 μ m, where CH₄ shows stronger absorptions with increasing wavelengths. Furthermore, the absorption around 2.0 μ m is partly cut out by the optical constants gap. Keeping this in mind, we calculated the H₂O integrated band depth by applying equation 1 with the parameters listed in Table 2 for the spectra of the geologic units having crystalline H₂O predicted by the models.

Fig. 17: Maps of variation of Crystalline H₂O areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

Figure 18 shows the mutual variation of the crystalline H₂O areal mass fraction, the H₂O integrated band depth, and the CH₄ shift parameter. Crystalline H₂O ice correlates well to the H₂O integrated band depth (top, left panel; $\rho=0.55$). No correlation, on the other hand, exists between the H₂O areal mass fraction (top, right panel), the H₂O integrated band depth (bottom, left panel), and the shift parameter ($\rho=-0.04$ and $\rho=-0.05$), suggesting that H₂O does not influence the CH₄ band shift.

Fig. 18: Mutual variation of the crystalline H₂O areal mass fraction, the H₂O integrated band depth, and the CH₄ shift index. Crystalline H₂O ice well correlates with the H₂O integrated band depth (top, left panel), while no correlation exists between the H₂O areal mass fraction (top, right panel) and the H₂O integrated band depth (bottom, left panel) and the shift parameter, suggesting that H₂O do not influence the CH₄ band shift.

The correlation between H₂O spectral indicators and CH₄ and N₂ integrated band depths is explored in Figure 19.

CH₄ integrated band depths in Ranges 1, 2, and 4 (Figure 19a-f) show a moderate anti-correlation with the crystalline H₂O areal mass fraction (panels a, b, c), and a strong anti-

correlation with the H₂O integrated band depth (panels d, e, f). Pearson correlation coefficient ranges between -0.90 and -0.96 for the plots on the right panels.

The correlation is less strong for the integrated band depths of CH₄ in Range 3 and at 1.48 μ m, and N₂ at 2.15 μ m. In the three left panels of Figure 19 (panels g, h, i), the Pearson coefficient's values are in the interval -0.26 to -0.33, while in the panels on the right (j, k, l) the parameter ranges between -0.06 and -0.78.

The geologic units having H₂O ice are the same forming group G2 in Figure 13a, or placed on the left side of group G1, characterized by low integrated band depths and low shift index values. The negative correlation observed in Figure 19a-f suggests that H₂O ice can contribute to the suppression of the strong CH₄ ice absorptions and can explain the anomalous trend observed in Figure 13a. For some units, though, H₂O is **neither** the only, **nor** the main, contributor.

Unit drt in Al-Idrisi and Baret Montes has the strongest absorptions in the 2.0 μ m region, but with moderate fractions of crystalline H₂O ice (28.5% and 18.1% respectively). The same is observed for unit abm in Zheng He and Hillary Montes. The discrepancy **between the crystalline H₂O areal mass function and the H₂O integrated band depths** suggests that crystalline H₂O is contributing to the absorption around 2.0 μ m, but the influence of some other material must be invoked to justify such deep absorptions in this spectral area. Because CH₄ integrated band depths are also very suppressed, we can deduce that H₂O and other contaminants are influencing the CH₄ **absorptions** in Ranges 1, 2, and 4 as well. Previous work (e.g. Cruikshank et al., 2015; Schmitt et al., 2017; Protopapa et al., 2017) has noticed a correlation between H₂O ice and tholins on Pluto, which in Sputnik Planitia is seen at the low-latitude mountain ranges of western Sputnik Planitia. It is therefore likely that tholins, or **other material with a positive spectral slope**, is significantly contributing to the suppression of CH₄

absorptions in Ranges 1, 2, and 4 in units like drt of Baret and Al-Idrisi Montes, and abm in Zheng He and Hillary Montes.

Unit drt in Hillary Montes shows weaker H₂O integrated band depth than the drt units in the other two provinces, but crystalline H₂O accounts for 22.6% of the total composition. The area of unit drt in Hillary Montes is less extensive than the units in Baret and Al-Idrisi Montes, and it is surrounded by units abm and ibm. Unit abm in Baret, Hillary and Zheng He Montes has the highest percentage of crystalline H₂O and significant H₂O absorption.

The amount of H₂O ice decreases moving south from the northwestern mountain ranges. Unit ibm shows a lower, but still considerable, amount of H₂O ice than abm. The lowest abundance of H₂O ice is seen in units lpp in Hillary Montes, abm and ibm in Tenzing Montes, lpp in Al-Idrisi Montes, and pmp and abm in Southwest buffer. These regions also show medium to low CO content, with the exception of unit abm in Southwest buffer, for which the CO integrated band depth has the deepest value (Figures 15 and 16).

Fig 19: (A-F) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the H₂O crystalline areal mass fraction (A, B, C), and with the H₂O integrated band depth (D, E, F). All the represented parameters show clear anti-correlations, suggesting that water ice can contribute to the suppression of the strong methane ice absorptions. For some units, though, H₂O is not the only, or the main, contributor. Unit drt in Al-Idrisi and Baret Montes, and unit abm in Zheng He and Hillary Montes have the strongest absorptions in the 2.0 μ m region, but moderate fractions of crystalline water ice. The discrepancy between the two water ice parameters suggests that crystalline H₂O is contributing to the absorption around 2.0 μ m, but the influence of some other material must be invoked to justify such deep absorptions in this spectral area. (G-L) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 3 (top), at 1.48 μ m (middle), and N₂ integrated band depth at 2.15 μ m (bottom) with the H₂O crystalline areal mass fraction (G, H, I), and with the H₂O integrated band depth (J, K, L). The correlation between these parameters is less pronounced than in the previous panels, and indication that crystalline H₂O minimally influence the depth of the CH₄ absorptions in Range 3 and at 1.48 μ m, and of N₂.

4.4 Negative spectral slope materials: NSS endmember and Pluto tholins

The MVIC instrument of the Ralph spectrometer revealed an extended region of material with positive spectral slope and low albedo, named Cthulhu Macula (Buie et al., 2010; Grundy et al., 2016), the existence of which was also inferred from previous ground-based observations (Cruikshank et al., 2015). This material also covers the low-latitude mountain ranges of western

807 Sputnik Planitia, seen here in units drt, abm and, in smaller amounts, ibm (Schmitt et al., 2017).
808 This material is interpreted to be tholins, organic compounds that assume colorations in the
809 visible spectrum - from yellow, to red, to brown - when bombarded with high-energy electrons
810 or UV radiation. Tholins don't have a clear spectral feature in the NIR range, but they can
811 **weaken** the CH₄ **absorption** band at 2.32 μm , within Range 4 (Schmitt et al., 2017), when the
812 two are mixed together. Comparing the spectrum of Cthulhu, rich in tholins, with that of Kiladze,
813 an impact crater within East Tombaugh Regio where H₂O is pure and abundant (Cook et al.,
814 2019), shows that around 2 μm they have similar shapes. Therefore, disentangling the
815 contribution to the resulting spectrum of H₂O from CH₄ and negative spectral slope material is
816 not easy.

817 Figures 20A and 20B show the distribution of areal mass fraction and grain size of the NSS
818 endmember across Sputnik Planitia.

819 The NSS endmember occurs mainly in units ibm, bct, drt of Al-Idrisi Montes, abm, ibm, dmp
820 and drt of Baret Montes, abm, ibm, dmp, drt and spp of Hillary Montes, pmp and spp of
821 Southwest buffer, and ibm and pmp of Tenzing Montes. The abundance ranges between 14% and
822 38.5%. In the northern regions of Sputnik Planitia, the NSS endmember accounts for 38.4% in
823 unit tbp and 26.9% in dcp, while in the east, this endmember composes between 20.7% and
824 33.2% of the sh units in the Colles provinces and the dpp and pmp units.

825 In the units where the NSS endmember is present, we observe a moderate negative trend of
826 the abundance of this component with the integrated band depths of CH₄ in Range 1 ($\rho = -0.34$),
827 Range 2 ($\rho = -0.48$), and Range 4 ($\rho = -0.55$; Figure 21a). The NSS endmember is not correlated
828 with the CH₄ in Range 3 ($\rho = -0.0007$), while it has a moderate and slight anti-correlation with

the CH₄ band at 1.48 μm ($\rho = -0.35$) and the N₂ absorption at 2.15 μm ($\rho = -0.28$; Figure 21b), respectively.

Unit drt in Baret and Al-Idrisi Montes hosts the highest amount of NSS endmember, followed by unit abm in Baret and Zheng He Montes, unit tbp in the Cellular plains, units dmp, drt and lpp in Hillary Montes, and unit dmp in Baret Montes. Unit drt and unit abm of Baret Montes also have very suppressed absorptions in the CH₄ Ranges 1, 2 and 4, the integrated band depth being close to 0.0. The same suppressed absorptions are also observed in Figure 21b for the CH₄ absorption at 1.48 μm , and for the N₂ feature.

Both Figures 21a and 21b do not show a north-south or east-west trend. Units belonging to provinces in the east and south of Sputnik Planitia share similar NSS endmember percentages, and analogous CH₄ integrated band depth values.

In Figure 22, the abundance of the NSS endmember is compared to the CH₄ shift index (top panel), the integrated band depth of H₂O ice (central panel), the areal mass fraction of crystalline H₂O ice (bottom panel).

The correlation coefficient of the top panel is equal to -0.36, denoting that a slight dependence between the shift value and the spectra's negative slope exists. In the other two panels, the represented quantities do not show any clear correlation. Indeed, if we do not consider units drt in the middle and bottom panels, the correlation coefficient drops close to 0. The trend in the middle panel of Figure 22 confirms the difficulty to disentangle H₂O from tholins in the spectrum, and the necessity to use a radiative transfer model.

Assuming that variations in scattering properties do not yield significant changes in the modeled parameters, we can conclude that tholins are primarily responsible for the suppression of CH₄ absorptions in Ranges 1, 2, and 4 in the units located on the west provinces of Sputnik

Planitia. For some of these units, like drt in Baret and Al-Idrisi Montes and abm in Baret Montes, tholins are the major contributors of the observed trend of Figure 13a. For the other units in the same area, tholins and H₂O ice both play a role in suppressing CH₄ signatures. Tholins and H₂O ice do not affect the shape and depth of CH₄ absorption in Range 3 and of N₂ feature at 2.15 μ m.

Fig. 20: Maps of variation of NSS endmember areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

Fig 21: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the NSS endmember areal mass fraction. A moderate negative trend between the abundance of the NSS endmember with the integrated band depths of CH₄ in Range 1, Range 2, and Range 4 is observed. (B) Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μ m (middle), and the N₂ integrated band depth at 2.15 μ m (bottom) with the NSS endmember areal mass fraction. The NSS endmember is not correlated with the CH₄ in Range 3, while it has a moderate and slight anti correlation with the CH₄ band at 1.48 μ m and the N₂ absorption at 2.15 μ m.

Fig 22: Scatter plot showing the correlation between the CH₄ band shift index (top), H₂O integrated band depth (middle), and crystalline H₂O areal mass fraction (bottom) versus the NSS endmember areal mass fraction. The top panel shows a slight dependence between the shift value and the negative spectral slope, while in the other two panels, the represented quantities do not show any clear correlation.

In our analysis, we examined several refractory materials that are featureless (i.e. they show no absorption bands) and only display a positive, neutral or negative spectral slope in the wavelength range we have examined (Figure 4). The use of kaolinite, a phyllosilicate, in our models consistently returned better fits to the data than any other material, including Plutonian tholins.

In general, hydrated materials display bands at around 1.4 and 1.9 μ m due to OH stretch, with the latter band being the stronger of the two. Because the optical constants for diluted CH₄ in N₂ are highly uncertain in the 1.82-2.11 μ m range, we have excluded this band from our work and therefore we cannot fully assess the presence (or absence) of a hydration band around 1.9 μ m. The weaker band around 1.4 μ m, which is in a spectral window that is analyzed in this work, is blended with several weak CH₄ bands.

Kaolinite also has an identifiable band around 2.3 μ m, but like the 1.9 μ m region, it is excluded from our analysis due to uncertain optical constants of diluted CH₄ in N₂. Thus, we cannot confirm if kaolinite specifically is present or not, but rather it likely shares spectral properties with what is **observed** – a negative spectral slope.

Tholins produced in Pluto's atmosphere and on Pluto's surface are a likely candidate for the negative spectral slope material on its surface. Tholins, which are typically red at visible wavelengths, can have a slope in the near-infrared spectral region that ranges from positive to negative. The fact that studies of the chemistry of Pluto's atmosphere (e.g. Bertrand & Forget, 2017; Cheng et al., 2017; Gladstone et al., 2016) produce tholins with a negative spectral slope at near-infrared wavelengths supports the idea that the negative spectral slope material present on Pluto is caused by tholins. To date, however, the optical constants for Plutonian tholins are limited, and their use in our analysis returns non-physical solutions.

As explained in Section 3.3, we selected four geologic units rich in red material to test the Plutonian tholins introduced by Cruikshank et al. (2016): unit drt in Al-Idrisi, Hillary, and Baret Montes, and sh in Columbia Colles. Figure 23 shows the LEISA average spectra superimposed upon the best fit model obtained by considering Plutonian tholins as a NSS endmember. Table 5 shows compositional details resulting from the modeling.

When Plutonian tholin is used as the NSS endmember, we typically find very small grain sizes (Table 5) and the Hapke code reaches the small grain limit for pure Hapke theory (0.8 μm diameter). The code, though, does not jump to the Rayleigh scattering regime (which accounts for particles smaller than 1 micron), likely because that would increase χ^2 . We also commonly find that the best fit temperature and dilution are increased, sometimes to the limits of our search space (maximum 60 K and 20% dilution CH_4 in N_2).

Specifically comparing models where the NSS endmember is kaolinite or the Plutonian tholin, those models with kaolinite had χ^2 values about a half that of models with Plutonian tholin.

These findings lead us to conclude that **a surface component with a negative spectral slope** must be present in the Sputnik Planitia regions we have examined, and which is perhaps uniformly present on Pluto, but our current understanding of Plutonian tholins is not sufficient to match the observations, and so more laboratory-based spectroscopic measurements are required.

* Some feature names mentioned in this paper are now formalized while others are informal

Figure 23: LEISA spectra, averaged for unit *drt* in Al-Idrisi, Hillary and Baret montes, and unit *sh* in Columbia Colles, overlapped by the corresponding Hapke theory-based best fit model. In this case, the modeling made use of the Pluto tholins optical constants, in place of the NSS endmember ones. The spectra are offset for clarity.

Table 5: Parameters used to model four LEISA spectra with a modified version of the Hapke theory (i.e. Hapke 1993, 2012), by using Pluto tholins.

Province*	T (K)	CH ₄ fraction (%)	Component	Unit	Mass fraction	Grain diameter (mm)	Fractional Area	Areal mass fraction (%)
DRT								
Baret Montes	44	11.1	N ₂ :CH ₄	A	1.000	32.1	0.159	15.9
			Pluto tholin		0.039	0.0008		3.3
			Crystalline H ₂ O	B	0.802	0.093	0.841	67.4
			Amorphous H ₂ O		0.159	0.003		13.4
Hillary Montes	44	0.70	pure CH ₄	A	0.001	0.58	0.625	0.1
			N ₂ :CH ₄		0.999	1,464.2		62.4
			Pluto tholin	B	2.0*10 ⁻⁰⁵	0.59	0.375	0.0
			Crystalline H ₂ O		1.000	0.008		37.5
Al-Idrisi Montes	49	2.9	N ₂ :CH ₄	A	1.000	18.8	0.192	19.2
			Pluto tholin		0.025	8.0*10 ⁻⁴		2.1
			Crystalline H ₂ O	B	0.384	0.072	0.808	31.0
			Amorphous H ₂ O		0.590	0.010		47.7
SH								
Columbia Colles	60	19.1	pure CH ₄		0.002	0.13		0.1
			N ₂ :CH ₄	A	0.028	5.96	0.573	1.6
			β-N ₂		0.970	634.9		55.6
			Pluto tholin	B	0.008	8.0*10 ⁻⁴	0.427	0.4
			Crystalline H ₂ O		0.992	0.038		42.3

5. Correlation of spectral results and observed geology

5.1 Blocky mountains and inter-block material.

The chaotic, angular, blocky mountains (unit abm), form a discontinuous buffer between Sputnik Planitia and the uplands to the west. The mountain blocks typically reach >10 km in diameter and are mostly contained within the ranges of Al-Idrisi, Baret, Hillary, Tenzing, and Zheng He Montes. Isolated mountain blocks are also seen within the dcp unit of the Cellular

* Some feature names mentioned in this paper are now formalized while others are informal

plains, the largest being Coleda de Dados Colles. The inter-block material (unit ibm) consists of chaotically oriented, close-packed blocks, typically reaching a few to several km across, that occur interstitially to and can also embay the abm unit. The blocks are similar to, but smaller than, the blocks forming the abm unit. The finer texture of unit ibm compared to abm may indicate breaking up of mountain blocks into smaller fragments and/or size filtering thereafter (White et al., 2017; O'Hara & Dombard, 2020). The mountain blocks that form these units are randomly oriented and have been hypothesized to consist of fragments of the H₂O ice crust that have been detached by tectonism and intruded, transported, and rotated by glacial N₂ ice (White et al., 2017).

Crystalline H₂O ice is indeed present to **various** degrees in both units, with areal mass fractions ranging between 9.3% and 47.1% (Figure 17a). The abundance of crystalline H₂O ice within unit abm is broadly constant between Al-Idrisi, Baret, and Hillary Montes (varying between 35.4% and 41.9%), although there is a dip to 25.1% at Zheng-He Montes. To the south of Hillary Montes, there is a substantial decrease in the abundance from 18.3% at the Southwest buffer to 9.3% at Tenzing Montes. The abundance of NSS endmember within abm reaches a maximum in the low northern latitudes: Al-Idrisi Montes shows none, Zheng He, Baret and Hillary Montes show 41.6%, 36.7%, and 27.8% respectively, and the Southwest buffer and Tenzing Montes show none. The NSS endmember maximum in the central Montes correlates to the occurrence of dark tholins coating Zheng He, Baret and Hillary Montes, which unlike Al-Idrisi and Tenzing Montes are co-latitudinal with the equatorial maculae that extend in a discontinuous belt around Pluto. The maculae are interpreted to represent tholins that have formed via ultraviolet irradiation of CH₄ in Pluto's atmosphere, settled out onto the surface, and accumulated to form a superficial, but contiguous, layer (Moore et al., 2016; Grundy et al.,

2018). This process occurs across Pluto's entire surface, but the low latitude uplands within the permanent diurnal zone are the only location where climatic conditions are mild enough on obliquity timescales such that the layer is not dissipated by regular volatile mobilization (Binzel et al., 2017; Earle et al., 2017, 2018). Grundy et al. (2018) estimated that unperturbed tholin accumulation would coat the surface to a thickness of ~3.5 m over 1 Gyr, a result supported by Johnson et al. (2020). The elevated abundance of NSS endmember within the abm unit of the central Sputnik mountain ranges, in combination with the observation that they are coated by a dark material whereas peaks in the northern and southern ranges are not, therefore indicates that these dislodged crustal blocks are sufficiently stable in their grounded state, surrounded by N₂ ice of Sputnik Planitia, to accumulate tholins to the extent that they form a contiguous layer over millions of years. As noted in Section 4, it is difficult to disentangle the effects of H₂O ice and negative spectral slope material at around 2 μm, and previous works (e.g. Cruikshank et al., 2015, Schmitt et al., 2017, Protopapa et al., 2017) have accordingly identified a correlation between the abundance of H₂O ice and tholins, which may form part of the explanation for the generally high abundance of H₂O ice within the central Sputnik mountain ranges (especially Baret Montes).

For both the abm and ibm units, there is a pronounced minimum in the abundance of volatile ices for the central Sputnik mountain ranges. The areal mass fraction of N₂:CH₄ and β-N₂ in abm is 64.6% at Al-Idrisi, which dips to 33.3% and 21.4% in Zheng He and Baret Montes respectively, before increasing to 34.7% in Hillary Montes, 81.3% in the Southwest buffer, and 89.3% at Tenzing Montes. We interpret this pattern to be a consequence of the extensive tholin coverage in the central ranges, and it is notable that it is anti-correlated to the NSS endmember, the abundance of which reaches a maximum in these ranges. For those ranges not coated with

tholins, the elevated abundance of volatiles in the southern mountain ranges (81.3-89.3%) relative to those in the north (64.6%) is interpreted to be a consequence of the highly variable insolation and climate zones across the latitudinal extent of Sputnik Planitia that derive from Pluto's high obliquity (presently 123°) (Hamilton et al., 2016; Binzel et al., 2017; Earle et al., 2017). Modeling of the N_2 cycles on Pluto over seasonal and astronomical timescales by Bertrand et al. (2018) shows that over one obliquity cycle in Pluto's current orbital configuration, the latitudes of Sputnik Planitia ($25^\circ S$ - $30^\circ N$) are dominated by N_2 condensation, entirely incorporating Tenzing Montes between $9^\circ S$ and $22^\circ S$, whereas the northern regions between $30^\circ N$ and $50^\circ N$ are dominated by N_2 sublimation, mostly incorporating Al-Idrisi Montes between ($25^\circ N$ - $42^\circ N$). This effect may explain the paucity of interstitial N_2 ice separating the mountain blocks of northern ranges such as Al-Idrisi (Fig. 25a), relative to the blocks of Tenzing Montes, the flanks of which appear to be inundated by N_2 ice plains that are elevated by as much as a kilometer above those of Sputnik Planitia (Fig. 25b), implying voluminous N_2 ice accumulation amongst the blocks here. The extensive coating of the southern mountains by such condensed volatiles likely explains the lower detections of H_2O ice here relative to the northern mountains, where the H_2O ice is more exposed. Volatile condensation is especially enhanced in southern Sputnik at present as these regions are entering winter, whereas the northern regions are entering summer.

A similar effect may be seen in the areal mass fraction of pure CH_4 ice in unit abm, which while forming less than a few percent of this unit, shows a general increase from north to south: it is absent at Al-Idrisi, Zheng He, Baret, and Hillary Montes, increases to 0.4% at the Southwest buffer, and to 1.4% at Tenzing Montes (the highest areal mass fraction for any unit in any province in the mapping area). For the latter range, N_2 absorption is especially suppressed (Fig.

10). N₂ and CH₄ will both deposit at low elevations, but the higher abundance of N₂ relative to CH₄ in Pluto's atmosphere, in combination with the warmer atmosphere at high elevations inhibiting N₂ precipitation (Moore et al., 2018; Bertrand et al., 2020a), means that deposition of N₂ dominates at lower elevations, whereas CH₄ is mostly deposited at high elevation. Therefore, both the very high elevation of Tenzing Montes (rising to >5 km above mean radius) and their equatorial latitude make them a natural setting for the precipitation of CH₄ ice under Pluto's present obliquity and seasonal conditions. The volatile transport modeling of Bertrand et al. (2019) found that at higher latitudes, CH₄ deposits are only stable on a seasonal timescale for Pluto's current orbital configuration, but at lower latitudes, such deposits at high elevation would grow thicker and potentially subsist across multiple Pluto years, as in the case of the bright CH₄ deposits that are seen to coat the summits of Pigafetta and Elcano Montes within Cthulhu Macula, the crests of which rise to almost 4 km above mean radius (Bertrand et al., 2020a). The CH₄ at Tenzing Montes is not **characterized by** a bright coating **unlike** the summits of the co-latitudinal Pigafetta and Elcano Montes, which may be due to (i) the overall low abundance of pure CH₄ ice here (1.4%), (ii) the lower albedo contrast between CH₄ frost and H₂O ice as compared to CH₄ frost and the dark blanket of tholins, and (iii) perhaps also the fact that Tenzing Montes were seen at a very high solar incidence angle (~77°) during the New Horizons flyby, which minimizes the visibility of the albedo contrast between the CH₄ frost and H₂O ice.

5.2 Bright chaotic terrain

The bright, chaotic terrain unit (bct) is confined to a single region to the north of Al-Idrisi Montes. It consists of high albedo plains interspersed with darker blocks reaching several km across. The unit is crossed by east-west oriented troughs and scarps, and is at a slightly lower

elevation (by ~0.5 km) than unit ibm to the south, making it amongst the lowest elevation regions of anywhere in Sputnik Planitia and its borders (reaching 3 km below mean radius). The fact that the unit displays a geomorphology that is more characteristic of the fluted, valleyed uplands to the north **led** White et al. (2017) to hypothesize that it may represent an early stage in the formation of the chaotic, angular, blocky mountains, whereby tectonically weakened H₂O ice crust is in the process of fragmenting as it is being infiltrated by glacial N₂ ice that has overflowed from Sputnik Planitia, or condensed directly onto it from the atmosphere in large quantities on account of the terrain's very low elevation. This hypothesis is supported by the composition of bct, very similar to the ibm unit, which is interpreted to represent small H₂O ice crustal blocks that have been dislodged and coated by the glacial N₂ ice. β - N₂ is the most abundant component in bct and ibm (54.8% and 41.2% respectively), followed by crystalline H₂O ice (25.5 % and 34.9%), the NSS endmember (14% and 21.3%), and N₂:CH₄ (5.7% and 2.5%). The abundance of N₂ in this area is also confirmed by LEISA spectra: Figures 6 and 10 show that unit bct has the highest CH₄ band shift parameter and deepest N₂ absorption band of any unit.

5.3 Dark, Ridged Terrain

The dark, ridged terrain (unit drt) consists of low albedo, subparallel ridges with crest-to-crest spacing of several hundred meters to a few km, which mainly separate Baret and Al-Idrisi Montes from the uplands of Viking Terra to the west, although a smaller occurrence is also seen separating Hillary Montes from the dark-pitted, marginal plains. The ridges tend to align parallel to the edge of Sputnik Planitia. Unit drt displays the highest areal mass fraction of the NSS endmember of any unit (38.5%-53.4%), followed by N₂:CH₄ (21.5%-38.7%), and H₂O ice

(18.1%-28.5%). The high abundance of NSS endmember reflects the fact that this unit displays the most contiguous and complete coverage by tholins of any unit. The ridges have been variously interpreted to be compressional in origin, whereby they form due to buoyant, mobile H₂O ice blocks being pushed towards the uplands by convective motions in Sputnik Planitia, with a weaker, darker, overlying layer folding in response to the compressive forces (White et al., 2017; Ahrens & Chevrier, 2019), or depositional, whereby they are recessional moraines of dark tholins deposited as the N₂ ice glaciers responsible for entraining and translating the H₂O ice mountains retreated (Howard et al., 2017). White et al. (2017) hypothesized that this dark material represents tholins like those coating Cthulhu Macula and Baret, Zheng He, and Hillary Montes, while Ahrens and Chevrier (2019) interpreted the ridges to be formed from a thin layer of CH₄-H₂O ice overlain on a H₂O ice-based glacier. Our spectral analysis and modeling does not suggest that the dark material is especially enriched in CH₄, with between 0.5% and 0.8% CH₄ being diluted in the N₂:CH₄ (Fig. 8A) that forms between 21.5% and 38.7% of the unit by areal mass fraction. The prevalence of the NSS endmember that characterizes this unit, and its very low albedo, **leads** us to conclude that the deformed layer is more likely composed of tholins rather than a CH₄-H₂O ice mixture.

There is always a sharp and well-defined boundary between unit drt and adjoining units – the dark tholins are always tightly confined to within the unit’s boundaries and do not spread beyond its borders, implying that whatever process has created this unit, it has acted to densely concentrate the tholins within the unit. In addition, whereas the drt units of Baret and Hillary Montes are mostly located within the equatorial, permanent diurnal zone (13°N to 13°S) that harbors the maculae and the tholin-covered mountain ranges, that of Al-Idrisi Montes extends to higher latitudes (20°N to 30°N), suggesting that accumulation directly via settling from the

atmosphere alone cannot explain the density of tholins here, as it can for the tholin coverage on the mountain ranges. Since the low albedo N₂ ice plains of northern Sputnik Planitia (encompassing units dcp and tbp, see section 5.5) are interpreted to have high levels of tholins entrained within them, the same compressive forces that White et al. (2017) and Ahrens and Chevrier (2019) hypothesized formed the ridges may have also concentrated tholins within N₂ ice separating the mountain blocks, dredged them to the surface, and formed them into the sub-parallel ridges. We further discuss unit drt in section 5.4, in which we argue that Columbia Colles, mapped by White et al. (2017) as scattered hills, displays geomorphological and spectral characteristics associated with unit drt.

5.4 Scattered hills

The scattered hills form a unit (sh) in eastern Sputnik Planitia consisting of km-sized hills with up to 500 m topographic relief that have been carried by N₂ ice valley glaciers flowing from East Tombaugh Regio into the Cellular plains of Sputnik Planitia (White et al., 2017). In addition, there are Challenger and Columbia Colles, larger conglomerations of such hills that form roughly rectangular masses measuring several tens of km across, and which have been interpreted to be grounded in shallow N₂ ice here at the edge of Sputnik basin (White et al., 2017). Given that these hills appear to be subject to the motions of N₂ ice (both glacial and convective) in this region of Sputnik Planitia, White et al. (2017) and Howard et al. (2017) hypothesized that they represent chunks of the pitted uplands that have been broken off through glacial erosion and transported in the N₂ ice. Geologic mapping of the pitted uplands and the CH₄ ice bladed terrain of Tartarus Dorsa to the east indicates that the pitted uplands are likely a lower-elevation extension of the bladed terrain that is experiencing deposition of volatile ices

that have sublimated from Sputnik Planitia (Moore et al., 2018). This would imply that the pitted uplands, and the scattered hills derived from them, are predominantly composed of CH₄ ice.

Our spectral modeling of the discrete ranges of hills that form unit sh shows a relatively consistent pattern: hills in the South-East pitted plains and Astrid, Challenger, and Soyuz Colles show a composition that is predominantly β -N₂ (64.4%-79%), followed by the NSS endmember (19.7%-32.4%), with a small areal mass fraction of N₂:CH₄ (1.3%-3.6%). These hills are located within the portion of Sputnik Planitia that is interpreted to be experiencing net N₂ ice deposition under Pluto's current climatic and obliquity conditions (White et al., 2017, Bertrand et al., 2018), and the dominance of β -N₂ in the spectra reflects this. In 315 m/pixel imaging of the hills, they show a similarly high albedo **with respect** to the surrounding N₂ ice plains, and their surface relief appears smoothened, indicating that they have accumulated a contiguous coating of N₂ ice (Fig. 26a). This coating is thick enough to obscure the spectral signal from the material composing the hills themselves, so we cannot confirm spectroscopically whether the hills are composed of H₂O or CH₄ ice (both of which are less dense than N₂ ice, allowing the hills to float, and both of which are rigid enough at Pluto conditions to support the topographic relief exhibited by the hills).

A notable exception to the trend is Columbia Colles, which displays a composition that is more similar to the dark, ridged terrain (unit drt) than the other scattered hills (cf. Fig. 24N to the drt units in Figs. 24A, B, and F). Like the other scattered hills, Columbia Colles displays substantial β -N₂ (45.5%) and NSS endmember (21.7%), with a small areal mass fraction of N₂:CH₄ (0.05%), but also displays a large areal mass fraction of crystalline H₂O (32.8%). The H₂O ice may be attributed to the fact that Columbia Colles are the only portion of the unit sh to display a consistent covering by dark red tholins, the spectral signature of which, as noted earlier,

1105 is difficult to distinguish from that of H₂O ice. Unit drt also shows significant crystalline H₂O
1106 (18.1%-28.5%) and NSS endmember (38.5%-53.4%), but with N₂:CH₄ (21.5%-38.7%) in place
1107 of β -N₂, which is absent. Portions of Columbia Colles display a quite well-developed ridged
1108 fabric, with ridge crests separated by 1-2 km (very similar to the separation of the ridge crests of
1109 unit drt, Figs. 26b and 26c). White et al. (2017) mapped Columbia Colles as part of unit sh on
1110 account of its proximity to the other scattered hills and close spatial relationship to Challenger
1111 Colles (a discontinuous “bridge” of hills 60 km long joins the two conglomerations). The
1112 distinct dark red color of Columbia Colles, its more explicitly ridged texture compared to
1113 anything seen elsewhere within unit sh, and the fact that Columbia Colles is the only portion of
1114 unit sh that contacts the surrounding uplands (as do the occurrences of unit drt in Baret and Al-
1115 Idrisi Montes, and possibly also that in Hillary Montes if the dark-pitted, marginal plains that
1116 bound it represent uplands terrain of Cthulhu Macula covered by thin N₂ ice), however, are
1117 characteristics that are more diagnostic of unit drt. Unit drt is interpreted to represent an
1118 accumulation of dark tholins superposed on lighter-toned H₂O ice blocks that have eroded from
1119 Pluto’s ancient H₂O ice crust along the western margin of Sputnik Planitia (section 5.3), whereas
1120 Columbia Colles, and the rest of the scattered hills, are interpreted to consist of blocks of CH₄ ice
1121 that were eroded more recently from the pitted uplands of East Tombaugh Regio. Therefore,
1122 while we hypothesize that the same processes have probably caused the concentration of dark
1123 surface material at the western dark ridged terrain as well as Columbia Colles, and its
1124 arrangement into subparallel ridges, the material forming Columbia Colles is still distinct
1125 stratigraphically and compositionally from that forming the western dark ridged terrain, and so
1126 mapping Columbia Colles as unit sh, rather than drt, remains justified. The processes forming the
1127 ridges are not known for certain, but compression of the underlying blocky material and glacial

recession have both been invoked (Howard et al., 2017; White et al., 2017; Ahrens and Chevrier, 2019).

5.5 Cellular plains

The Cellular plains of Sputnik Planitia represent the portion of the N₂ ice sheet that is experiencing solid-state convection from thermal input within or below the glacier (Stern et al., 2015; Moore et al., 2016; McKinnon et al., 2016; Trowbridge et al., 2016). The plains dominate the central and northern portions of Sputnik Planitia, i.e. the part of Sputnik Planitia corresponding to the Sputnik basin itself, where the N₂ ice is sufficiently thick (>1 km) to support convection (McKinnon et al., 2016). The cells tend to be ovoid in planform, are defined by a reticulate network of troughs with central ridges, and exhibit pitting on a scale of hundreds of meters to a few km (Moore et al., 2016; White et al., 2017). The timescale of surface renewal via convection has been estimated to be ~420,000 to ~890,000 years (McKinnon et al., 2016; Trowbridge et al., 2016; Buhler & Ingersoll, 2018). White et al. (2017) divided the Cellular plains into three units based primarily on albedo. The bright, Cellular plains (unit bcp) occupy the central portion of Sputnik Planitia, extending to ~30°N. They display a normal reflectance of 0.78 to 0.86 (Buratti et al., 2017) and are interpreted to be the region of Cellular plains that are presently experiencing net deposition of fresh, bright N₂ frost from the northern regions of Sputnik Planitia (Protopapa et al. 2017; Bertrand et al., 2018, 2020b). The dark, Cellular plains (unit dcp, with a normal reflectance of ~0.69), and dark, trough-bounding plains (unit tbp, with a normal reflectance of ~0.52-0.60) occur in the northern and western portions of Sputnik Planitia, and are interpreted to be presently experiencing net sublimation (Protopapa et al. 2017; Bertrand

et al., 2018, 2020b). With the exception of Alcyonia Lacus in Al-Idrisi Montes, all three units of the Cellular plains are confined to the Cellular plains in this study.

Unsurprisingly, the most abundant component of all three units is N₂ ice, the CH₄ fraction diluted in N₂ always being below 1%. This observation is also confirmed by the high values of the CH₄ band shift index, and by the depth of N₂ absorption band. Unit bcp is dominated by N₂:CH₄, which accounts for 99.9% of its areal mass fraction, corroborating the interpretation that the high albedo of unit bcp is due to current deposition of fresh N₂ frost on its surface White et al. (2017). Units dcp and tbp are instead dominated by β-N₂ ice: dcp shows 68.2% β-N₂ and 4.9% N₂:CH₄, whereas tbp shows 53.9% β-N₂ and 7.6% N₂:CH₄. The remainders of these units are mainly occupied by NSS endmember: 26.9% for dcp and 38.4% for tbp. Based on the results of Protopapa et al. (2017) and Schmitt et al. (2017), White et al. (2017) interpreted unit dcp to be representative of the material filling the Sputnik basin, specifically N₂ ice that **is associated with** a relatively high concentration of tholins that first settled onto the surface by katabatic and condensation flows (Bertrand et al., 2020b) and then became entrained within the ice by convective motion across the history of the existence of Sputnik Planitia (White et al., 2017). This N₂/tholin mixture is only exposed in the north and west where the net sublimation of the N₂ ice means that it is not blanketed by a fresh layer of bright N₂ frost as seen in the rest of Sputnik Planitia, including unit bcp (Bertrand et al., 2018, 2020b). In the case of the lower albedo unit tbp, confined to the northern edge of Sputnik Planitia, White et al. (2017) interpreted this to be where tholins in the N₂ ice had become especially concentrated at cell boundaries through a combination of convective motion of the ice and the very high sublimation rates encountered here (higher than anywhere else in Sputnik Planitia across an obliquity cycle). In accordance with this hypothesis, we find that the proportions of NSS endmember within these three Cellular

1173 plains units correlate to their albedos, and indicate a progressively increasing tholin content
1174 within darker plains.

1175 Alcyonia Lacus is an irregular, 30 km long by 10 km wide expanse of N₂ ice plains that is
1176 surrounded by units abm and ibm of Al-Idrisi Montes, and which was mapped as dcp by White et
1177 al. (2017) (Fig. 27a). While the plains do show the same albedo as unit dcp within Sputnik
1178 Planitia, they are separated from the Cellular plains by the mountain range, so cannot strictly be
1179 described as “cellular”. The absence of pits indicates that it is being resurfaced by some means
1180 other than sublimation, and/or that its rheology is unable to support pit topography. Its relatively
1181 smooth boundaries, whereby the surrounding mountains and hills do not intrude into its interior,
1182 indicate that this feature may have actively modified its boundaries. It has variously been
1183 interpreted as once being a “pond” of liquid N₂ maintained during an era of high atmospheric
1184 pressure, and which has since frozen (Stern et al., 2017), or an active glacial feature in which
1185 flow of the N₂ ice closes any sublimation pits and shepherds blocky H₂O ice material to its edges
1186 (White et al., 2017). Spectral modeling shows that its composition is broadly similar to that of
1187 the dcp unit proper within Sputnik Planitia, exhibiting 53.9% β-N₂, 20.7% NSS endmember, and
1188 1.9% N₂:CH₄, but with an additional H₂O ice component, comprising 23.6%. Sub-resolution
1189 H₂O ice fragments floating within the N₂ ice of the lacus may cause this. The presence of the
1190 NSS endmember suggests that, like unit dcp within the Cellular plains, Alcyonia Lacus also
1191 consists of “mature” N₂ ice that has entrained a high concentration of tholins within its volume
1192 over the course of its existence, but given its geographic isolation from Sputnik Planitia (the two
1193 are separated by 65 km), it most likely formed independently from Sputnik Planitia and
1194 separately acquired its tholins. White et al. (2017) hypothesized that the lacus may be situated at
1195 a localized zone of high geothermal flux that is mobilizing the N₂ ice and causing any blocky

1196 H₂O fragments within the zone of mobilization to drift to its edges, and if the lacus is long-lived,
1197 then it is possible that such continual mobilization has also allowed gradual entrainment of
1198 tholins within the N₂ ice to levels comparable to that seen within unit dcp of the Cellular plains.

1199

1200 *5.6 Non-Cellular plains*

1201 The non-Cellular plains of Sputnik Planitia are those that are interpreted to not be currently
1202 experiencing solid-state convection. These plains dominate the southern and eastern regions of
1203 Sputnik Planitia, but there are also small occurrences seen interstitially to mountain and Cellular
1204 plains units at the western and northern boundaries. As with the Cellular plains, these plains
1205 exhibit pitted textures, but the pits can reach much larger diameters (typically >1 km). The
1206 transition from cellular to non-Cellular plains is interpreted to reflect thinning of the volatile ice
1207 layer, and perhaps also declining heat flow (McKinnon et al., 2016). The non-Cellular plains are
1208 not convecting, but they have nevertheless very recently resurfaced via glacial flow of the N₂ ice
1209 from which they are formed, possibly on a timescale as short as tens of thousands of years (Wei
1210 et al., 2018). The non-Cellular plains universally show a high normal reflectance (0.78 to 0.86),
1211 like that of the bright Cellular plains. This is true even for the small patches of non-Cellular
1212 plains located at the northern and western edges of Sputnik Planitia (the North pitted plains and
1213 West pitted plains provinces), which are situated within the portion of Sputnik Planitia that is
1214 currently experiencing net sublimation and which abut the darker plains units (dcp and tbp)
1215 (White et al., 2017; Bertrand et al., 2018, 2020b).

1216 β -N₂ and N₂:CH₄ are the most abundant components of the non-Cellular plains: in the
1217 southern region of Sputnik Planitia, the deeply pitted plains (unit dpp), lightly pitted plains (unit
1218 lpp), sparsely pitted plains (unit spp), patchy, pitted, marginal plains (unit pmp), and dark-pitted

1219 marginal plains (unit dmp) display between 59.2% and 100% $N_2:CH_4$ and $\beta-N_2$ by areal mass
1220 fraction. The proportion of $N_2:CH_4$ and $\beta-N_2$ versus NSS endmember within these plains appears
1221 to correlate to the extent to which the plains display deep pits. The plains units exhibiting the
1222 largest pits (typically reaching ~1 km in diameter, but which can reach several km) are the
1223 deeply pitted plains, which are primarily concentrated in the southernmost region of Sputnik
1224 Planitia where they dominate the South pitted plains province, and the dark-pitted, marginal
1225 plains, which form a buffer between the mountain ranges of Hillary and Baret Montes and the
1226 uplands of Cthulhu Macula. The pits in both of these units tend to cluster together in tightly
1227 packed swarms that form curved, wavelike patterns (White et al., 2017), and where they are large
1228 enough for their floors to be resolved and not obscured by shadows cast by the pit walls, the
1229 floors invariably display a low albedo (<0.17 normal reflectance, Buratti et al., 2017). This low
1230 albedo material has been interpreted to be tholins covering the pit floors (White et al., 2017),
1231 which in the case of dpp may be tholins entrained within the N_2 ice that have been released via
1232 sublimation to build up on the floors of the pits as a lag, and in the case of dmp may be tholins of
1233 Cthulhu Macula, whereby the N_2 ice covering the macula is thin enough for the pits to extend all
1234 the way through the ice, exposing the tholins of Cthulhu Macula underneath. Our models show
1235 that both units exhibit NSS endmember: 20.7% for dpp in the South pitted plains, and 38.9% to
1236 61.4% for dmp in Baret and Hillary Montes respectively. The high abundance of NSS
1237 endmember in the latter may be a consequence of the lower solar incidence angle of the imaging
1238 covering unit dmp relative to dpp, meaning that shorter shadows are cast by the pit walls across
1239 pit floors in dmp, and so higher proportions of the pit floors are visible. Pits within dpp in
1240 southern Sputnik Planitia are mostly small enough for shadows to cast across their entire floors.

In contrast to these plains units that display large and deep pits, the lightly pitted plains and sparsely pitted plains were interpreted by White et al. (2017) to be experiencing only superficial sublimation of N₂ ice, and are instead undergoing mantling by ongoing deposition of N₂ frost, as well as glacial creep of the N₂ ice that is infilling any large pits that do exist. Any sublimation occurring within these plains is therefore insufficient to counter these processes and to create large pits that expose tholins entrained within the N₂ ice, meaning that neither of these units is interpreted to display non-volatile components (i.e. NSS endmember) in their composition. Accordingly, both of these units are dominated by N₂:CH₄ and β-N₂ in the South and East pitted plains (>99% by areal mass fraction), with no NSS endmember observed.

The patchy, pitted marginal plains (unit pmp) are interpreted to represent relatively thin N₂ ice (probably no more than a few hundred meters) that has condensed on rugged, low-lying uplands terrain bordering Sputnik Planitia, explaining why this unit shows a hummocky texture on a scale of several km, whereas the other plains units of Sputnik Planitia are flat. Unit pmp borders the plains of southern Sputnik Planitia, which we interpret to be a geologic consequence of the preferential deposition of volatile ices that is presently occurring within this equatorial, permanently diurnal zone (Bertrand et al., 2018), a phenomenon that is also manifested compositionally by the deeper N₂ band depth in N₂ ice plains at southerly latitudes (Fig. 10). As described in section 5.1, it is for this same reason that we interpret unit abm of Tenzing Montes, which is embayed by elevated N₂ ice plains of unit pmp, to display a high areal mass fraction of N₂:CH₄ compared to the northern mountain ranges. The elevated N₂ ice plains of unit pmp that cover the southeast margin of Sputnik Planitia (Fig. 27b) show some geomorphological similarities to the elevated plains that separate the blocks of Tenzing Montes, including scarps leading from unit pmp down to Sputnik Planitia. Unit pmp shows a similarly dense concentration

of pits to units dpp and dmp, although the pits of pmp show a smaller size range, never reaching >1 km in diameter. The presence of NSS endmember within unit pmp (areal mass fractions range between 20.8% and 33.2%), however, indicates that its pits do display tholins on their floors that are detectable by LEISA.

The non-Cellular plains at the eastern and southern boundaries of Sputnik Planitia are dominated by β -N₂ ice, with typically only a few percent of N₂:CH₄. But of this N₂:CH₄, Figure 8a shows that the percentage of CH₄ diluted in N₂ is generally high (>4%), whereas it is low for the rest of the plains of Sputnik Planitia (generally <2%). For the southern plains (unit dpp in South pitted plains), the elevated CH₄ content may be interpreted as a manifestation of the general increase in volatile abundance that is seen towards the southern end of Sputnik Planitia, whereby the low insolation that is presently encountered here is conducive to deposition of both CH₄ and N₂ in low-lying areas (deposition of N₂ at low elevation tends to dominate at more northerly, and more insulated, latitudes). Yet the elevated CH₄ content that is seen along Sputnik Planitia's eastern boundary may instead be an indication of CH₄-rich material being transported from the pitted uplands of East Tombaugh Regio by the N₂ ice glaciers that lead from there into Sputnik Planitia. As noted in section 5.4, the pitted uplands likely represent a lower-elevation extension of the bladed terrain, and so their composition is likely CH₄-based (Moore et al., 2018), and the scattered hills (unit sh) have accordingly been interpreted as km-sized blocks of such material that have been transported into Sputnik Planitia (albeit which are coated by freshly-deposited N₂ ice). Yet given that these eastern non-Cellular plains incorporate the active glaciers leading from the uplands, their elevated CH₄ content may be an indication of recently eroded, sub-resolution CH₄-rich material that is being carried on the surface of the glaciers – the lateral moraine trails that have been identified at these glaciers (White et al., 2017, Howard et al.,

1287 2017) likely represent such sub-resolution material (Fig. 27c). As this material is transported
1288 farther to the west, into the interior of Sputnik Planitia, it becomes dissipated, lowering its
1289 concentration within the N₂ ice, and it becomes coated by freshly deposited N₂ ice (as has
1290 happened to the large scattered hills), resulting in low CH₄ percentages here.

1291 While the non-Cellular plains are concentrated within southern and eastern Sputnik Planitia,
1292 units dpp and spp also form small expanses at its western and northern edges (the North and
1293 West pitted plains provinces), surrounded by the mountains and Cellular plains. Units dpp and
1294 spp within these provinces display a high albedo that is akin to the bright plains of central and
1295 southern Sputnik Planitia, and which contrasts with the darker plains of the surrounding Cellular
1296 plains (Fig. 27d). That the north and west pitted plains provinces are located within the portion of
1297 Sputnik Planitia that is presently experiencing net sublimation of N₂ ice from the surface, and yet
1298 still present a high albedo, implies two possible scenarios: (i) the plains may be experiencing net
1299 sublimation like the surrounding dark Cellular plains, with the exception that the body of the N₂
1300 ice forming them does not contain a high concentration of tholins that would be exposed at the
1301 surface by the sublimation, or (ii) the plains are in fact localized zones of net deposition of N₂ ice
1302 rather than sublimation, causing them to be coated by a fresh, bright layer of N₂ frost in the same
1303 manner as the plains in the south and east of Sputnik Planitia. These bright northern and western
1304 plains differ in composition from their southeastern counterparts: they display units dpp and spp
1305 and are composed almost entirely of N₂:CH₄ (>99%), in contrast to the β-N₂ and NSS
1306 endmember that form unit dpp in the south, and the β-N₂ and N₂:CH₄ that form unit spp in the
1307 south (Fig. 24). The most notable compositional difference is the absence of NSS endmember
1308 from unit dpp in the northern and western plains. This suggests that tholins are not covering pit
1309 floors here, in contrast to pits in unit dpp in the southern and eastern plains, and indicates that

1310 tholins are not entrained within the N₂ ice of unit dpp in the north and west. Sublimation of the
1311 N₂ ice to form the pits is not exhuming any entrained tholins, meaning that none can build up as
1312 a lag on the pit floors. If these northern and western plains are experiencing net sublimation, like
1313 the darker, cellular plains surrounding them, then the absence of entrained tholins means that the
1314 albedo of the plains will remain high regardless of how much N₂ ice sublimates from the surface.
1315 In fact, the presence of localized plains that consistently display a high albedo, and which are
1316 therefore consistently cooler than the surrounding darker plains, may actually act to partially
1317 offset the predominant sublimation that occurs within this part of Sputnik Planitia, and allow
1318 them to retain more of the bright N₂ ice that does deposit on them, in what would essentially be a
1319 runaway albedo effect (see point 3 in section 5.7).

1320 This does require, however, that the plains are bright to begin with, which is related to the
1321 question of how bright, non-Cellular plains were established in these marginal areas of Sputnik
1322 Planitia. They evidently represent portions of the plains at the margins of Sputnik Planitia where
1323 the N₂ ice is insufficiently thick to support convection, and within which entrained tholins are
1324 absent, in contrast to the dark, adjacent Cellular plains. This observation seems to imply that
1325 convection within the Cellular plains is an efficient process for entraining tholins and ensuring
1326 that they remain trapped within the convection cells and cannot migrate to adjacent N₂ ice that is
1327 not convecting. The fact that dark pit floors are seen in pitted plains of the southern non-Cellular
1328 plains suggests that glacial flow of N₂ ice from the center of Sputnik Planitia to its southern
1329 regions may play a role in transferring tholin-entrained N₂ ice of the convective cells outside of
1330 the convective regime. There is evidence for this in the form of elongated, “extinct” cells
1331 extending from the southern boundary of the bright Cellular plains that are defined by chains of
1332 joined, dark-floored pits that describe polygonal outlines (Fig. 27e), and which White et al.

(2017) interpreted to be formerly active convection cells that were moved southwards and their planforms distorted by lateral flow of the ice in this region of Sputnik Planitia. In the case of the bright, non-Cellular plains of the North and West pitted plains, however, it may be that convective motion in the adjacent Cellular plains acts to effectively segregate any tholins entrained within the non-Cellular plains and trap them in the convection cells, thereby brightening the non-Cellular plains and initiating the runaway albedo effect whereby sublimation of N₂ ice remains dominant in the dark Cellular plains, but becomes less effective relative to deposition of N₂ ice in the bright, non-Cellular plains.

5.7 Possible processes responsible for the observed diversity of ice mixtures in Sputnik Planitia

The diversity of ice mixtures and N₂ or CH₄ enrichment at the surface of the plains of Sputnik Planitia may in part be a consequence of various phenomena that would not manifest in geomorphology that is resolvable by New Horizons imaging. These include: (1) Differences in ice thickness (related to different bedrock topography and glacial flow), which would impact deep ice convection and entrainment of tholins, as well as the subsurface heat flow. Within the convective cells, the subsurface heat flow would be larger at the centers than at the edges of the cells. (2) Eolian processes disrupting the surface ice (changes in albedo, composition, grain size, etc.) such as (a) warming by the atmospheric downward sensible flux, (b) mechanical erosion, and (c) atmospheric transport, surface accumulation of haze particles or dark materials and subsequent darkening of the ice (or brightening if ice grains are transported too). Bertrand et al. (2020b) investigated these processes and showed that the former and the latter could significantly impact the surface ice and the volatile sublimation-condensation rates and therefore

the surface composition. (3) Albedo and composition positive feedbacks have been shown to be very efficient in Sputnik Planitia (Earle et al., 2018, Bertrand et al., 2020b). In particular, Bertrand et al. (2020b) showed that a local decrease in N₂ ice surface albedo from 0.7 to 0.65 during northern spring is sufficient to turn a N₂ condensation-dominated region into a sublimation-dominated region (see Fig. 16 in Bertrand et al., 2020b). The processes mentioned in (1) and (2) can locally trigger a change in surface albedo and composition that is likely to amplify with time (e.g. local deposition of N₂ ice on bright surfaces and removal on dark surfaces) (4) The composition of the surface ice can also be impacted by ice segregation (e.g. formation of a CH₄-rich layer on top of a N₂-rich ice) and by the relaxation of the surface ice toward a ternary phase equilibrium, whose timescale and properties can vary locally depending on the local surface and atmospheric conditions (Protopapa et al., 2017, Schmitt et al., 2017, Tan and Kargel, 2019). (5) Transport of gaseous CH₄ by the near-surface winds in Sputnik Planitia can also favor CH₄ saturation above the surface at specific locations, and subsequent condensation and enrichment of the ice in CH₄. This is illustrated by Figure 28, which shows the diurnal mean near surface CH₄ atmospheric mixing ratio and the diurnal net CH₄ deposition in Sputnik Planitia, as predicted for July 2015 by global climate modeling of Pluto (Bertrand et al., 2020b). The 3D simulations show that the near-surface air in Sputnik Planitia is enriched in N₂ (depleted in CH₄) compared to the air outside the basin. This is due to N₂ sublimation in Sputnik Planitia (and subsequent injection of cold N₂-rich air in the atmosphere) and to the confinement of this N₂-rich air by the high relief boundaries of the basin (Forget et al., 2017, Bertrand et al., 2020b). The near-surface northern regions of Sputnik Planitia were particularly depleted in CH₄ in 2015 due to the north-to-south sublimation flow that transports gaseous CH₄ southward. Note that the wind patterns predicted by the model inside Sputnik Planitia become different at ~1 km

above the surface, with a strong western boundary current and an anticlockwise wind spiral (see Bertrand et al., 2020b). Figure 28 (left) shows that higher amounts of near-surface gaseous CH₄ are obtained locally near the boundaries of the basin, or near the blocky mountains of the western and southern sides. This is due to downslope transport of the air which is outside the basin or above the blocky mountains and which is enriched in gaseous CH₄ (due to the absence of N₂ sublimation or the occurrence of local sublimation of CH₄-rich frosts that formed on these terrains). As a result, CH₄ deposition onto the plains of Sputnik Planitia is favored in the western, eastern and southern edge of Sputnik Planitia, and in particular near the blocky mountains and near the steepest slopes of the eastern side of Sputnik Planitia (Figure 28, right), where the air is highly enriched in gaseous CH₄ coming from the sublimation of the CH₄-rich Bladed Terrains.

Figure 24 A-O: Pie plots summarizing the composition of the geologic units in each province, as returned by the application of the Hapke-based spectral modeling.

Figure 25. Contrast between the northernmost mountain range of Al-Idrisi Montes and the southernmost range of Tenzing Montes. (a) Al-Idrisi Montes show minimal interstitial N₂ ice plains between mountain blocks. LORRI image is 76 m/pixel and centered at 37.6°N, 156.3°E, with illumination from the top. (b) Several of the mountain blocks of Tenzing Montes are partly engulfed by N₂ ice plains that are elevated by up to a kilometer above the surrounding N₂ ice plains of Sputnik Planitia, and separated from them by scarps (white arrows). MVIC image is 315 m/pixel and centered at 13.6°S, 176.7°E, with illumination from the top.

Figure 26. Scattered hills (unit sh) and dark ridged terrain (unit drt). (a) Scattered hills of Astrid and Soyuz Colles, which display smooth topographic relief and a high albedo, indicating that the hills, like the surrounding plains, have been coated by ongoing N₂ ice deposition. MVIC image is 315 m/pixel and centered at 14.7°N, 184.5°E, with illumination from the left. (b) Dark ridges situated between Baret Montes and dark-pitted, marginal plains of Sputnik Planitia, which were mapped as unit drt by White et al. (2017). White arrows indicate ridges spaced 1-2 km apart that align roughly parallel to the border of the unit with the N₂ ice plains. LORRI image is 117 m/pixel and centered at 11.4°N, 157.5°E, with illumination from the top. (c) Columbia Colles, located at the eastern margin of Sputnik Planitia, which were mapped as unit sh by White et al. (2017.) White arrows indicate ridges spaced 1-2 km apart that resemble those highlighted in (a). The comparable geomorphology and albedo of Columbia Colles to occurrences of unit drt in the west suggest that similar processes have affected Columbia Colles, which are otherwise separated stratigraphically and compositionally from unit drt. MVIC image is 315 m/pixel and centered at 28.7°N, 196.5°E, with illumination from the left.

Figure 27. Plains units of Sputnik Planitia described in sections 5.5 and 5.6. (a) Alcyonia Lacus, mapped by White et al. (2017) as an isolated occurrence of dark Cellular plains surrounded by mountains and blocky material of Al-Idrisi Montes. LORRI image is 117 m/pixel and centered at 36.4°N, 151.6°E, with illumination from the top-right. (b) Hummocky N₂ ice plains of unit pmp covering low-lying uplands of Krun Macula (dark terrain at lower right). Scarps (white arrows) separate unit pmp from the flat plains of Sputnik Planitia, similar to those seen at Tenzing Montes (Fig. 26b). MVIC image is 315 m/pixel and centered at 5.8°S, 191.2°E, with illumination from the left. (c) Glacial flow of nitrogen ice from the bright pitted uplands of East Tombaugh Regio (bottom) into Sputnik Planitia. Dark, converging flow bands (white arrows) are seen in valleys that connect upland flats to Sputnik Planitia, and are interpreted to be moraine trails consisting of CH₄-rich material eroded from the pitted uplands by N₂ ice glaciation. MVIC image is 315 m/pixel and centered at 3.7°N, 193.6°E, with illumination from the top-right. (d) High-albedo, pitted plains of units dpp and spp located at the western edge of Sputnik Planitia, occurring interstitially to convective cells of the dark, Cellular plains (unit dcp). MVIC image is 315 m/pixel and centered at 20.3°N, 155.1°E, with illumination from the top. (e) Dense fields of aligned (unit dpp) in southern Sputnik Planitia. Across the center of the image, they are seen to form chains of

joined, dark-floored pits that trace elongated, polygonal outlines that enclose sparsely pitted plains (unit spp), and which extend southwards from the bright, Cellular plains (unit bcp) at top left. MVIC image is 315 m/pixel and centered at 6.0°S, 179.7°E, with illumination from the left.

Figure 28: Results from the global climate model of Pluto obtained for July 2015 from simulations similar to those presented in Bertrand et al., 2020b. Left: Diurnal mean near-surface (~20 m) atmospheric CH₄ mass mixing ratio in the region of Sputnik Planitia, with near-surface winds. Right: Net diurnal CH₄ deposition onto the surface.

6. Conclusions

In this study of Sputnik Planitia, we have compared spectroscopic data of this region acquired by New Horizons' LEISA instrument to the geomorphology as mapped by White et al. (2017) using visible and panchromatic imaging acquired by the LORRI and LEISA instruments.

Sputnik Planitia is a unique geologic formation in our Solar System: it is a young and deep impact crater basin, hosting a large variety of diverse terrain types, whose surface veneer is made up of volatile ices captured by the cold trap created by its peculiar morphological shape. Terrain units typical of the basin's western rims, were also found inside the cellular plains, like the abm mountains, while the pitted plains covering the whole eastern edge of the planitia, are also frequent, in small patches, in most of the western territory.

The idea behind this work was then to comprehend if, and in which amount, the processes responsible for the ice deposition inside the basin influence the surface composition of units belonging to the very same geological type, but that are spatially separated.

We fit the units' average spectra with and Hapke theory-based modeling, and we created scatter plots comparing the integrated band depths of the main endmember's absorptions, to have a better vision of how the different surface components influence each other, and how this is reflected in the resulting surface spectra.

The analysis of the CH₄ integrated band depths in five wavelength ranges revealed their different sensitivities to variations in composition, grain size, and scattering properties.

We expected to observe an anticorrelation between the CH₄ absorptions and the CH₄ shift index, and a positive trend between the N₂ integrated band depth and the shift parameter: spectral units hosting a large amount of N₂-rich ice would show high values of the shift parameter, whereas in areas where the CH₄-rich ice dominates, the CH₄ absorptions should manifest as small or null shifts. For three out of these six spectral indicators, the results were actually the opposite. The scatter plot of the CH₄ integrated band depths versus the shift index in Ranges 1, 2, and 4 showed, in fact, a positive correlation. We further noticed that the geologic units having weak CH₄ absorptions but small values of the CH₄ shift index are all located within the western mountain ranges, in addition to Columbia Colles. These units are also those that display the deepest absorptions relating to H₂O and tholins, leading us to the conclusion that the weakness of the CH₄ absorptions in Ranges 1, 2, and 4 for these units is not a consequence of low abundance of this material, but rather of a high concentration of other materials that mask its spectral signature or that surface particles in these units are more backscattering than those in the cellular plains. The broad CH₄ absorptions in Ranges 1, 2, and 4 saturate quickly, even though not linearly, with increasing CH₄ abundance, grain size, or forward scattering, while the absorption in Range 3 and the band centered at 1.48 μm , being weaker, require a larger quantity of CH₄ for reaching the saturation level. This conclusion is also supported by the absence of trends between the CH₄ absorptions in Ranges 1, 2, and 4 and the band in Range 3 (Figure 14).

We explored the correlation between the CH₄ and N₂ absorptions with the other endmembers considered - CO, H₂O, NSS endmember - to understand which one is the most responsible for the unexpected suppression of the absorptions in Ranges 1, 2, and 4 observed in Figure 13A.

From the comparison between the trends in Figure 13A and Figure 16A (CH₄ integrated band depths in Ranges 1, 2, and 4 versus the CO integrated band depth), we notice that geologic units

showing deeper CH₄ absorptions and higher values of the CH₄ shift index also have strong CO bands. CH₄ in Range 3 and N₂, on the other hand, do not show any correlation to CO (Figure 16B). Grundy et al. (2013, 2014) and Schmitt et al. (2017) noticed, however, a strong correlation between CO and N₂, but not between CO and CH₄. Comparing the CO abundance map (Figure 15) to the areal mass fraction maps of N₂:CH₄ (Figure 11a) and pure β-N₂ (Figure 12a) confirms the observed connection between CO and N₂. The fact that this link doesn't manifest in the scatter plots of Figure 16 can signify that the contaminants affect the depth of the CO absorption as well, and that CO is not responsible for the observed anomaly in Figure 13A.

We then explored the mutual variation of the CH₄ and N₂ integrated band depths with the abundance of crystalline H₂O and the NSS endmember returned by the modeling. The results (from Figure 18 to Figure 22) indicate that the NSS endmember (likely tholins) or more backscattering particles are primarily responsible for the suppression of CH₄ absorptions in Ranges 1, 2, and 4 in the western mountainous units of Sputnik Planitia.

The Hapke theory-based modeling is a powerful tool to investigate the nature of the endmembers covering a planetary surface, but it is limited by the availability and the quality of the optical constants. For instance, in our modeling we could not include the contribution of the CO because of lack of reliable optical constants, making its important contribution to the observed spectra only partially explored. The same can be concluded for the refractory non-ice material responsible for the observed negative spectral slope in the NIR spectra. Because there is very little published information on the optical constants for tholins with a composition relevant to Pluto's surface, the nature of the non-ice material is still unknown.

The spectroscopic analyses of this study have provided additional insight into the geological processes that have shaped Sputnik Planitia, and in some instances they reveal aspects of the

1497 geology that is not apparent within the visible and panchromatic imaging that was used to define
1498 the geological units in the mapping of White et al. (2017). For non-plains units, a general
1499 increase in volatile abundance from the north to the south of Sputnik Planitia is seen, manifested
1500 especially by the higher areal mass fraction of $\text{N}_2\text{:CH}_4$ at the expense of H_2O ice for the
1501 southernmost mountains (unit abm) as compared to the northernmost ones. Higher amounts of
1502 pure CH_4 are also seen at the southern mountains, which are a natural site for CH_4 deposition
1503 owing to their high elevation and the lower insolation they are presently receiving; the existence
1504 of a thin veneer of pure CH_4 ice is only apparent in the spectra, and not in the visible imaging.
1505 Topography within southern Sputnik Planitia (specifically the scattered hills, Tenzing Montes
1506 and Krun Macula) that appears inundated by N_2 ice is interpreted as a geomorphological
1507 consequence of the increased deposition of volatiles occurring here, which is predicted by
1508 climate modeling (Bertrand et al., 2018; 2020b). The NSS endmember that has been identified
1509 in the spectra correlates to the existence of tholins within certain units, and are coating the low-
1510 latitude mountain ranges of Zheng He, Baret, and Hillary Montes (i.e. those that are co-
1511 latitudinal with the tholin-covered Cthulhu Macula in the uplands to the west) and the dark
1512 ridged terrain (unit drt); covering the floors of large pits within non-cellular plains; and are
1513 entrained within the exposed N_2 ice of Sputnik Planitia within the northern dark cellular plains
1514 and trough-bounding plains (units dcp and tbp). Our spectral and geomorphological
1515 observations have also revealed that Columbia Colles, which belong to the CH_4 ice-based
1516 scattered hills that have been eroded from the pitted uplands of East Tombaugh Regio (unit sh),
1517 appear to have been affected by processes somewhat similar to those that have formed the dark
1518 ridged terrain along the western boundary of Sputnik Planitia, which is based on much older,
1519 H_2O ice-based crustal material that also forms the western mountain ranges. Elevated CH_4

1520 concentrations within N₂:CH₄ ice of the eastern non-cellular plains may represent sub-resolution,
1521 CH₄-rich material that has been recently eroded from the pitted uplands of East Tombaugh
1522 Regio, and which is being transported into Sputnik Planitia by N₂ ice glaciers. The spectral
1523 analysis has also revealed compositional and/or directional scattering differences between the
1524 handful of occurrences of northern non-cellular plains and the surrounding cellular plains, all of
1525 which are located within the portion of Sputnik Planitia that is presently experiencing net
1526 sublimation of volatiles, and which do not therefore exhibit a surface layer of bright, freshly-
1527 deposited N₂ ice. The compositional differences between the cellular and non-cellular plains
1528 here hint at the effectiveness of convection in entraining and trapping tholins within the body of
1529 the cellular plains, while preventing the spread of such tholins to abutting non-cellular plains.

1530 The results of this paper form a testament to the dynamism of volatile mobilization within the
1531 plains of Sputnik Planitia and its mountain ranges, with many factors including surface elevation,
1532 Pluto's highly variable climate with latitude, and endogenous factors (i.e. convection) all playing
1533 important roles in explaining our spectroscopic and geomorphological observations. As
1534 described by Bertrand et al. (2020b) Sputnik Planitia does represent the “beating heart” of Pluto
1535 that regulates its atmospheric circulation through such volatile mobilization, and the effects of
1536 this have consequences across the rest of the dwarf planet. Outside of Sputnik Planitia, both
1537 latitudinal and longitudinal variations in the distribution of surface volatiles have been described.
1538 The eastwards sequence of equatorial terrains from the bright pitted uplands of East Tombaugh
1539 Regio through the bladed terrain deposits of Tartarus Dorsa to the dark, tholin covered, cratered
1540 plains of Cthulhu Macula appear to manifest a surficial composition sequence from dominance
1541 by nitrogen directly to the east of Sputnik Planitia, to increasing dominance of methane ice
1542 farther to the east culminating in the bladed terrain deposits (Moore et al., 2018), eventually

1543 terminating at the volatile-poor expanse of Cthulhu Macula to the west of Sputnik Planitia.
1544 Development of albedo contrasts is heightened in the equatorial region, owing to its relatively
1545 stable climate (Earle et al., 2018), and is a powerful driving force behind the very pronounced
1546 segregation of volatile-rich and -poor terrains at the equator. The drastic climate cycles
1547 experienced by the northern latitudes promotes mixing of volatiles and causes them to neither be
1548 substantially eroded nor accumulated relative to the equatorial region, but longitudinal variation
1549 is still apparent, from the smooth, mantled, undulating uplands of Hayabusa and Pioneer Terrae
1550 to the northeast of Sputnik Planitia, to the very flat, heavily cratered, partly eroded plains of
1551 Vega and Venera Terrae to the northwest. At both at low and high latitudes, the observed
1552 longitudinal variation of uplands geomorphology may indicate an origin related to the
1553 retrorotation of Pluto's atmosphere that is controlled by Sputnik Planitia, and both further high-
1554 resolution, long-term global climate model simulations and comprehensive analysis of the
1555 spectral properties of terrains beyond Sputnik Planitia will complement geological observations
1556 to expand our understanding of volatile mobilization across Pluto in general.
1557

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Appendix

Table: CH ₄ shift parameter and integrated band depths calculated for the average spectra of the 48 provinces of Sputnik Planitia								
Province *	CH ₄ shift parameter	Integrated band depths						
		CH ₄ Range 1 1.30 - 1.43 μm	CH ₄ Range 2 1.59 - 1.83 μm	CH ₄ Range 3 1.90 - 2.00 μm	CH ₄ Range 4 2.09 - 2.48 μm	CH ₄ 1.48 μm	N ₂ 2.15 μm	CO 1.58 μm
ABM								
Baret Montes	0.003	0.08	0.07	0.05	0.12	0.02	0.02	0.009
Cellular plains	0.004	0.29	0.36	0.06	0.58	0.04	0.03	0.04
Hillary Montes	0.001	0.17	0.18	0.08	0.31	0.03	0.01	0.003
Southwest buffer	0.003	0.29	0.32	0.11	0.50	0.04	0.02	0.04
Tenzing Montes	0.002	0.23	0.27	0.10	0.45	0.04	0.01	0.02
Zheng He Montes	0.001	0.19	0.21	0.07	0.36	0.02	0.01	0.00
Al-Idrisi Montes	0.005	0.15	0.23	0.04	0.42	0.17	0.16	0.009
BCP								
Cellular plains	0.006	0.29	0.41	0.05	0.62	0.04	0.06	0.03
BCT								
Al-Idrisi Montes	0.007	0.08	0.18	0.02	0.46	0.004	0.08	0.002
DCP								
Cellular plains	0.005	0.27	0.36	0.05	0.58	0.04	0.04	0.02
Al-Idrisi Montes	0.007	0.14	0.26	0.02	0.48	0.03	0.06	0.01
DMP								
Baret	0.002	0.29	0.34	0.07	0.52	0.05	0.03	0.01

* Some feature names mentioned in this paper are now formalized while others are informal

Montes								
Hillary Montes	0.003	0.29	0.34	0.08	0.52	0.04	0.03	0.02
DPP								
Hillary Montes	0.002	0.27	0.31	0.09	0.49	0.05	0.04	0.01
North pitted plains	0.005	0.25	0.36	0.05	0.58	0.04	0.06	0.02
Cellular plains	0.004	0.30	0.38	0.06	0.58	0.05	0.04	0.02
East pitted plains	0.005	0.29	0.40	0.06	0.59	0.05	0.04	0.03
South pitted plains	0.004	0.30	0.39	0.07	0.60	0.05	0.06	0.02
West pitted plains	0.003	0.30	0.36	0.06	0.57	0.04	0.06	0.02
DRT								
Baret Montes	0.002	0.06	0.05	0.04	0.09	0.008	0.01	0.00
Hillary Montes	0.004	0.15	0.16	0.09	0.27	0.02	0.02	0.00
Al-Idrisi Montes	0.003	0.06	0.05	0.05	0.12	0.002	0.02	0.009
IBM								
Baret Montes	0.003	0.16	0.18	0.07	0.33	0.04	0.02	0.01
Hillary Montes	0.002	0.24	0.28	0.08	0.43	0.04	0.04	0.01
Tenzing Montes	0.003	0.25	0.32	0.10	0.51	0.04	0.03	0.03
Al-Idrisi Montes	0.005	0.11	0.20	0.04	0.40	0.01	0.04	0.008
LPP								
Hillary Montes	0.003	0.31	0.35	0.07	0.57	0.04	0.06	0.00
East pitted plains	0.005	0.30	0.41	0.06	0.62	0.04	0.06	0.03
South pitted plains	0.006	0.27	0.40	0.04	0.62	0.03	0.08	0.03
Cellular plains	0.005	0.29	0.39	0.04	0.60	0.04	0.05	0.04
Al-Idrisi Montes	0.005	0.21	0.30	0.06	0.49	0.03	0.02	0.004
PMP								
East pitted plains	0.004	0.30	0.40	0.07	0.59	0.05	0.04	0.02
Southwest buffer	0.003	0.31	0.36	0.10	0.55	0.05	0.02	0.02

South pitted plains	0.004	0.29	0.39	0.07	0.58	0.05	0.03	0.02
Tenzing Montes	0.003	0.25	0.36	0.07	0.57	0.03	0.02	0.03
SH								
Astrid Colles	0.005	0.27	0.39	0.05	0.59	0.05	0.04	0.03
Challenger Colles	0.003	0.26	0.34	0.06	0.52	0.03	0.04	0.02
Columbia Colles	0.003	0.18	0.23	0.04	0.40	0.03	0.04	0.01
Soyuz Colles	0.005	0.33	0.40	0.06	0.60	0.04	0.008	0.03
East pitted plains	0.005	0.30	0.40	0.07	0.61	0.03	0.04	0.02
SPP								
Hillary Montes	0.003	0.33	0.39	0.08	0.59	0.04	0.05	0.01
East pitted plains	0.005	0.30	0.38	0.06	0.60	0.02	0.05	0.03
South pitted plains	0.005	0.29	0.40	0.05	0.61	0.04	0.08	0.03
North pitted plains	0.005	0.27	0.35	0.03	0.59	0.04	0.07	0.01
Cellular plains	0.005	0.29	0.38	0.03	0.60	0.04	0.05	0.03
Southwest buffer	0.003	0.33	0.41	0.08	0.62	0.05	0.06	0.03
West pitted plains	0.003	0.30	0.37	0.06	0.59	0.05	0.07	0.02
TBP								
Cellular plains	0.005	0.22	0.21	0.04	0.54	0.02	0.04	0.01

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Figure 1: Geologic units identified in Sputnik Planitia by White et al. (2017) through analysis of New Horizons LORRI images. The original 15 units initially identified were reduced to 13 here, to include only the geologic units within and around Sputnik Planitia. The basemap mosaic is a combination of 12 LORRI images, with a spatial resolution of 386 m/px.

Figure 2: The 15 provinces that we have divided the Sputnik Planitia geologic map into, with each province containing one or more geologic unit. Indeed, some geologic unit covers areas that are spatially distant and surrounded by very diverse terrain types. For example, the spp unit can be found in 5 different provinces: in the northernmost part of Sputnik Planitia (North Pitted Plains), embedded in the cellular plains; in the West Pitted Plains, again close to the cellular plains, but also to the blocky mountains; in the Hillary Montes region, surrounded by inter-blocky material; in the South-West Buffer and the South-East Pitted Plains, where the other types of pitted plains dominate.

Figure 3: Average spectra of the 13 geologic units identified by White et al. (2017). The boxes indicate the location of the main absorption bands of CH_4 , CO and N_2 .

Figure 4: LEISA spectra of unit drt in Baret overlapped by seven Hapke theory-based best fit models, calculated by considering the optical constants of seven different materials to account for the observed negative spectral slope. The spectra are offset for clarity.

Figure 5A-M: Comparison between LEISA spectra, averaged for each geologic unit in the 15 provinces, and the models calculated by applying the Hapke theory. Each panel also reports the components used in the models, with their fractional area.

Figure 6: Variation of the CH_4 band shift index across the geologic units of Sputnik Planitia. The highest values of the band shift index in the map (light grey) indicate areas characterized by N_2 -rich ice, while the lowest values (dark grey) indicate CH_4 -rich ice.

Figure 7 A-E: Maps of variation of the integrated band depths of the main CH_4 absorptions: Range 1 ($1.30\text{-}1.43 \mu\text{m}$; A), Range 2 ($1.59\text{-}1.83 \mu\text{m}$; B), Range 3 ($1.90\text{-}2.00 \mu\text{m}$; C), Range 4 ($2.09\text{-}2.48 \mu\text{m}$; D), and the single band at $1.48 \mu\text{m}$ (E). The Range 3 map (C) shows opposite trends compared to the other four spectral ranges, a behavior that was previously observed also in other studies (e.g. Schmitt et al, 2017).

Figure 8A-B: Maps of percentage variation of CH_4 diluted in N_2 -rich ice (A) and temperatures (B) estimated by the spectral modeling.

Figure 9A-B: Maps of variation of pure CH₄ areal mass fraction (A) and grain size (A) estimated by the spectral modeling. Pure CH₄ covers almost all geologic units in Sputnik Planitia, but its percentage is very low, below 1.5%.

Figure 10: Map of variation of the integrated band depth of N_2 at $2.15 \mu m$.

Figure 11A-B: Maps of variation of $N_2:CH_4$ areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

Figure 12A-B: Maps of variation of pure $\beta-N_2$ areal mass fraction (A) and grain size (B) estimated in the spectral modeling.

Figure 13: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the CH₄ shift index. The data are split into two groups, separated by a dotted curve. The points belonging to group G1, above the curve, show increasing band strength with increasing values of the shift parameter. The second group (G2), below the dotted line, also shows a positive trend, but the points are more dispersed. Furthermore, the values of the CH₄ integrated band depths in G2 are lower than the units in G1. The positive trends in both groups contradicts the definition of the CH₄ shift index, i.e. higher index values correspond to lower of CH₄-rich ice amount. Therefore, a trend opposite of what observed in panel A is expected: the CH₄ integrated band depth should be less intense - or, the abundance of methane should decrease - with increasing values of the shift index. **(B)** Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μm (middle), and the N₂ integrated band depth at 2.15 μm (bottom) with the CH₄ shift index. As opposite to the three plots in panel A, these spectral parameters show a clear and single trend with the CH₄ shift index, in agreement with the definition of the CH₄ shift index.

Figure 14: Scatter plot showing the correlation between the CH₄ integrated band depths in Ranges 1 (top), 2 (middle), and 4 (bottom) versus the CH₄ integrated band depth in Range 3. The plots clearly show a lack of correlation between the represented parameters, indicating that the factor influencing the depth of the CH₄ absorptions in Ranges 1, 2, and 4 doesn't have any (or it has negligible) effect on the absorption in Range 3.

Figure 15: Maps of variation of CO integrated band depth at 1.58 μm.

Figure 16: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the CO integrated band depth. Because the data shows to different trends, we split them into two groups, separated by a vertical dotted line. The units on the left side have a positive trend but a sparse distribution, the points on the right portion of the plots show a flat distribution. **(B)** Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μm (middle), and the N₂ integrated band depth at 2.15 μm (bottom) with the CO integrated band depth. The only clear correlation occurs between CO and the band at 1.48 μm , while the correlation coefficient for CH₄ band in Range 3 and N₂ are negligible.

Figure 17A-B: Maps of variation of Crystalline H₂O areal mass fraction (A) and grain size(B) estimated by the spectral modeling

Figure 18: Mutual variation of the crystalline H₂O areal mass fraction, the H₂O integrated band depth, and the CH₄ shift index. Crystalline H₂O ice well correlates with the H₂O integrated band depth (top, left panel), while no correlation exists between the H₂O areal mass fraction (top, right panel) and the H₂O integrated band depth (bottom, left panel) and the shift parameter, suggesting that H₂O do not influence the CH₄ band shift.

Figure 19: (A-F) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the H₂O crystalline areal mass fraction (A, B, C), and with the H₂O integrated band depth (D, E, F). All the represented parameters show clear anti-correlations, suggesting that water ice can contribute to the suppression of the strong methane ice absorptions. For some units, though, H₂O is not the only, or the main, contributor. Unit drt in Al-Idrisi and Baret Montes, and unit abm in Zheng He and Hillary Montes have the strongest absorptions in the 2.0 μ m region, but moderate fractions of crystalline water ice. The discrepancy between the two water ice parameters suggests that crystalline H₂O is contributing to the absorption around 2.0 μ m, but the influence of some other material must be invoked to justify such deep absorptions in this spectral area.

Figure 19: (G-L) Scatter plot showing the correlation between the CH_4 integrated band depth in Ranges 3 (top), at $1.48 \mu\text{m}$ (middle), and N_2 integrated band depth at $2.15 \mu\text{m}$ (bottom) with the H_2O crystalline areal mass fraction (G, H, I), and with the H_2O integrated band depth (J, K, L). The correlation between these parameters is less pronounced than in the previous panels, and indication that crystalline H_2O minimally influence the depth of the CH_4 absorptions in Range 3 and at $1.48 \mu\text{m}$, and of N_2 .

Figure 20: Maps of variation of NSS endmember areal mass fraction (A) and grain size (B) estimated by the spectral modeling.

Figure 21: (A) Scatter plot showing the correlation between the CH₄ integrated band depth in Ranges 1 (top), 2 (middle), and 4 (bottom) with the NSS endmember areal mass fraction. A moderate negative trend between the abundance of the NSS endmember with the integrated band depths of CH₄ in Range 1, Range 2, and Range 4 is observed. (B) Scatter plot showing the correlation between the CH₄ integrated band depth in Range 3 (top), at 1.48 μm (middle), and the N₂ integrated band depth at 2.15 μm (bottom) with the NSS endmember areal mass fraction. The NSS endmember is not correlated with the CH₄ in Range 3, while it has a moderate and slight anti correlation with the CH₄ band at 1.48 μm and the N₂ absorption at 2.15 μm .

Figure 22: Scatter plot showing the correlation between the CH₄ band shift index (top), H₂O integrated band depth (middle), and crystalline H₂O areal mass fraction (bottom) versus the NSS endmember areal mass fraction. The top panel shows a slight dependence between the shift value and the NSS slope, while in the other two panels, the represented quantities do not show any clear correlation.

Figure 23: LEISA spectra, averaged for unit drt in Al-Idrisi, Hillary and Baret montes, and unit sh in Columbia Colles, overlapped by the corresponding Hapke theory-based best fit model. In this case, the modeling made use of the Pluto tholins optical constants, in place of the NSS endmember ones. The spectra are offset for clarity.

Geological units composition of provinces

Al-Idrisi Montes (a)

Baret Montes (b)

Zheng He Montes (c)

North pitted plains (d)

West pitted plains (e)

Hillary Montes (f)

Cellular plains (g)

South-West buffer (h)

Tenzing Montes (i)

East pitted plains (j)

South pitted plains (k)

Astrid Colles (l)

Challenger Colles (m)

Columbia Colles (n)

Soyuz Colles (o)

Figure 24 A-O: Pie plots summarizing the composition of the geologic units in each province, as returned by the application of the Hapke-based spectral modeling.

Figure 25: Contrast between the northernmost mountain range of Al-Idrisi Montes and the southernmost range of Tenzing Montes. (a) Al-Idrisi Montes show minimal interstitial N₂ ice plains between mountain blocks. LORRI image is 76 m/pixel and centered at 37.6°N, 156.3°E, with illumination from the top. (b) Several of the mountain blocks of Tenzing Montes are partly engulfed by N₂ ice plains that are elevated by up to a kilometer above the surrounding N₂ ice plains of Sputnik Planitia, and separated from them by scarps (white arrows). MVIC image is 315 m/pixel and centered at 13.6°S, 176.7°E, with illumination from the top.

Figure 26: Scattered hills (unit sh) and dark ridged terrain (unit drt). (a) Scattered hills of Astrid and Soyuz Colles, which display smooth topographic relief and a high albedo, indicating that the hills, like the surrounding plains, have been coated by ongoing N_2 ice deposition. MVIC image is 315 m/pixel and centered at 14.7°N, 184.5°E, with illumination from the left. (b) Dark ridges situated between Baret Montes and dark-pitted, marginal plains of Sputnik Planitia, which were mapped as unit drt by White et al. (2017). White arrows indicate ridges spaced 1-2 km apart that align roughly parallel to the border of the unit with the N_2 ice plains. LORRI image is 117 m/pixel and centered at 11.4°N, 157.5°E, with illumination from the top. (c) Columbia Colles, located at the eastern margin of Sputnik Planitia, which were mapped as unit sh by White et al. (2017). White arrows indicate ridges spaced 1-2 km apart that resemble those highlighted in (a). The comparable geomorphology and albedo of Columbia Colles to occurrences of unit drt in the west suggest that similar processes have affected Columbia Colles, which are otherwise separated stratigraphically and compositionally from unit drt. MVIC image is 315 m/pixel and centered at 28.7°N, 196.5°E, with illumination from the left.

Figure 27: Plains units of Sputnik Planitia described in sections 5.5 and 5.6. (a) Alcyonia Lacus, mapped by White et al. (2017) as an isolated occurrence of dark cellular plains surrounded by mountains and blocky material of Al-Idrisi Montes. LORRI image is 117 m/pixel and centered at 36.4°N, 151.6°E, with illumination from the top-right. (b)

Hummocky N_2 ice plains of unit pmp covering low-lying uplands of Krun Macula (dark terrain at lower right). Scarps (white arrows) separate unit pmp from the flat plains of Sputnik Planitia, similar to those seen at Tenzing Montes (Fig. 26b). MVIC image is 315 m/pixel and centered at $5.8^\circ S$, $191.2^\circ E$, with illumination from the left. (c) Glacial flow of nitrogen ice from the bright pitted uplands of East Tombaugh Regio (bottom) into Sputnik Planitia. Dark, converging flow bands (white arrows) are seen in valleys that connect upland flats to Sputnik Planitia, and are interpreted to be moraine trails consisting of CH_4 -rich material eroded from the pitted uplands by N_2 ice glaciation. MVIC image is 315 m/pixel and centered at $3.7^\circ N$, $193.6^\circ E$, with illumination from the top-right. (d) High-albedo, pitted plains of units dpp and spp located at the western edge of Sputnik Planitia, occurring interstitially to convective cells of the dark, cellular plains (unit dcp). MVIC image is 315 m/pixel and centered at $20.3^\circ N$, $155.1^\circ E$, with illumination from the top. (e) Dense fields of aligned (unit dpp) in southern Sputnik Planitia. Across the center of the image, they are seen to form chains of joined, dark-floored pits that trace elongated, polygonal outlines that enclose sparsely pitted plains (unit spp), and which extend southwards from the bright, cellular plains (unit bcp) at top left. MVIC image is 315 m/pixel and centered at $6.0^\circ S$, $179.7^\circ E$, with illumination from the left.

Figure 28: Results from the global climate model of Pluto obtained for July 2015 from simulations similar to those presented in Bertrand et al., 2020b. Left: Diurnal mean near-surface (~ 20 m) atmospheric CH_4 mass mixing ratio in the region of Sputnik Planitia, with near-surface winds. Right: Net diurnal CH_4 deposition onto the surface.