



HAL
open science

Chemical composition of Pluto aerosol analogues

Lora Jovanovic, Thomas Gautier, Véronique Vuitton, Cédric Wolters, Jérémy Bourgalais, Arnaud Buch, François-Régis Orthous-Daunay, Ludovic Vettier, Laurène Flandinet, Nathalie Carrasco

► **To cite this version:**

Lora Jovanovic, Thomas Gautier, Véronique Vuitton, Cédric Wolters, Jérémy Bourgalais, et al.. Chemical composition of Pluto aerosol analogues. *Icarus*, 2020, 346, pp.113774. 10.1016/j.icarus.2020.113774 . insu-02533967

HAL Id: insu-02533967

<https://insu.hal.science/insu-02533967v1>

Submitted on 3 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Chemical composition of Pluto aerosol analogues**

2 Lora Jovanović¹, Thomas Gautier¹, Véronique Vuitton², Cédric Wolters², Jérémy Bourgalais¹,
3 Arnaud Buch³, François-Régis Orthous-Daunay², Ludovic Vettier¹, Laurène Flandinet²,
4 Nathalie Carrasco¹

5

6 ¹ LATMOS/IPSL, UVSQ - Université Paris-Saclay, Sorbonne Université, CNRS, Guyancourt,
7 France

8 ² Université Grenoble Alpes, CNRS, IPAG, Grenoble, France

9 ³ LGPM, CentraleSupélec, Université Paris-Saclay, Gif-sur-Yvette, France

10

11 **Keywords**

12 Pluto; Pluto, Atmosphere; Atmospheres, Chemistry; Organic chemistry

13

14 **Abstract**

15 Photochemical aerosols were observed in Pluto atmosphere during the *New Horizons* flyby on
16 July 14th, 2015, as several thin haze layers extending at more than 350 km of altitude. This flyby
17 has raised numerous questions on the aerosols formation processes and their impact on Pluto
18 radiative transfer and climate. In order to gain a better understanding, we synthesized Pluto
19 aerosol analogues in a room-temperature dusty plasma experiment and inferred their chemical
20 composition from infrared spectroscopy, elemental composition analysis and very high-
21 resolution mass spectrometry (ESI+/Orbitrap device). Three types of samples were synthesized
22 at 0.9 ± 0.1 mbar, called P₄₀₀, P₆₀₀ and P_{CO-free}. The samples P₄₀₀ and P₆₀₀ were produced from
23 gas mixtures mimicking Pluto atmosphere at around 400 and 600 km of altitude, respectively,
24 in order to determine if CH₄ mixing ratio has an influence on the chemical composition of the
25 aerosols. The sample P_{CO-free} was produced from a gas mixture similar to the one forming the
26 sample P₄₀₀, but without carbon monoxide, in order to identify the impact of CO.

27 Our study shows that the molecules constituting samples P₄₀₀ and P₆₀₀ are very rich in nitrogen
28 atoms (up to 45 % in mass of N elements) and, compared to the molecules constituting the P_{CO-}
29 _{free} sample, a significant incorporation of oxygen atoms was detected. Moreover, our results on
30 the variation of CH₄ mixing ratio demonstrate that different ratios lead to different reactivity
31 between N₂, CH₄ and CO. In particular, more nitrogen and oxygen atoms are detected in the
32 bulk composition of the analogues P₄₀₀. Due to the presence of nitrogenated and oxygenated
33 molecules in the analogues of Pluto aerosols, we suggest that these aerosols will have an impact
34 on Pluto radiative transfer, and thus on climate, that will differ from predictions based on the
35 optical constants of Titan aerosol analogues.

36

37

38 I. Introduction

39 Since 1988, ground-based observations have shown that Pluto is surrounded by a tenuous
40 atmosphere (Elliot et al., 1989; Hubbard et al., 1988), which is seasonal due to Pluto elliptic
41 orbit. This atmosphere is supplied by the sublimation of the surface ices composed of molecular
42 nitrogen N₂, methane CH₄ and carbon monoxide CO (Forget et al., 2017; Grundy et al., 2016;
43 Owen et al., 1993; Stern et al., 2015). These observations motivated the establishment of the
44 *New Horizons* mission, whose one of the goals was to characterize the structure, composition
45 and variability of neutral atmosphere of Pluto (Young et al., 2008). The *New Horizons*
46 spacecraft flew by Pluto at closest approach on July 14th, 2015, providing important information
47 about Pluto atmosphere thanks to its suite of instruments.

48 From radio occultation data measured by the REX (Radio Experiment) instrument, the average
49 surface pressure was measured at approximately 11 μbar, while the temperature near surface
50 was estimated at about 45 K (Gladstone et al., 2016; Hinson et al., 2017). The composition of
51 Pluto atmosphere was confirmed from solar ultraviolet occultation data recorded by the ALICE
52 spectrograph (Young et al., 2018). Pluto atmosphere is mainly composed of N₂ – in vapor-
53 pressure equilibrium with N₂ ice – and CH₄. In addition to these molecules, 515 ± 40 ppm of
54 CO was detected with submillimeter observations by ALMA (Lellouch et al., 2017) and few
55 hydrocarbons (C_xH_y) are also part of the atmosphere as trace species (Young et al., 2018).

56 Considering this atmospheric composition – a nitrogen-based atmosphere containing a
57 substantial fraction of methane – and the presence of spikes in the lightcurve of the stellar
58 occultation by Pluto on June 9th, 1988, the presence of photochemical aerosols was suspected
59 and discussed since the 1990's (Elliot et al., 1989; Krasnopolsky and Cruikshank, 1999; Lara
60 et al., 1997; Lellouch, 1994; Stansberry et al., 1989). These aerosols were finally evidenced
61 when Pluto was investigated by *New Horizons*, by means of forward scattering observations
62 and solar occultations. Pluto aerosols aggregate into several optically thin haze layers of about
63 a few kilometers, extending at an altitude of > 350 km and accounting for about 0.1 ppmv of
64 the atmosphere (Cheng et al., 2017; Gladstone et al., 2016; Stern et al., 2015; Young et al.,
65 2018). The blue color of the observed haze and the UV extinction exceeding unity are consistent
66 with very small and forward-scattering particles (Rayleigh scatterers, with radius $r \sim 10$ nm),
67 while the large forward scatter-to-back scatter ratio in the visible suggests much larger particles
68 ($r > 0.1$ μm). Thus, the haze might be composed of randomly-shaped aggregates of spherical
69 particles with different sizes (Cheng et al., 2017; Gladstone et al., 2016; Stern et al., 2015).

70 These aerosols may have a deep impact on Pluto atmospheric chemistry, for instance through
71 the depletion from the atmosphere of small hydrocarbons that stick to the negatively-charged
72 aerosols and may form complex hydrocarbons (Luspay-Kuti et al., 2017). They may also impact
73 the climate of Pluto, such as playing the role of condensation nuclei for clouds (Lavvas et al.,
74 2016; Luspay-Kuti et al., 2017). They can also influence the radiative cooling by absorbing
75 1 to 5 % of incident solar radiations, explaining why Pluto atmosphere, at about 400 km of
76 altitude, is around 30 K colder than predicted by the models (Gladstone et al., 2016; Zhang et
77 al., 2017; Zhu et al., 2014). Studying Pluto aerosols is thus of prime importance to understand
78 the physics and the chemistry of Pluto atmosphere.

79 Recent photochemical models have been developed to explain the formation of aerosols in Pluto
80 atmosphere, based on two processes (Cheng et al., 2017; Gladstone et al., 2016; Luspay-Kuti
81 et al., 2017; Wong et al., 2017).

82 At lower altitudes, between 200 and 400 km, the condensation of volatiles onto photochemical
83 aerosols dominates (Luspay-Kuti et al., 2017; Mandt et al., 2017; Wong et al., 2017). This
84 condensation concerns C₂ hydrocarbons – C₂H₂, C₂H₄, C₂H₆ – HCN, CH₂NH, C₃H₄, C₃H₆,
85 CH₃CN, C₄H₂, HC₃N, C₂H₃CN, C₂N₂, CH₃C₂CN and C₆H₆ (Gao et al., 2017; Krasnopolsky
86 and Cruikshank, 1999; Lara et al., 1997; Luspay-Kuti et al., 2017; Mandt et al., 2017; Wong et
87 al., 2017).

88 In the upper atmosphere, above 400 km of altitude, the aerosols formation is dominated by
89 photochemistry (Gladstone et al., 2016; Wong et al., 2017; Young et al., 2018). By analogy
90 with Titan, whose atmosphere is mainly composed of molecular nitrogen and methane, a
91 complex photochemistry is initiated in Pluto upper atmosphere by far-ultraviolet sunlight and
92 by solar photons that are scattered back to the Solar System by hydrogen present in
93 interplanetary medium (Gladstone et al., 2016, 2015). This photochemistry involves neutral and
94 ionic molecules generated from the ionization and the dissociation of N₂, CH₄ and CO, leading
95 to the formation of complex hydrocarbons, nitriles and oxygenated organic molecules. Some of
96 the molecules formed by photochemistry can then polymerize, resulting in the formation of
97 aerosols. Nevertheless, the exact reactive pathways leading to the formation of Pluto
98 photochemical aerosols are not well constrained yet.

99 In this study, we used the experimental setup PAMPRE developed at LATMOS (Guyancourt,
100 France) to produce analogues of Pluto photochemical aerosols. This experimental device
101 simulates the formation of aerosols by polymerization of molecules in the gas phase. The
102 condensation of volatiles as occurring at low altitudes in Pluto atmosphere is therefore not
103 reproduced in the simulation chamber, and is beyond the scope of this study.

104 Additionally, as Pluto aerosols are seen at least as high as 350 km of altitude, they are certainly
105 formed higher in the atmosphere, but are there initially too small to scatter the photons in the
106 UV-Visible range. Moreover, the data obtained by the ALICE spectrograph (Young et al., 2018)
107 showed that the mixing ratio of CH₄ varies from 0.5 % at the surface to 50 % at about 1450 km
108 of altitude. Due to this variability in atmospheric composition, it is legitimate to wonder about
109 the variability in chemical composition of these aerosols.

110 The aim of this work is to constrain the chemical composition and the formation pathways of
111 Pluto photochemical aerosols. We performed for this purpose very high-resolution mass
112 spectrometry, infrared spectroscopy and elemental composition analyses of Pluto aerosol
113 analogues.

114

115

116

117

118

119 **II. Experimental setup and analyses protocol**

120 **1. PAMPRE**

121 Pluto aerosol analogues were produced using the PAMPRE experimental setup, already
122 described in detail in Szopa et al. (2006) and Alcouffe et al. (2010). PAMPRE is a Radio-
123 Frequency Capacitively Coupled Plasma (RF CCP) generated in a gas mixture by a 13.56 MHz
124 generator (*SAIREM GRP OIKE*). The interaction between the electrons from the
125 discharge – mimicking the energy distribution of the solar photons (Szopa et al., 2006) – and
126 the injected molecules produces a plasma in which the aerosol analogues are formed in volume.
127 Before each experiment, the reactor is cleaned, heated and pumped down to a secondary
128 vacuum of 1.5×10^{-6} mbar. The gas mixture is introduced in the stainless-steel reactor through
129 the meshed polarized electrode, as a homogeneous and continuous flow, and is extracted by a
130 primary vane pump (*Adixen by Pfeiffer Vacuum Pascal 2015 SD*). In this work, the gas mixture
131 introduced in the reactor, expected to be representative of Pluto atmosphere, is composed of
132 molecular nitrogen N_2 and methane CH_4 – in variable proportions – and 500 ppm of carbon
133 monoxide CO (*Air Liquide*, with impurities $H_2O < 3$ ppm, $O_2 < 2$ ppm and $C_xH_y < 0.5$ ppm).

134 For the experiments presented here, the total flow rate was set at 55 sccm (standard cubic
135 centimeters per minute), controlled by gas flow controllers (*MKS*), resulting in an overall
136 plasma pressure of 0.9 ± 0.1 mbar, at ambient temperature. Note that the pressure and
137 temperature are higher in the experiment than in Pluto upper atmosphere ($\sim 10^{-2}$ μ bar and ~ 65
138 K at 400 km of altitude and $\sim 10^{-4}$ μ bar and ~ 65 K at 600 km of altitude (Gladstone and Young,
139 2019)). However, the most important parameter, the ionization rate, is the same and in the order
140 of ppm_v. As ion-molecule reaction rates are relatively insensitive to low temperatures (Anicich
141 et al., 2003; Böhme, 2000; Imanaka and Smith, 2009), the lower temperature in Pluto upper
142 atmosphere (65 K instead of 293 K in our experiment) is not an issue in our case. The higher
143 pressure induces shorter mean free path for the molecules, which main implication is just faster
144 kinetics in the experiment. This remains true as long as the pressure is low enough to minimize
145 trimolecular reactions (a few mbar), which is the case in all our experiments. In contrast, using
146 similar ionization rate enables a realistic contribution of ions into the whole ion-neutral coupled
147 chemical network and thus better represents Pluto atmospheric chemistry.

148 The plasma is confined in a cylindrical metallic cage where the particles form. The cage
149 contains grid apertures allowing the aerosol analogues to be ejected out of the plasma and to
150 accumulate as a brownish powder on glass vessel walls surrounding the confining cage. The
151 aerosol analogues were finally collected at atmospheric pressure for the *ex situ* analyses
152 presented below.

153 **2. Sample synthesis: Pluto aerosol analogues**

154 In this work, two types of Pluto aerosol analogues were synthesized. The first one was produced
155 from a gaseous mixture containing 99 % of N_2 , 1 % of CH_4 and 500 ppm of CO, representative
156 of the aerosols forming at 400 km of altitude in Pluto atmosphere – we will thereafter call it
157 P_{400} . The second type was produced from a gaseous mixture containing 95 % of N_2 , 5 % of CH_4
158 and 500 ppm of CO, which is representative of aerosols that could form at 600 km of altitude –
159 thereafter called P_{600} (Lellouch et al., 2017; Young et al., 2018).

160 In order to understand the impact of the presence of CO in Pluto atmosphere, aerosol analogues
 161 were also synthesized from a plasma containing 99 % of N₂ and 1 % of CH₄, but without CO.
 162 This type of analogue, afterward called *P_{CO-free}* – equivalent to Titan aerosol analogues– has
 163 been studied for decades (Cable et al., 2012; Coll et al., 2013, 1999; Imanaka et al., 2004;
 164 Imanaka and Smith, 2010; Khare et al., 1984; McDonald et al., 1994; Sciamma-O’Brien et al.,
 165 2017; Sekine et al., 2008; Szopa et al., 2006) (Table 1).

166 Table 1: Table presenting the three samples analyzed in this study.

Composition of the reactive mixture			Corresponding altitude on Pluto	Acronym of the aerosol analogues
N ₂	CH ₄	CO		
99 %	1 %	500 ppm	400 km	P ₄₀₀
95 %	5 %	500 ppm	600 km	P ₆₀₀
99 %	1 %	-	-	P _{CO-free}

167

168 3. Infrared spectroscopy by the Attenuated Total Reflectance technique

169 The infrared spectra of Pluto aerosol analogues were acquired using an Attenuated Total
 170 Reflectance (ATR) accessory on the *Thermo Scientific Nicolet 6700* spectrometer, driven by
 171 *OMNIC* software. The purpose of this analysis was to characterize the chemical functions
 172 present in the molecules constituting the samples.

173 A spatula tip of the aerosol analogues was deposited on a zinc selenide (ZnSe) crystal. Direct
 174 contact between the sample and the crystal was facilitated by applying pressure to the sample.
 175 An IR beam was directed onto the crystal at an angle of incidence greater than a critical angle.
 176 Under these conditions, an evanescent wave was generated and passed through the sample for
 177 a few micrometers (0.5 to 5 μm). Depending on the chemical functions present in the molecules
 178 constituting the aerosol analogues, the evanescent wave is absorbed at different characteristic
 179 wavelengths. The resulting altered wave was collected by a DTGS KBr (deuterated-triglycine
 180 sulfate, potassium bromide) detector.

181 The spectrum presented here results from the accumulation of 250 scans, acquired between 500
 182 and 4000 cm⁻¹, with a resolution of 4 cm⁻¹ corresponding to a digital increment of 1.928 cm⁻¹.
 183 Background spectrum was also acquired before the sample analysis, to remove the contribution
 184 of ambient atmosphere.

185 4. Sample preparation for very high-resolution mass spectrometry analysis

186 To analyze the molecular composition of the aerosol analogues by very high-resolution mass
 187 spectrometry (ESI+/Orbitrap technique), we dissolved about 1 mg of the samples in 1 mL of a
 188 50/50 % (v/v) methanol/acetonitrile (*Carlo Erba*, UHPLC-MS quality) mixture (MeOH/ACN)
 189 in a polypropylene vial at ambient conditions. The choice of the solvent was based on Titan
 190 aerosol analogues literature, extracting most of the soluble fraction (Carrasco et al., 2009;
 191 Somogyi et al., 2005). The vials were then agitated and centrifuged for few minutes and then,
 192 the supernatants were diluted at 0.5 mg/mL in order to stabilize the ionization source and to
 193 optimize the ionization yield.

194 5. Very High-Resolution Mass Spectrometry by the ESI+/Orbitrap technique

195 In order to determine the stoichiometric formulae of the molecules constituting the soluble
196 fraction of Pluto aerosol analogues, we analyzed them by Very High-Resolution Mass
197 Spectrometry (VHRMS). We used the analytical instrument *LTQ Orbitrap™ XL*
198 (*ThermoFisher Scientific*) installed at IPAG (Grenoble, France), a Fourier Transform mass
199 spectrometer combining two mass analyzers: a Linear Trap Quadrupole (LTQ) and an Orbitrap
200 (Makarov et al., 2006; Perry et al., 2008). The LTQ selects the ions belonging to a specific mass
201 range and brings them to the C-trap. The C-trap then accumulates the ions and focalizes them
202 to the Orbitrap, which acts as mass analyzer. The ionization source was the ElectroSpray
203 Ionization (ESI) in positive mode (ESI+) (Banks and Whitehouse, 1996; Yamashita and Fenn,
204 1984). ESI+ is a “soft” ionization method producing mainly mono-charged (and few multi-
205 charged) ions by adding protons (H⁺) without any substantial fragmentation of the molecules.
206 This positive mode of ionization has been widely used for Titan aerosol analogues analysis in
207 the literature (Sarker et al., 2003; Somogyi et al., 2016, 2012, 2005; Vuitton et al., 2010) and,
208 as a “soft” ionization method, gives access to the pristine molecules present in the soluble
209 fractions of interest. Furthermore, elemental composition analysis of Titan aerosol analogues
210 produced with different proportions of CO has shown that nitrogen and oxygen atoms are
211 substantial components of the samples (Fleury et al., 2014). The ESI+ source is thus adapted to
212 the analysis of our samples due to the proton affinity of the nitrogen and oxygen atoms
213 constituting our analyzed molecules (Rodgers et al., 2005). Nevertheless, it should be kept in
214 mind that this technique can only study the soluble fraction of the samples, which probably
215 represents only 20 to 35 % of the total solid mass of Pluto aerosol analogues (Carrasco et al.,
216 2009).

217 The sample was injected into the ESI+ source using a syringe through a polyetheretherketone
218 (PEEK) capillary (direct infusion) with a fixed flow of 3 μL/min. The capillaries were
219 systematically washed with methanol between each sample analysis. The analyses were
220 performed using *Thermo Tune Plus* software, with the following ESI+ source parameters: a
221 spray voltage of 3.5 kV, a sheath gas flow rate of 5 (arbitrary unit), an aux gas flow rate of
222 0 (arbitrary unit), a sweep gas flow rate of 0 (arbitrary unit), a capillary voltage of 34 V, a
223 capillary temperature of 275 °C and a tube lens voltage of 50 V.

224 As we estimated that no unequivocal molecular assignment can be made above m/z 300 due to
225 the high complexity of the material analyzed (Gautier et al., 2014), we restricted our analysis
226 from m/z 50 to m/z 300.

227 In order to increase the signal/noise ratio, each mass spectrum is the mean of 4 scans and each
228 scan is the sum of 128 microscans. The maximum ion injection time allowed into the Orbitrap
229 was 500 ms. The mass spectra were acquired with a resolution $m/\Delta m$ set to 100,000 at m/z 400.

230 6. Calibration of the VHRMS data and identification of the molecules

231 Prior to the analyses, the Orbitrap was externally calibrated with a mixture of caffeine, MRFA
232 peptide and Ultramark. No internal calibration was used. Mass spectra of blanks (solvent only)
233 were also acquired before each analysis of the samples P_{CO-free}, P₄₀₀ and P₆₀₀. Molecules present
234 in the blanks were subsequently removed from the samples analyses (see an example of blank

235 mass spectrum in Supplementary Material, Figure A). The external calibration was not
236 sufficient on a small m/z scale, because the lightest calibrator, the caffeine, was at m/z 195.
237 Thus, *Attributor*, a software developed at IPAG (Grenoble, France) (Orthous-Daunay et al.,
238 2019), was also used to improve the calibration of the data. We used the masses of molecules
239 known to be present in the P_{CO-free} sample (Gautier et al., 2014) to refine the calibration curve
240 to correct the mass spectra of Pluto aerosol analogues: C₃N₂H₅⁺ at m/z 69.045 and C₄N₂H₇⁺ at
241 m/z 83.060.

242 *Attributor* was also used to attribute the stoichiometric formulae to the molecules constituting
243 the samples. For the molecules assignment, we excluded the peaks whose intensity was four
244 orders of magnitude lower than the most intense peak. The attribution was based on a
245 combination of x carbon, y hydrogen, z nitrogen and w oxygen (C _{x} H _{y} N _{z} O _{w}). The considered
246 isotopes were: ¹²C, ¹H, ¹⁴N and ¹⁶O. To avoid aberrant formulae, we used some restrictions.
247 The minimum numbers of carbon, hydrogen and nitrogen atoms were set to 1 and there were
248 no maximum numbers. The minimum number of oxygen atom was set to 0 and the maximum
249 number limited to 3; due to the low proportion of CO injected in the reactor, it is unlikely to
250 form highly-oxygenated molecules. Theoretical m/z with a deviation more than ± 5 ppm were
251 excluded (according to the instrument specifications in external calibration mode). An
252 additional filter was applied to screen out unrealistic molecules with H/C > 5 and N/C > 3 ratios,
253 which would be molecules with extremely exotic structures and/or C atoms with more than four
254 bonds.

255 7. Elemental composition analysis

256 An elemental composition analysis of P₄₀₀ and P₆₀₀ samples was performed to determine their
257 carbon, hydrogen, nitrogen and oxygen mass percentages.

258 The determination of C, H and N was performed using a FlashSmart™ elemental analyzer
259 (*ThermoFisher Scientific*) under flash combustion at 930 °C. About 1-2 mg of each sample,
260 with 1 mg of vanadium pentoxide (V₂O₅) for complete combustion, were precisely weighed
261 into a tin container. For the determination of O, the system operated in pyrolysis mode at
262 1050 °C. About 1-2 mg of each sample were weighed into a silver container. Then, tin and
263 silver capsules were individually introduced into the combustion reactor via the *Thermo*
264 *Scientific*™ *MAS Plus Autosampler*. After combustion (C, H and N) and pyrolysis (O), the
265 resulting gases – CO₂, H₂O and N₂ – were transported by a helium flow to a copper-filled layer
266 and then swept through a gas chromatography (GC) column to separate the combustion gases.
267 Finally, they were detected by a Thermal Conductivity Detector (TCD).

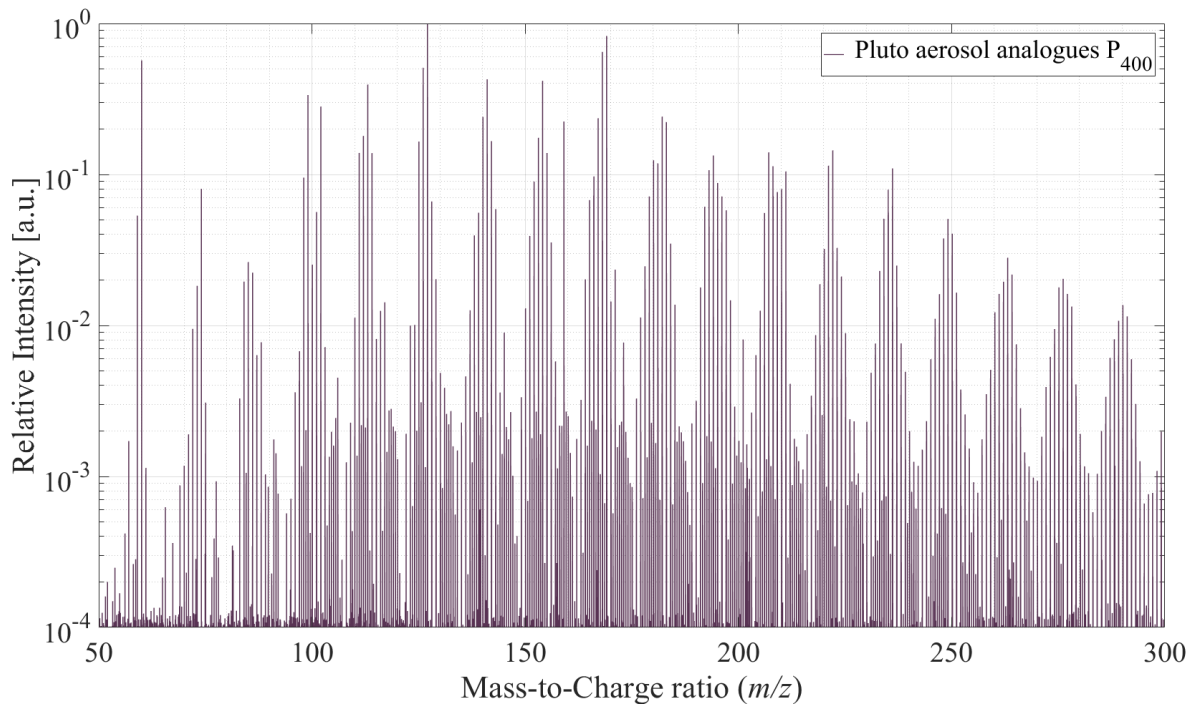
268 Two calibration curves have been created: one for C, H and N measurements and one for O
269 measurements. For this purpose, 0.5-5 mg of BBOT (2,5-Bis(5-ter-butyl-benzoxazol-2-yl)
270 thiophene, C₂₆H₂₆N₂O₂S) (*Fisher Scientific*, 99 % purity) were analyzed as a standard using K
271 factor as the calibration method.

272

273 III. Results

274 1. ESI+/Orbitrap analysis

275 Figure 1 presents the ESI+/Orbitrap mass spectrum of the soluble fraction of Pluto aerosol
276 analogues P₄₀₀, from m/z 50 to m/z 300. Intensity was normalized to the most intense peak in
277 the mass spectrum (m/z 127.0725).



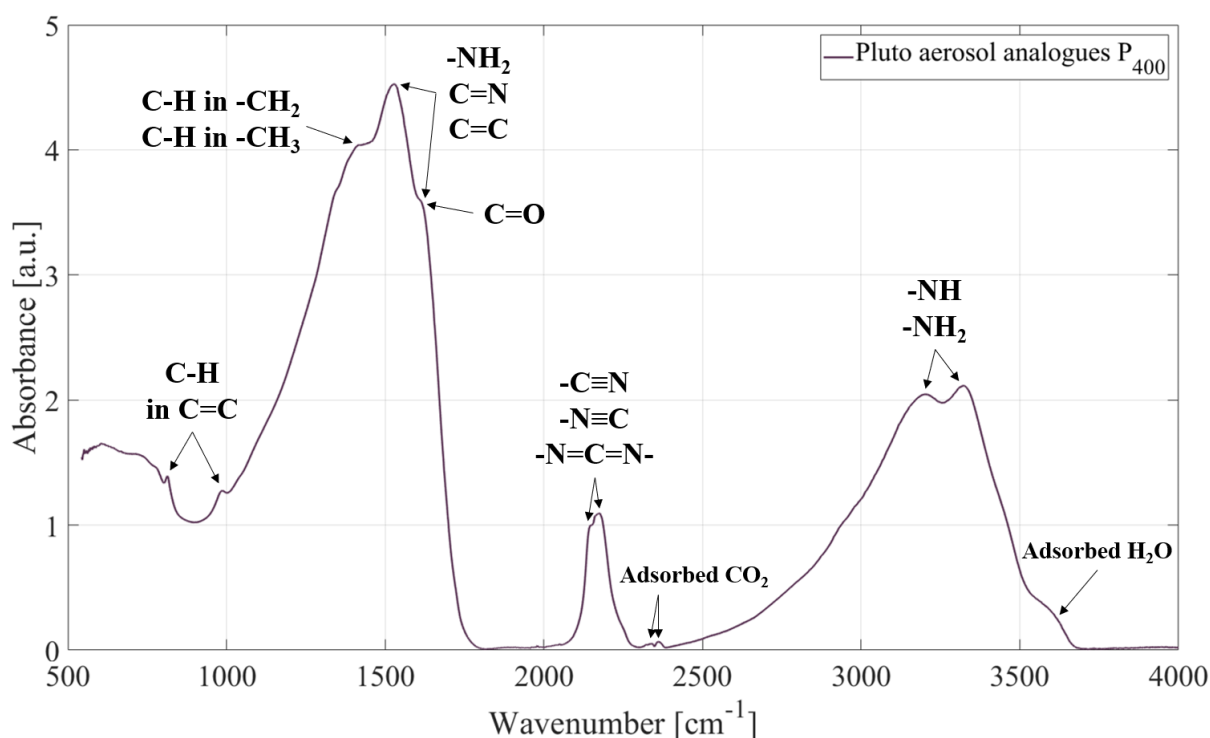
278

279 Figure 1: ESI+/Orbitrap mass spectrum of the soluble fraction of Pluto aerosol analogues P₄₀₀. The x -axis
280 corresponds to the Mass-to-Charge ratio (m/z), while the y -axis corresponds to the relative intensity of the peaks,
281 normalized to the most intense peak (m/z 127.0725). The small peaks in dark purple color are due to an aliasing
282 effect.

283 In the mass spectrum (Figure 1), thousands of peaks are seen; hence, the soluble fraction of
284 Pluto aerosol analogues is a complex mixture requiring such a high-resolution and high-
285 precision analysis. The peaks are grouped in several periodic clusters similar to those observed
286 in the mass spectrum of Titan aerosol analogues. This analogy suggests that the molecules
287 detected in the soluble fraction of Pluto aerosol analogues, using ESI+/Orbitrap, are of a
288 random-copolymeric nature, composed at least partially of a repetition of a $(\text{CH}_2)_m(\text{HCN})_n$
289 pattern (Gautier et al., 2017; Maillard et al., 2018; Pernot et al., 2010).

290 2. Chemistry with N₂ and CO

291 From laboratory studies of Titan atmosphere we have learnt that not only methane, but also
292 nitrogen plays a critical role in the atmospheric chemistry of Titan and in the formation and the
293 growth of the aerosols (Carrasco et al., 2012; Dubois et al., 2019; Gautier et al., 2011; He and
294 Smith, 2014, 2013; Hörst et al., 2018; Imanaka et al., 2004; Imanaka and Smith, 2010; Trainer
295 et al., 2012). Our results emphasize the importance of nitrogen chemistry on Pluto as well.



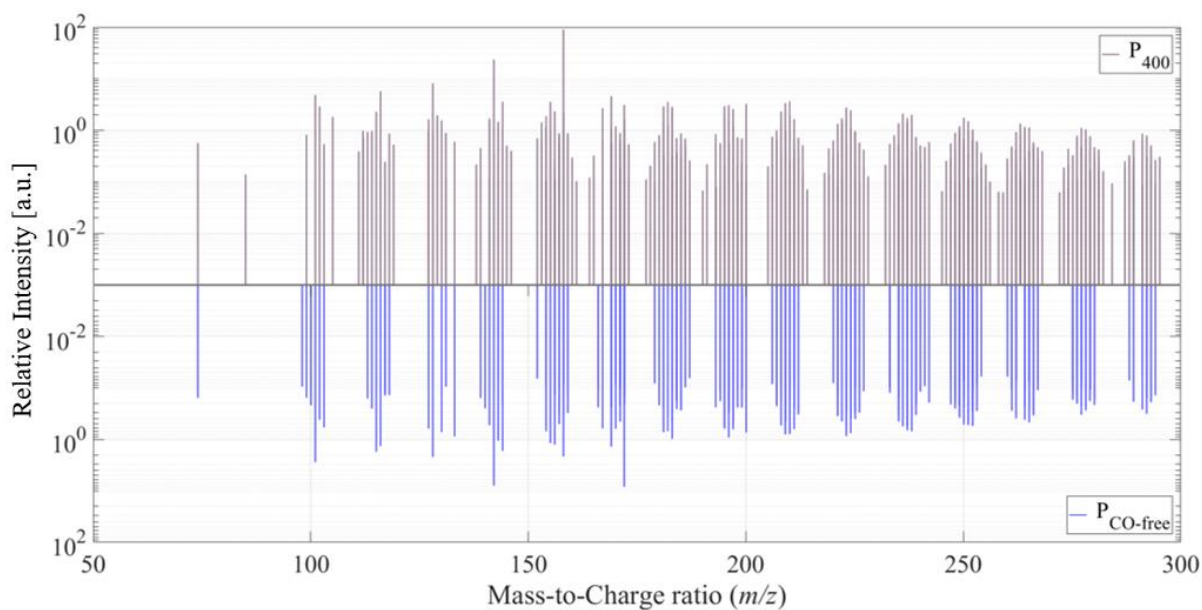
296

297 Figure 2: Infrared spectrum of Pluto aerosol analogues P₄₀₀, acquired by the ATR technique. At 2340 and
 298 2360 cm⁻¹, small absorption bands are attributed to CO₂ adsorbed on the sample, while the shoulder at
 299 3600 cm⁻¹ corresponds to water adsorbed on the analogues as hydroxyl -OH.

300 Figure 2 presents the infrared spectrum of Pluto aerosol analogues P₄₀₀, obtained by the ATR
 301 technique. In this spectrum, the importance of N-bearing chemical functions is clearly shown
 302 (Gautier et al., 2012). At 1550 cm⁻¹, a strong absorption band can be attributed to the
 303 deformation vibrations of aromatic and aliphatic amines -NH₂ and of double bonds C=C and
 304 C=N in aromatic and hetero-aromatic cycles. The bands at 2150 and 2170 cm⁻¹ can be attributed
 305 to nitriles -C≡N, isocyanides -N≡C and carbodiimides -N=C=N-. At 3200 and 3330 cm⁻¹,
 306 there are two strong large bands, characteristic of primary and secondary amines -NH and
 307 -NH₂.

308 According to the IR spectrum (Figure 2) and due to the selectivity of the ESI+ source (Rodgers
 309 et al., 2005), we expect to detect with the Orbitrap a large amount of N-bearing organic
 310 molecules in the soluble fraction of P₄₀₀ and P₆₀₀ samples. The presence of oxygenated organic
 311 molecules is also expected. In contrast, we do not expect to detect hydrocarbons without
 312 heteroatoms, since this kind of molecules is minor in similar samples (Derenne et al., 2012;
 313 Gautier et al., 2016, 2014; Morisson et al., 2016). In addition, the ESI+ source is not the most
 314 adequate to detect them due to their low proton affinity (Molnárné Guricza and Schrader, 2015).

315 In order to understand if the presence of CO in Pluto atmosphere has an impact on the molecular
 316 composition of Pluto aerosols via the presence of oxygenated organic molecules, we compared
 317 the intensities of the oxygenated molecules present in the soluble fraction of Pluto aerosol
 318 analogues P₄₀₀ and of aerosol analogues produced without CO (Figure 3). The intensities of the
 319 oxygenated molecules were normalized to the intensity of the most intense peak in the mass
 320 spectrum (*m/z* 127.0725 for P₄₀₀ sample and *m/z* 60.0551 for P_{CO-free} sample, respectively).



321
 322 Figure 3: Normalized intensities of only the oxygenated molecules present in the soluble fraction of Pluto aerosol
 323 analogues P₄₀₀ (in purple) and of aerosol analogues produced without CO (P_{CO-free}, in blue). The spectra were
 324 acquired with the ESI+/Orbitrap technique. Intensities were normalized to the most intense peak of each mass
 325 spectrum (m/z 127.0725 for P₄₀₀ sample and m/z 60.0551 for P_{CO-free} sample, respectively).

326 Upper panel in Figure 3 displays in purple the normalized intensities of oxygenated molecules
 327 present in the soluble fraction of Pluto aerosol analogues P₄₀₀. Lower panel (in mirror) shows
 328 in blue the normalized intensities of oxygenated molecules present in the soluble fraction of
 329 hypothetical Pluto aerosol analogues P_{CO-free}.

330 Considering the composition of the gas mixture producing the aerosol analogues without CO,
 331 oxygenated molecules should not be present. However, in this case, the small proportion of
 332 oxygenated molecules are produced by partial oxidation of the surface of the particles during
 333 the air exposure when collecting the samples (Carrasco et al., 2016; Fleury et al., 2014).

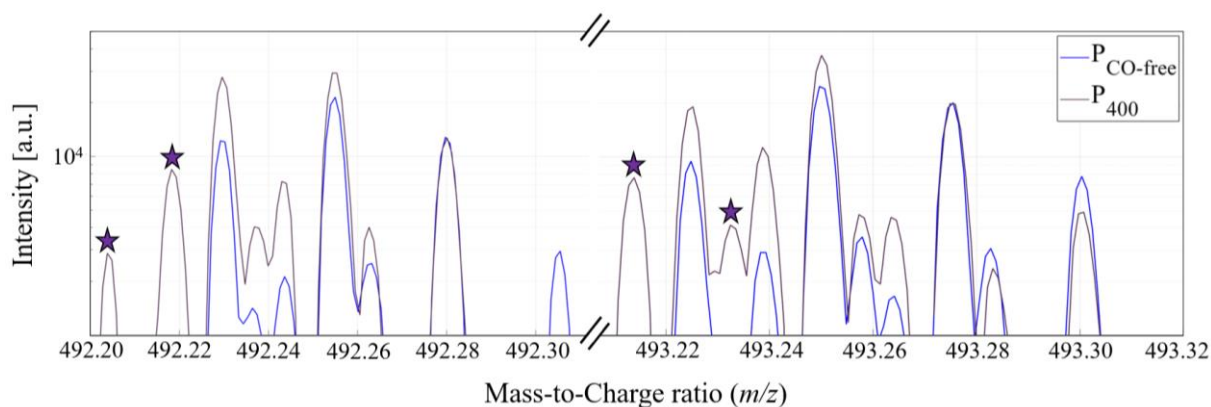
334 In Figure 3, the oxygenated molecules detected with ESI+/Orbitrap in Pluto aerosol analogues
 335 P₄₀₀ appear to be similar to the oxygenated molecules contaminating the aerosol analogues
 336 without CO (P_{CO-free}). However, regarding the normalized intensities of these oxygenated
 337 molecules, it appears that they are significantly higher in P₄₀₀ analogues than in P_{CO-free},
 338 demonstrating an effective reactivity of CO.

339 The oxygenated molecules are detected at the same m/z ratios, within the accuracy of the
 340 Orbitrap, so that the chemical formulae attributions are the same. This means that the reactive
 341 pathways leading to their formation for P₄₀₀ in the experiment might be, at least partially, similar
 342 to the oxidation pathways affecting P_{CO-free}. The oxygenated molecules present in P₄₀₀ are
 343 produced both by reactions within the plasma simulating Pluto atmospheric chemistry and by
 344 surface oxidation of the particles during the collecting exposed to air. Both processes might
 345 involve the same oxidizing agents.

346 Future experiments would provide information on the oxidizing agents involved in the plasma
 347 oxidation pathways: analysis of the gas phase chemical composition of the plasma simulating
 348 Pluto atmosphere and synthesis of Pluto aerosol analogues with C¹⁸O.

349 Figure 4 shows the molecules present in P₄₀₀ (in purple) and P_{CO-free} (in blue) samples, between
350 m/z 492.20 and m/z 493.32 (arbitrary zooming for example purpose). The purple stars point out
351 molecules that are present only in the sample P₄₀₀. Although the resolution of the analytical
352 instrument is not sufficient above m/z 300 to strictly identify molecules, Figure 4 demonstrates
353 that CO reactivity impacts the aerosols composition even at large masses.

354



355

356 Figure 4: Mass spectra of P₄₀₀ (in purple) and P_{CO-free} (in blue) samples, between m/z 492.20 and m/z 493.32. The
357 x -axis was cropped (//) for a better visualization of the peaks. The purple stars correspond to molecules that are
358 detected only in the analogues P₄₀₀.

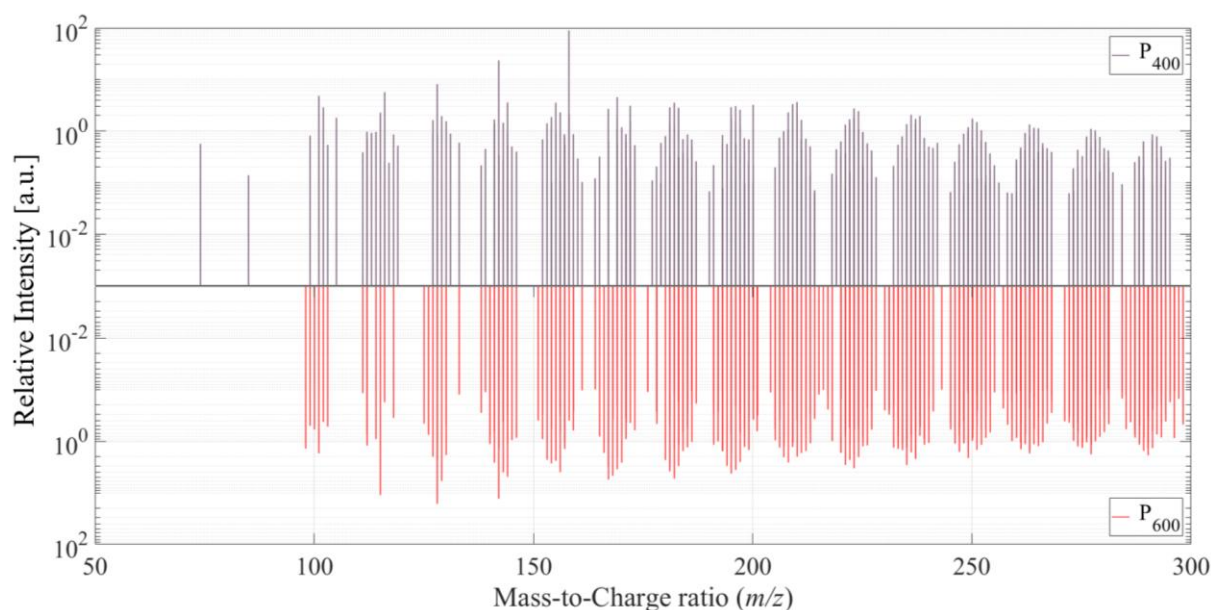
359 In Figure 4, we count 19 peaks. Of these, 14 stoichiometric formulae are common to both P₄₀₀
360 and P_{CO-free} samples, 1 formula is present only in the sample P_{CO-free}, while 4 formulae – those
361 pointed out by the purple stars – are present only in the sample P₄₀₀. We can therefore conclude
362 that the presence of CO in the reactive mixture, even in a small proportion (500 ppm), has an
363 impact on the chemistry leading to the formation of aerosols on Pluto, from light gas-phase
364 molecules to large macromolecular polymeric structures incorporated in the aerosols.

365 3. Effect of the altitude of aerosols formation

366 The mixing ratio of CH₄ in Pluto atmosphere strongly varies with the altitude (Young et al.,
367 2018). This variation can have an impact on the molecular composition and thus on physical
368 properties of Pluto aerosols.

369 As the abundance of CO is nearly constant all along Pluto atmosphere, the CO/CH₄ ratio varies
370 with the variation of CH₄ mixing ratio, from 0.1 at the surface to 0.001 at around 1450 km of
371 altitude. We therefore also study the distribution of the oxygenated molecules in Pluto aerosol
372 analogues P₆₀₀.

373 In Figure 5, we compare the normalized intensities of the oxygenated molecules detected with
374 ESI+/Orbitrap in the soluble fraction of P₄₀₀ (upper panel, in purple) and P₆₀₀ (lower panel, in
375 mirror, in red). The intensities of the oxygenated molecules were normalized to the intensity of
376 the most intense peak in the mass spectrum (m/z 127.0725 for P₄₀₀ sample and m/z 60.0551 for
377 P₆₀₀ sample, respectively).



378

379 Figure 5: Normalized intensities of only the oxygenated molecules present in the soluble fraction of Pluto aerosol
 380 analogues P₄₀₀ (in purple) and P₆₀₀ (in red). The spectra were acquired with the ESI+/Orbitrap technique. The
 381 intensities of the peaks identified as oxygenated molecules have been normalized to the most intense peak of each
 382 mass spectrum (m/z 127.0725 for P₄₀₀ sample and m/z 60.0551 for P₆₀₀ sample, respectively).

383 Regarding the mass spectra on Figure 5, it seems that the clusters in P₆₀₀ are shifted leftward
 384 compared to P₄₀₀, suggesting that the oxygenated molecules in the soluble fraction of P₆₀₀ are
 385 different from those constituting the soluble fraction of P₄₀₀. This would imply that the chemical
 386 pathways leading to the formation of oxygenated molecules are quite different in Pluto aerosols
 387 depending on their altitude of formation. Due to the leftward shifting of the clusters, we can
 388 suppose that the oxygenated organic molecules detected in the soluble fraction of the sample
 389 P₆₀₀ include less hydrogen atoms than the molecules present in the soluble fraction of P₄₀₀.
 390 Oxygenated organic molecules in P₆₀₀ are therefore more unsaturated. From this observation,
 391 we can conclude that the increase in the mixing ratio of CH₄ (thus being at higher altitude on
 392 Pluto) leads to an increased formation of unsaturated molecules in the soluble fraction of Pluto
 393 aerosol analogues. This conclusion was also made for Titan aerosol analogues produced from
 394 N₂:CH₄ gas mixtures with different CH₄ mixing ratios (Derenne et al., 2012; Gautier et al.,
 395 2014). This implies that this effect is likely due to the variation in the mixing ratio of CH₄ itself
 396 and not to the presence of CO in the reactive mixture.

397 In order to determine the abundances of C, H, N and O atoms in Pluto aerosol analogues, we
 398 performed an elemental composition analysis of P₄₀₀ and P₆₀₀ samples and obtained the results
 399 presented in Table 2.

400

401

402

403 **Table 2: Mass percentages of C, H, N and O elements present in Pluto aerosol analogues P₄₀₀ and P₆₀₀.**
404 **Given uncertainties correspond to $\pm 3\sigma$.**

Mass percentage (%)	P ₄₀₀	P ₆₀₀
C	42.1 \pm 0.2	49.0 \pm 0.2
H	3.7 \pm 0.06	4.8 \pm 0.07
N	45.1 \pm 0.2	36.0 \pm 0.2
O	1.9 \pm 0.03	1.7 \pm 0.03

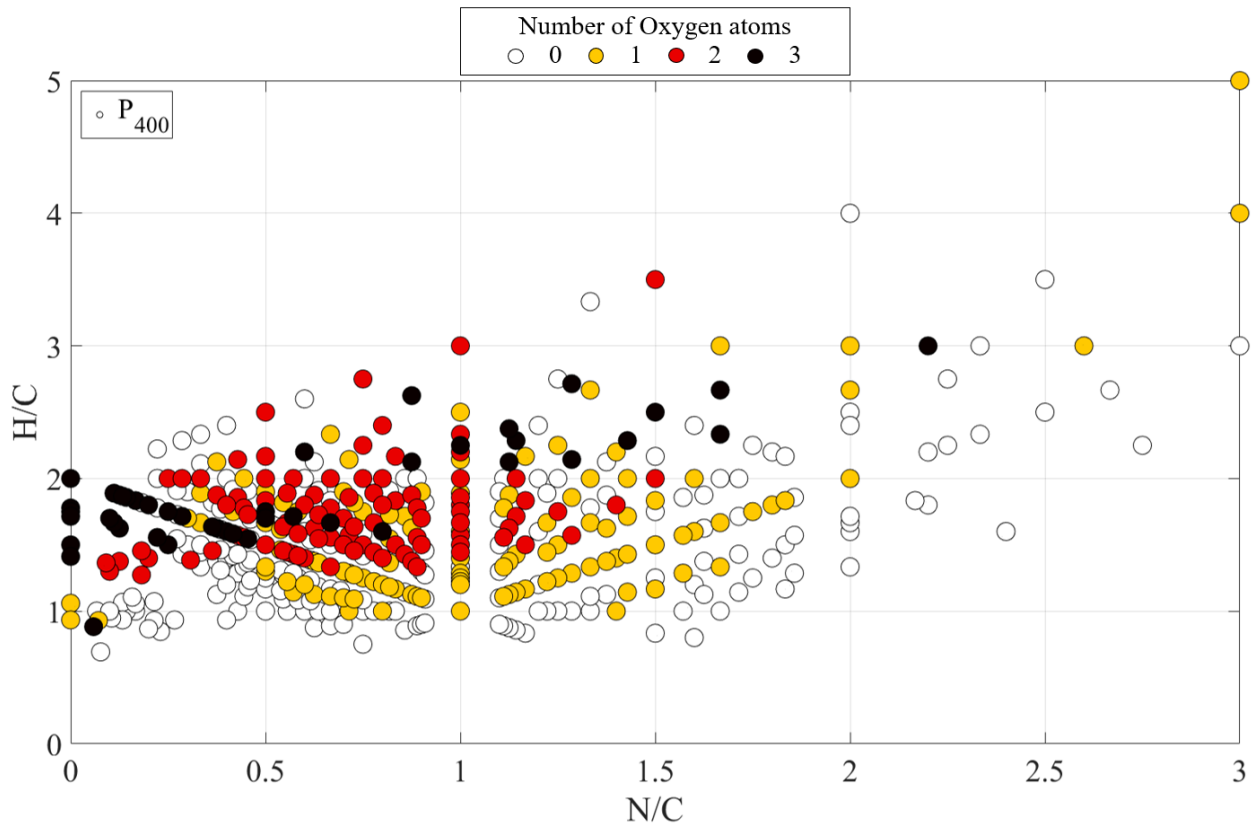
405

406 Table 2 displays the mass percentages of the elements C, H, N and O present in Pluto aerosol
407 analogues P₄₀₀ and P₆₀₀. Note for both samples that the sum of the mass percentages does not
408 equal 100 %. This is due to uncertainties related to the fact that the measurement of the mass
409 percentage of the element O is not carried out at the same time, nor with the same technique, as
410 the measurement of the mass percentages of the elements C, H and N.

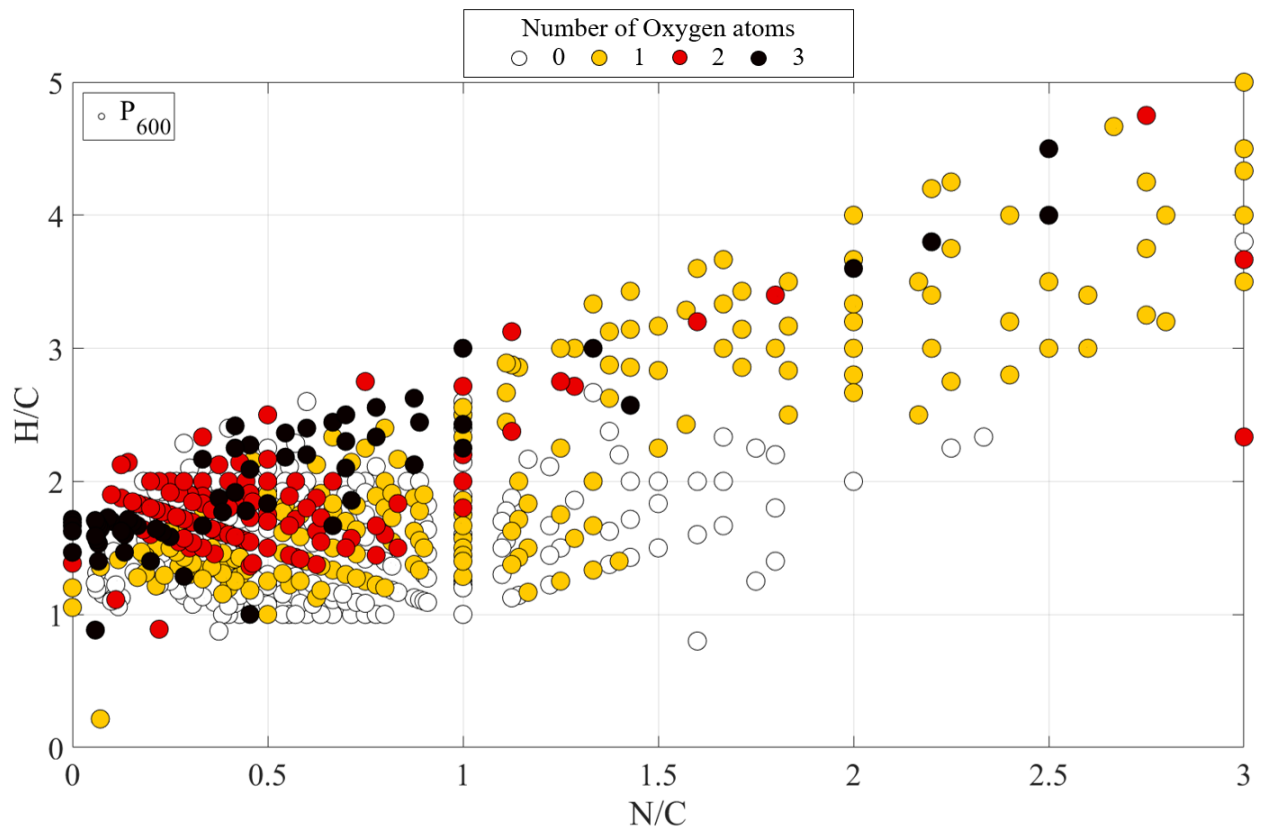
411 Two observations can be deduced from Table 2: (1) sample P₆₀₀ contains more carbon and
412 hydrogen in mass, but less nitrogen than sample P₄₀₀; (2) sample P₄₀₀ contains more oxygen in
413 mass than sample P₆₀₀. The first observation can be explained by the fact that the sample P₆₀₀
414 is synthesized with a higher CH₄ mixing ratio; whereby more C and H atoms and less N atoms
415 are present in the reactive mixture. The second one, in agreement with the conclusion of He et
416 al. (2017), is due to the fact that the sample P₄₀₀ is produced with a higher CO/CH₄ ratio.

417 To further visualize the chemical differences between the soluble fraction of the samples P₄₀₀
418 and P₆₀₀, we modified conventional van Krevelen [H/C versus O/C] diagrams. The van
419 Krevelen diagrams were proposed in 1950 to study the structure and reactions processes of coal.
420 Since then, this type of representation has been frequently applied on data obtained with high-
421 resolution mass spectrometry (Kim et al., 2003; Marshall and Rodgers, 2008; Rodgers et al.,
422 2005; Wu et al., 2004). More recently, this tool was expanded to the analysis of complex organic
423 mixtures of terrestrial and planetary interests, using [H/C versus N/C] axes (Danger et al., 2016;
424 Gautier et al., 2014; Imanaka and Smith, 2010; Pernot et al., 2010; Somogyi et al., 2012; Tziotis
425 et al., 2011).

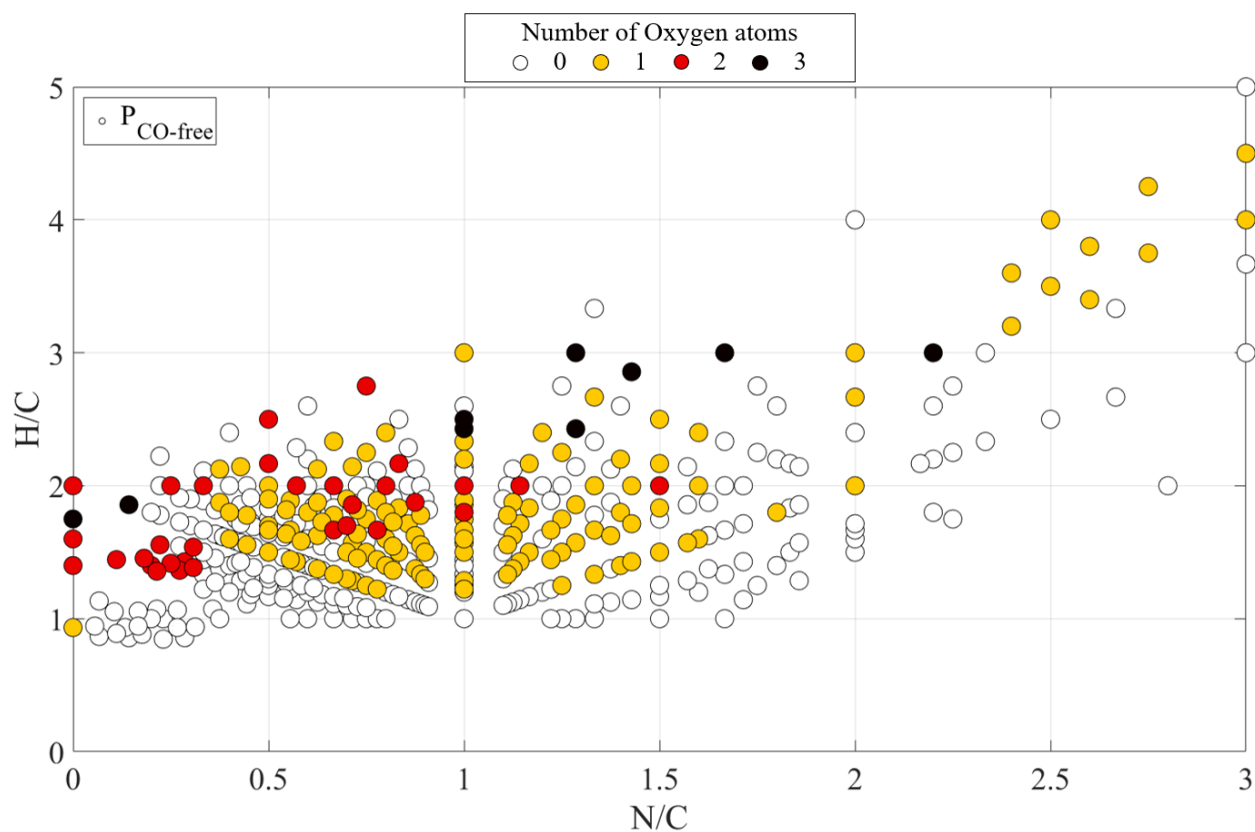
426 Figure 6 shows the modified van Krevelen diagrams of all the molecules identified in the
427 soluble fraction of the samples P₄₀₀ (top), P₆₀₀ (middle) and P_{CO-free} (bottom). The *x*-axis
428 corresponds to Nitrogen-to-Carbon (N/C) ratio and the *y*-axis corresponds to Hydrogen-to-
429 Carbon (H/C) ratio. Each point represents a given molecule constituting the soluble fraction of
430 the sample analyzed by ESI+/Orbitrap. The colors correspond to the number of oxygen atoms
431 included in the molecule. As the oxygen is not supposed to take part to the co-polymeric growth,
432 due to its bivalence and its affinity to labile hydrogen (Decker and Jenkins, 1985; Ligon et al.,
433 2014), but instead to be randomly included in the molecules, we have chosen to represent the
434 data with the number of oxygen atoms present in the molecules and not with Oxygen-to-Carbon
435 (O/C) ratio.



436



437



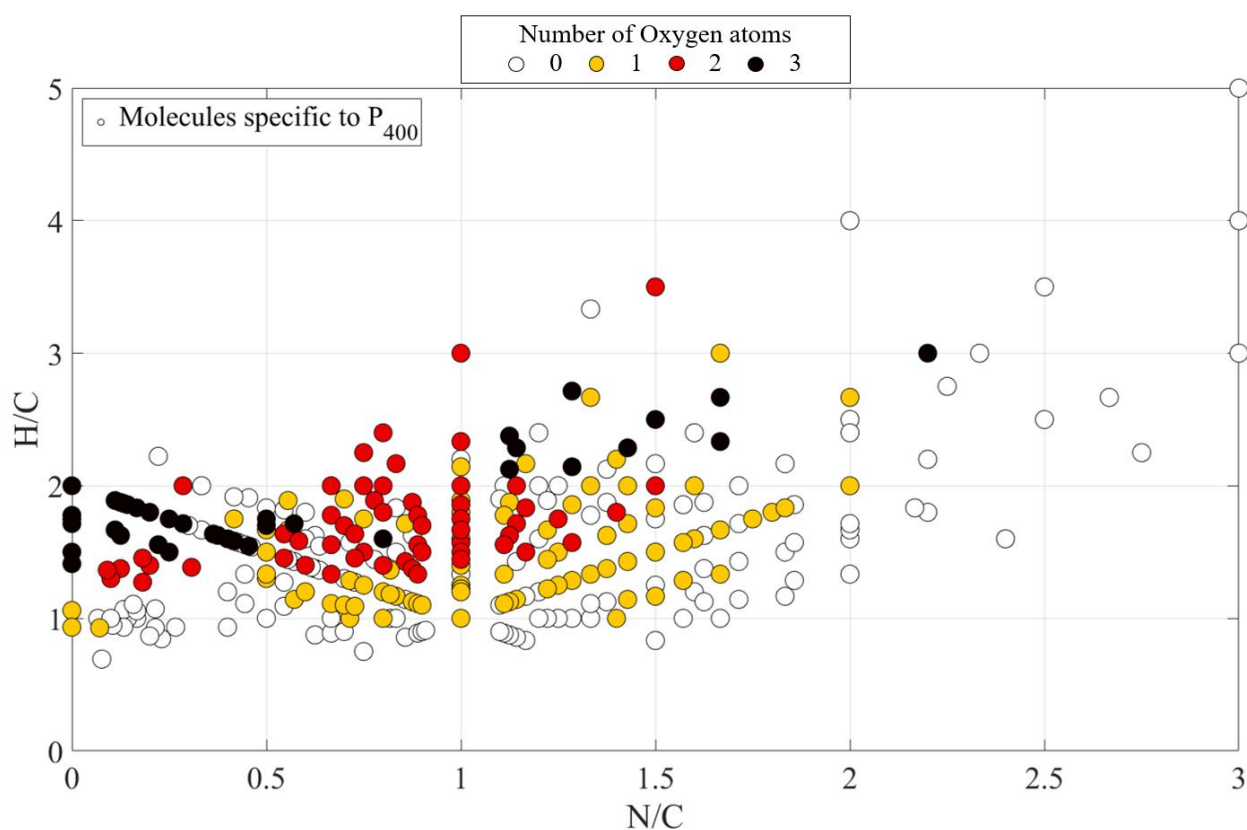
438

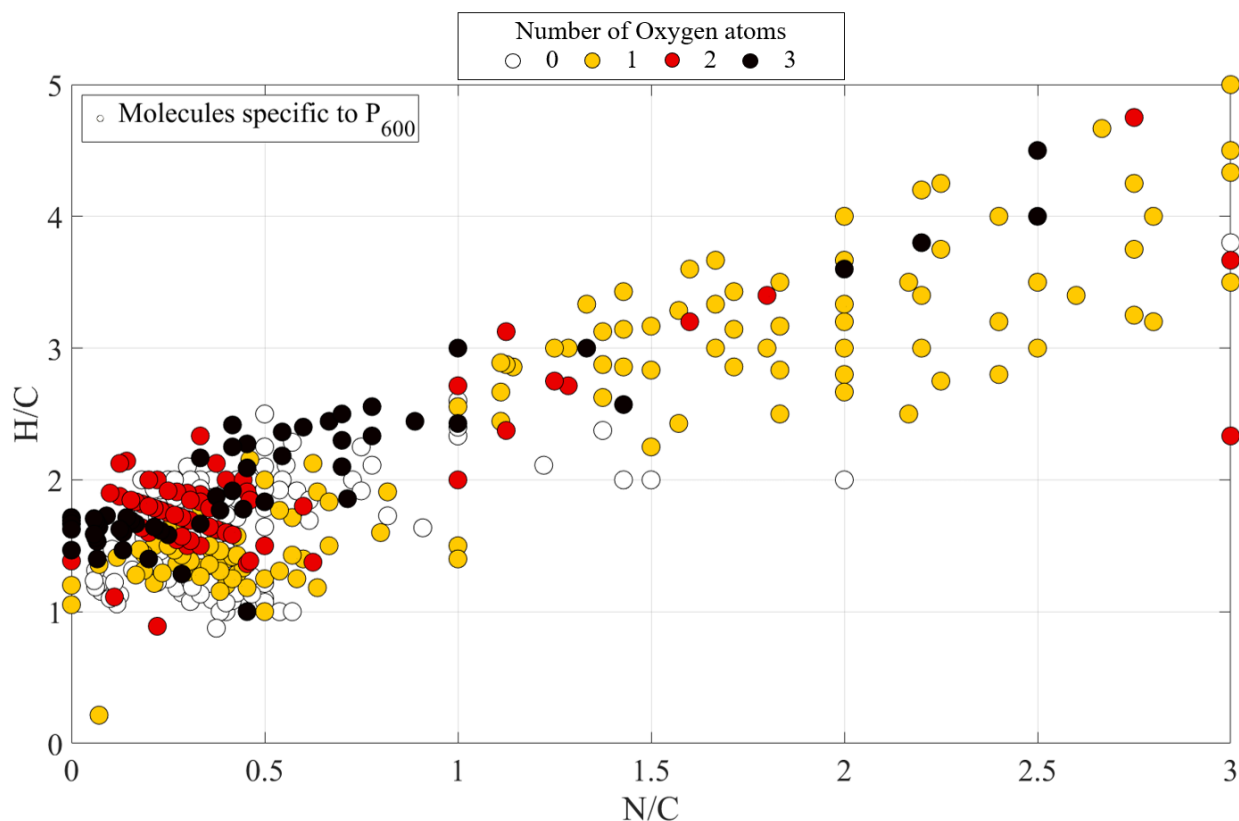
439 Figure 6: Modified van Krevelen diagrams. The samples were analyzed with the ESI+/Orbitrap technique and the
 440 molecules were identified with *Attributor* software. Each dot corresponds to a specific molecule characterized by
 441 its Hydrogen-to-Carbon (H/C) and Nitrogen-to-Carbon (N/C) ratios. The colors correspond to the number of
 442 oxygen atoms included in the molecules: White ⇔ Zero O atom; Yellow ⇔ One O atom; Red ⇔ Two O atoms;
 443 Black ⇔ Three O atoms. Top: P₄₀₀ sample. Middle: P₆₀₀ sample. Bottom: P_{CO-free} sample.

444 In Figures 6.top, middle and bottom, we notice that the molecules with one oxygen atom
 445 (yellow dots) are scattered all over the distribution for the samples P₄₀₀, P₆₀₀ and P_{CO-free}. This
 446 means that incorporating one atom of oxygen in a molecule does not depend on its nature (light
 447 or heavy, low or high H/C and N/C ratios). The second important point is that the oxygenated
 448 molecules due to contamination in P_{CO-free} sample essentially correspond to molecules with one
 449 oxygen atom. Thus, the molecules with two and three oxygen atoms (red and black dots,
 450 respectively), that are abundantly detected in the soluble fraction of P₄₀₀ and P₆₀₀ samples, are
 451 very likely produced by CO chemistry. These molecules are mainly present in a specific area
 452 of the diagrams, characterized by the following elemental ratios: $[1 < H/C < 2.5 \text{ and } 0 < N/C < 1]$.
 453 The fact that N/C ratio is lower than one suggests that the incorporation of more than one
 454 oxygen atom in the molecules constituents of the aerosols is done at the expense of nitrogen
 455 incorporation. There may be a competition between N₂ and CO chemistries, as suggested by
 456 He et al. (2017). The presence of molecules with two or three oxygen atoms at N/C ratio of less
 457 than one could also be explained by the incorporation of O atoms into the molecules in the form
 458 of carbonyl –C=O or carboxyl –COOH chemical functions. The incorporation of oxygen with
 459 carbon into a molecule would therefore necessarily decrease the N/C ratio.

460 Figure 7 presents the modified van Krevelen diagrams of molecules that are exclusively
 461 detected in either the P₄₀₀ (top) or P₆₀₀ (bottom) sample. In Figure 7.top and bottom, we can see

462 that the molecules specific to P₄₀₀, oxygenated or not, are scattered all over the distribution,
463 whereas in the sample P₆₀₀, the molecules group into two distinct areas, suggesting again
464 different reactive pathways for both samples. The area [1 < H/C < 2.5 and 0 < N/C < 1] is
465 composed of a patchwork of heavier molecules including or not oxygen atoms (white, yellow,
466 red and black dots), while the area [2 < H/C < 5 and 1.25 < N/C < 3] is essentially composed
467 of lighter molecules with one oxygen atom (essentially yellow dots). This reinforces the idea
468 that when the percentage of methane increases, the mixing ratio of molecular nitrogen
469 decreases, while there is likely competition between CO and N₂ chemistries (He et al., 2017).
470 Incorporating more than one oxygen atom in heavier molecules, probably in the form of
471 chemical functions -C=O or -COOH, is done at the expense of N-incorporation.





473

474 Figure 7: Modified van Krevelen diagrams of the molecules exclusively detected in the soluble fraction of
 475 P₄₀₀ (top) and P₆₀₀ (bottom) samples. The samples were analyzed with the ESI+/Orbitrap technique and the
 476 molecules were identified with *Attributor* software. Each dot corresponds to a specific molecule characterized by
 477 its Hydrogen-to-Carbon (H/C) and Nitrogen-to-Carbon (N/C) ratios. The colors correspond to the number of
 478 oxygen atoms included in the molecules: White ⇔ Zero O atom; Yellow ⇔ One O atom; Red ⇔ Two O atoms;
 479 Black ⇔ Three O atoms.

480 In Gautier et al. (2014), a high-resolution mass spectrometry study was carried out on Titan
 481 aerosol analogues produced with the PAMPRE experimental setup. This study showed the
 482 impact on the molecular composition of Titan aerosol analogues when the methane percentage
 483 varies. In particular, there are less molecules formed with N/C < 1 when the percentage of
 484 methane increases.

485 Previous studies have also shown that when CH₄ percentage increases, more hydrogen is
 486 available in the gas phase leading to the aerosols, and that this hydrogen tends to inhibit the
 487 growth of the aerosol analogues (DeWitt et al., 2009; Sciamma-O'Brien et al., 2010). We can
 488 exclude this to be the case here since we do not see a depletion of the “N/C < 1” molecules in
 489 the P₆₀₀ sample. This suggests that N₂ and CH₄ chemistry is strongly impacted by the presence
 490 of CO, even in a small proportion. Hörst and Tolbert (2014) and He et al. (2017) also studied
 491 the effect of carbon monoxide on planetary atmospheric chemistry and on the formation of
 492 aerosol analogues and proposed two hypotheses: (1) in presence of carbon monoxide, oxygen
 493 radicals coming from CO react with atomic and molecular hydrogen coming from CH₄ and
 494 removes them from the chemical system; (2) in presence of CO, there is more carbon available
 495 without increasing the quantity of available hydrogen that inhibits the aerosols growth, resulting
 496 in a less reducing environment allowing the production of more unsaturated molecules.
 497 According to our results, the first hypothesis of Hörst and Tolbert (2014) and He et al. (2017)

498 may be an explanation to the lack of depletion of the molecules with $N/C < 1$ when the CH_4
499 percentage increases. On the contrary, the second hypothesis cannot explain our results. On one
500 hand, the sample P_{600} presents more molecules with higher N/C (and H/C) ratios than P_{400} ,
501 meaning that less carbon is incorporated in these molecules. On the other hand, as shown in
502 Figure 4, the soluble fraction of P_{600} contains more unsaturated molecules than that of the P_{400}
503 sample, even though the sample P_{600} is produced with a lower CO/CH_4 ratio.

504

505 **IV. Discussion**

506 Long before the *New Horizons* era, the photochemical models of Pluto atmosphere scarcely
507 took into consideration N_2 and CO chemistries (Krasnopolsky and Cruikshank, 1999; Lara et
508 al., 1997; Stansberry et al., 1989). It was thought that the formation of the aerosols would be
509 essentially driven by the photolysis of CH_4 by Lyman- α photons. This was also the case on
510 Titan before the *Cassini-Huygens* mission that revealed that not only methane, but also
511 molecular nitrogen plays a key role in Titan atmospheric chemistry and in the formation of
512 N-bearing organic aerosols. In light of this discovery, the latest photochemical models of Pluto
513 atmosphere compensated this misconception by including the chemistry from N_2 , but the
514 question of the CO chemistry still remains unsolved (Luspay-Kuti et al., 2017; Wong et al.,
515 2017). CO serves as a source of oxygen for incorporation in haze particles, leading to the
516 formation of prebiotic molecules in the aerosols. This was pointed out by Hörst et al. (2012)
517 who detected amino acids and nucleotide bases in the solid products produced with the
518 PAMPRE experimental setup in a plasma of $N_2:CH_4:CO$ gas mixture. However, even Titan
519 aerosol analogues studies usually do not include CO despite its substantial mixing ratio
520 (47 ± 8 ppm $_v$) in the hazy atmosphere of Titan (de Kok et al., 2007). Additionally, few studies
521 on exoplanetary atmospheres also emphasized the link between the presence of carbon
522 monoxide and haze layers (Barman et al., 2015; Deming et al., 2013; He et al., 2018a, 2018b;
523 Hörst et al., 2018a; Konopacky et al., 2013; Pont et al., 2013).

524 For Pluto, an endeavor has recently been done by Luspay-Kuti et al. (2017) and Krasnopolsky,
525 (2020) to incorporate the most important reactions of CO chemistry in their models. Our results
526 obtained by elemental composition analysis highlight an important incorporation of both
527 nitrogen and oxygen atoms in the molecules constituting Pluto aerosol analogues and thus
528 active N_2 and CO chemistries influencing the gas phase composition and density. We thus
529 strongly advise to keep focusing on the effect of CO in Pluto atmospheric chemistry and make
530 sure to include extensive oxygen and nitrogen reactive pathways in future Pluto photochemical
531 models.

532 From our analyses, we conclude that the molecules constituting the soluble fraction of Pluto
533 aerosol analogues are mainly composed of N-bearing organic molecules, with a significant
534 proportion of oxygenated molecules. Unsaturated molecules may also be present in large
535 amount. These heavy, unsaturated N-bearing organic molecules and oxygenated species are
536 likely very reactive and may therefore catalyze and self-sustain the synthesis of other molecules
537 constituting the aerosols. Furthermore, by interacting with molecules in the gas phase, they may
538 also act as cloud condensation nuclei (Broekhuizen et al., 2004; Fan et al., 2016; Kumar et al.,
539 2003; Lavvas et al., 2016; Luspay-Kuti et al., 2017), impacting the climate of Pluto. Seven

540 Pluto clouds candidates have been identified by Stern et al. (2017) from *New Horizons* image
541 dataset. These clouds could be the result of the condensation of HCN, C₂H₂, C₂H₆, C₂H₄ or
542 CH₄. One interesting question is whether the condensation of clouds on Pluto aerosols is
543 affected by the proportion of O-bearing molecules in the hazes. The study of the wettability of
544 Pluto aerosol analogues to HCN, C₂H₂, C₂H₆, C₂H₄ or CH₄ may provide answers to this
545 question.

546 Pluto atmosphere is around 30 K colder than theoretically predicted, at about 400 km of altitude
547 (Gladstone et al., 2016; Zhang et al., 2017; Zhu et al., 2014). Because of Pluto thermal structure,
548 expected to be in radiative-convective equilibrium, atmospheric gas molecules such as HCN or
549 water vapor are not sufficient to explain Pluto temperature profile. Zhang et al. (2017) proposed
550 that Pluto haze, rather than its atmospheric gases, could explain Pluto cold atmosphere. Their
551 study was performed using the optical properties of Titan aerosol analogues, which are oxygen-
552 free. Our results obtained by elemental composition analysis and ESI+/Orbitrap showed a
553 significant incorporation of oxygen atoms in the molecules constituting Pluto aerosol analogues
554 and that this O-incorporation depends on CH₄ mixing ratio. As more oxygen is incorporated,
555 the real and imaginary refractive indices of haze particles change, resulting in different optical
556 properties that may reduce UV wavelengths from reaching Pluto surface and influence Pluto
557 radiative cooling. While Zhang et al. (2017) showed a dependency of Pluto climate to the
558 aerosols simulated optical constants, Gavilan et al. (2017) have shown that when the percentage
559 of oxygen increases in organic aerosols, the absorption at longer UV wavelengths is
560 significantly higher. The experimental determination of the UV-Visible refractive indices of
561 Pluto aerosol analogues is thus of prime importance to further advance our understanding of
562 Pluto cold atmosphere.

563 V. Conclusion

564 In this study, we produced Pluto aerosol analogues using the PAMPRE experimental setup. The
565 sample P₄₀₀ is expected to be representative of aerosols that form at 400 km of altitude in Pluto
566 atmosphere. The sample P₆₀₀ is an analogue of aerosols that could form at 600 km of altitude.
567 To determine the chemical composition of these analogues of Pluto aerosols, we performed
568 infrared spectroscopy and elemental composition analyses on them. The samples were also
569 analyzed using very high-resolution mass spectrometry, with the ESI+/Orbitrap technique. Our
570 results show:

- 571 (1) Substantial incorporation of nitrogen atoms in Pluto aerosol analogues: nitrogen
572 accounts for about 36 and 45 % in mass of Pluto aerosol analogues P₆₀₀ and P₄₀₀,
573 respectively. The N-bearing chemical functions essentially correspond to primary and
574 secondary amines –NH and –NH₂, C=N double bonds in aromatic and hetero-aromatic
575 cycles, nitriles –C≡N, isocyanides –N≡C and carbodiimides –N=C=N–.
- 576 (2) A significant proportion of O-bearing molecules is formed by chemistry of CO: about
577 1.9 and 1.7 % of oxygen in mass in samples P₄₀₀ and P₆₀₀, respectively.
- 578 (3) An impact of methane percentage – and thus the altitude of aerosols formation on
579 Pluto – on the chemical composition of the aerosols. This impact strongly affects the
580 nitrogen and oxygen contents of the hazes. In particular, we show that the bulk sample
581 of aerosols produced at low altitude (P₄₀₀) contains more nitrogen and oxygen than the
582 bulk sample of aerosols produced at high altitude (P₆₀₀).

583 Pluto aerosols have a strong impact on Pluto climate, acting as condensation nuclei or affecting
584 the atmosphere radiative balance (Luspay-Kuti et al., 2017; Zhang et al., 2017). However, these
585 exact interactions are still poorly understood and further experimental work is needed on the
586 aerosols-gas interactions and the aerosols optical properties to further refine Pluto atmospheric
587 models.

588 Finally, Sebree et al. (2018) have recently detected prebiotic molecules in aerosols formed from
589 an AC glow discharge in a N₂:CH₄:CO gas mixture with a high CO mixing ratio, and a recent
590 review was also published by Cruikshank et al. (2019) about the implications of Pluto for the
591 prebiotic chemistry. In our data, we detected at *m/z* 111.043 the following chemical formula
592 C₄H₅N₃O, which can correspond to cytosine, the easiest produced nucleobase. To confirm the
593 presence of this biomolecule in Pluto aerosol analogues, it would be necessary to analyze them
594 by chromatography coupled to mass spectrometry, in order to get structural information of the
595 molecules.

596

597

598

599 Acknowledgements

600 We are grateful to the European Research Council Starting Grant *PrimChem* for funding this
601 work (grant agreement n° 636829).

602 **References**

- 603 Alcouffe, G., Cavarroc, M., Cernogora, G., Ouni, F., Jolly, A., Boufendi, L., Szopa, C., 2009.
604 Capacitively coupled plasma used to simulate Titan's atmospheric chemistry. *Plasma*
605 *Sources Sci. Technol.* 19, 15008. <https://doi.org/10.1088/0963-0252/19/1/015008>
- 606 Anicich, V.G., Wilson, P., McEwan, M.J., 2003. Termolecular ion-molecule reactions in
607 Titan's atmosphere. IV. A search made at up to 1 micron in pure hydrocarbons. *J. Am.*
608 *Soc. Mass Spectrom.* 14, 900–915. [https://doi.org/10.1016/S1044-0305\(03\)00218-6](https://doi.org/10.1016/S1044-0305(03)00218-6)
- 609 Banks, J.F., Whitehouse, C.M., 1996. Electrospray Ionization Mass Spectrometry. *Methods*
610 *Enzymol.* 270, 486–519. [https://doi.org/10.1016/s0076-6879\(96\)70023-x](https://doi.org/10.1016/s0076-6879(96)70023-x)
- 611 Barman, T.S., Konopacky, Q.M., Macintosh, B., Marois, C., 2015. Simultaneous Detection of
612 Water, Methane and Carbon Monoxide in the Atmosphere of Exoplanet HR 8799 b.
613 *Astrophys. J.* 804, 61. <https://doi.org/10.1088/0004-637x/804/1/61>
- 614 Böhme, D.K., 2000. Experimental studies of positive ion chemistry with flow-tube mass
615 spectrometry: birth, evolution, and achievements in the 20th century. *Int. J. Mass*
616 *Spectrom.* 200, 97–136. [https://doi.org/https://doi.org/10.1016/S1387-3806\(00\)00299-2](https://doi.org/https://doi.org/10.1016/S1387-3806(00)00299-2)
- 617 Broekhuizen, K.E., Thornberry, T., Kumar, P.P., Abbatt, J.P.D., 2004. Formation of cloud
618 condensation nuclei by oxidative processing: Unsaturated fatty acids. *J. Geophys. Res.*
619 *Atmos.* 109. <https://doi.org/10.1029/2004JD005298>
- 620 Cable, M.L., Hörst, S.M., Hodyss, R., Beauchamp, P.M., Smith, M.A., Willis, P.A., 2012.
621 Titan Tholins: Simulating Titan Organic Chemistry in the Cassini-Huygens Era. *Chem.*
622 *Rev.* 112, 1882–1909. <https://doi.org/10.1021/cr200221x>
- 623 Carrasco, N., Gautier, T., Es-sebbar, E., Pernot, P., Cernogora, G., 2012. Volatile products
624 controlling Titan's tholins production. *Icarus* 219, 230–240.
625 <https://doi.org/https://doi.org/10.1016/j.icarus.2012.02.034>
- 626 Carrasco, N., Jomard, F., Vigneron, J., Etcheberry, A., Cernogora, G., 2016. Laboratory
627 analogues simulating Titan's atmospheric aerosols: Compared chemical compositions of
628 grains and thin films. *Planet. Space Sci.* 128, 52–57.
629 <https://doi.org/https://doi.org/10.1016/j.pss.2016.05.006>
- 630 Carrasco, N., Schmitz-Afonso, I., Bonnet, J.-Y., Quirico, E., Thissen, R., Dutuit, O., Bagag,
631 A., Laprévotte, O., Buch, A., Giuliani, A., Adandé, G., Ouni, F., Hadamcik, E., Szopa, C.,
632 Cernogora, G., 2009. Chemical Characterization of Titan's Tholins: Solubility,
633 Morphology and Molecular Structure Revisited. *J. Phys. Chem. A* 113, 11195–11203.
634 <https://doi.org/10.1021/jp904735q>
- 635 Cheng, A.F., Summers, M.E., Gladstone, G.R., Strobel, D.F., Young, L.A., Lavvas, P.,
636 Kammer, J.A., Lisse, C.M., Parker, A.H., Young, E.F., Stern, S.A., Weaver, H.A., Olkin,
637 C.B., Ennico, K.A., 2017. Haze in Pluto's atmosphere. *Icarus* 290, 112–133.
638 <https://doi.org/https://doi.org/10.1016/j.icarus.2017.02.024>
- 639 Coll, P., Coscia, D., Smith, N.S., Gazeau, M.-C., Ramírez, S.I., Cernogora, G., Israël, G.,

- 640 Raulin, F., 1999. Experimental laboratory simulation of Titan's atmosphere: aerosols and
641 gas phase. *Planet. Space Sci.* 47, 1331–1340.
642 [https://doi.org/https://doi.org/10.1016/S0032-0633\(99\)00054-9](https://doi.org/https://doi.org/10.1016/S0032-0633(99)00054-9)
- 643 Coll, P., Navarro-González, R., Szopa, C., Poch, O., Ramírez, S.I., Coscia, D., Raulin, F.,
644 Cabane, M., Buch, A., Israël, G., 2013. Can laboratory tholins mimic the chemistry
645 producing Titan's aerosols? A review in light of ACP experimental results. *Planet. Space*
646 *Sci.* 77, 91–103. <https://doi.org/https://doi.org/10.1016/j.pss.2012.07.006>
- 647 Cruikshank, D.P., Materese, C.K., Pendleton, Y.J., Boston, P.J., Grundy, W.M., Schmitt, B.,
648 Lisse, C.M., Runyon, K.D., Keane, J.T., Beyer, R.A., Summers, M.E., Scipioni, F.,
649 Stern, S.A., Dalle Ore, C.M., Olkin, C.B., Young, L.A., Ennico, K.A., Weaver, H.A.,
650 Bray, V.J., 2019. Prebiotic Chemistry of Pluto. *Astrobiology* 19, 831–848.
651 <https://doi.org/10.1089/ast.2018.1927>
- 652 Danger, G., Fresneau, A., Abou Mrad, N., de Marcellus, P., Orthous-Daunay, F.-R.,
653 Duvernay, F., Vuitton, V., Le Sergeant d'Hendecourt, L., Thissen, R., Chiavassa, T.,
654 2016. Insight into the molecular composition of laboratory organic residues produced
655 from interstellar/pre-cometary ice analogues using very high resolution mass
656 spectrometry. *Geochim. Cosmochim. Acta* 189, 184–196.
657 <https://doi.org/https://doi.org/10.1016/j.gca.2016.06.014>
- 658 de Kok, R., Irwin, P.G.J., Teanby, N.A., Lellouch, E., Bézard, B., Vinatier, S., Nixon, C.A.,
659 Fletcher, L., Howett, C.J.A., Calcutt, S.B., Bowles, N.E., Flasar, F.M., Taylor, F.W.,
660 2007. Oxygen compounds in Titan's stratosphere as observed by Cassini CIRS. *Icarus*
661 186, 354–363. <https://doi.org/https://doi.org/10.1016/j.icarus.2006.09.016>
- 662 Decker, C., Jenkins, A.D., 1985. Kinetic approach of oxygen inhibition in ultraviolet- and
663 laser-induced polymerizations. *Macromolecules* 18, 1241–1244.
664 <https://doi.org/10.1021/ma00148a034>
- 665 Deming, D., Wilkins, A., McCullough, P., Crouzet, N., Burrows, A., Fortney, J.J., Agol, E.,
666 Dobbs-Dixon, I., Madhusudhan, N., Desert, J.-M., Knutson, H.A., Line, M., Gilliland,
667 R.L., Haynes, K., Magic, Z., Mandell, A.M., Clampin, M., Ranjan, S., Charbonneau, D.,
668 Seager, S., 2013. Infrared Transmission Spectroscopy of the Exoplanets HD 209458b
669 and XO-1b using the Wide Field Camera-3 on the Hubble Space Telescope. *Astrophys.*
670 *J.* 774, 17. <https://doi.org/DOI:101088/0004-637X/774/2/95>
- 671 Derenne, S., Coelho, C., Anquetil, C., Szopa, C., Rahman, A.S., McMillan, P.F., Corà, F.,
672 Pickard, C.J., Quirico, E., Bonhomme, C., 2012. New insights into the structure and
673 chemistry of Titan's tholins via ¹³C and ¹⁵N solid state nuclear magnetic resonance
674 spectroscopy. *Icarus* 221, 844–853.
675 <https://doi.org/https://doi.org/10.1016/j.icarus.2012.03.003>
- 676 DeWitt, H.L., Trainer, M.G., Pavlov, A.A., Hasenkopf, C.A., Aiken, A.C., Jimenez, J.L.,
677 McKay, C.P., Toon, O.B., Tolbert, M.A., 2009. Reduction in Haze Formation Rate on
678 Prebiotic Earth in the Presence of Hydrogen. *Astrobiology* 9, 447–453.
679 <https://doi.org/10.1089/ast.2008.0289>

680 Dubois, D., Carrasco, N., Petrucciani, M., Vettier, L., Tigrine, S., Pernot, P., 2019. In situ
681 investigation of neutrals involved in the formation of Titan tholins. *Icarus* 317, 182–196.
682 <https://doi.org/https://doi.org/10.1016/j.icarus.2018.07.006>

683 Elliot, J.L., Dunham, E.W., Bosh, A.S., Slivan, S.M., Young, L.A., Wasserman, L.H., Millis,
684 R.L., 1989. Pluto's atmosphere. *Icarus* 77, 148–170.
685 [https://doi.org/https://doi.org/10.1016/0019-1035\(89\)90014-6](https://doi.org/https://doi.org/10.1016/0019-1035(89)90014-6)

686 Fan, J., Wang, Y., Rosenfeld, D., Liu, X., 2016. Review of Aerosol-Cloud Interactions:
687 Mechanisms, Significance, and Challenges. *J. Atmos. Sci.* 73, 4221–4252.
688 <https://doi.org/10.1175/JAS-D-16-0037.1>

689 Fleury, B., Carrasco, N., Gautier, T., Mahjoub, A., He, J., Szopa, C., Hadamcik, E., Buch, A.,
690 Cernogora, G., 2014. Influence of CO on Titan atmospheric reactivity. *Icarus* 238, 221–
691 229. <https://doi.org/https://doi.org/10.1016/j.icarus.2014.05.027>

692 Forget, F., Bertrand, T., Vangvichith, M., Leconte, J., Millour, E., Lellouch, E., 2017. A post-
693 New Horizons global climate model of Pluto including the N₂, CH₄ and CO cycles.
694 *Icarus* 287, 54–71. <https://doi.org/https://doi.org/10.1016/j.icarus.2016.11.038>

695 Gao, P., Fan, S., Wong, M.L., Liang, M.-C., Shia, R.-L., Kammer, J.A., Yung, Y.L.,
696 Summers, M.E., Gladstone, G.R., Young, L.A., Olkin, C.B., Ennico, K.A., Weaver,
697 H.A., Stern, S.A., 2017. Constraints on the microphysics of Pluto's photochemical haze
698 from New Horizons observations. *Icarus* 287, 116–123.
699 <https://doi.org/https://doi.org/10.1016/j.icarus.2016.09.030>

700 Gautier, T., Carrasco, N., Buch, A., Szopa, C., Sciamma-O'Brien, E., Cernogora, G., 2011.
701 Nitrile gas chemistry in Titan's atmosphere. *Icarus* 213, 625–635.
702 <https://doi.org/https://doi.org/10.1016/j.icarus.2011.04.005>

703 Gautier, T., Carrasco, N., Mahjoub, A., Vinatier, S., Giuliani, A., Szopa, C., Anderson, C.M.,
704 Correia, J.-J., Dumas, P., Cernogora, G., 2012. Mid- and far-infrared absorption
705 spectroscopy of Titan's aerosols analogues. *Icarus* 221, 320–327.
706 <https://doi.org/https://doi.org/10.1016/j.icarus.2012.07.025>

707 Gautier, T., Carrasco, N., Schmitz-Afonso, I., Touboul, D., Szopa, C., Buch, A., Pernot, P.,
708 2014. Nitrogen incorporation in Titan's tholins inferred by high resolution orbitrap mass
709 spectrometry and gas chromatography–mass spectrometry. *Earth Planet. Sci. Lett.* 404,
710 33–42. <https://doi.org/https://doi.org/10.1016/j.epsl.2014.07.011>

711 Gautier, T., Schmitz-Afonso, I., Touboul, D., Szopa, C., Buch, A., Carrasco, N., 2016.
712 Development of HPLC-Orbitrap method for identification of N-bearing molecules in
713 complex organic material relevant to planetary environments. *Icarus* 275, 259–266.
714 <https://doi.org/https://doi.org/10.1016/j.icarus.2016.03.007>

715 Gautier, T., Sebree, J.A., Li, X., Pinnick, V.T., Grubisic, A., Loeffler, M.J., Getty, S.A.,
716 Trainer, M.G., Brinckerhoff, W.B., 2017. Influence of trace aromatics on the chemical
717 growth mechanisms of Titan aerosol analogues. *Planet. Space Sci.* 140, 27–34.
718 <https://doi.org/https://doi.org/10.1016/j.pss.2017.03.012>

- 719 Gavilan, L., Broch, L., Carrasco, N., Fleury, B., Vettier, L., 2017. Organic Aerosols in the
720 Presence of CO₂ in the Early Earth and Exoplanets: UV–Vis Refractive Indices of
721 Oxidized Tholins. *Astrophys. J.* 848, L5. <https://doi.org/10.3847/2041-8213/aa8cc4>
- 722 Gladstone, G.R., Pryor, W.R., Stern, S.A., 2015. Ly α @Pluto. *Icarus* 246, 279–284.
723 <https://doi.org/https://doi.org/10.1016/j.icarus.2014.04.016>
- 724 Gladstone, G.R., Stern, S.A., Ennico, K.A., Olkin, C.B., Weaver, H.A., Young, L.A.,
725 Summers, M.E., Strobel, D.F., Hinson, D.P., Kammer, J.A., Parker, A.H., Steffl, A.J.,
726 Linscott, I.R., Parker, J.W., Cheng, A.F., Slater, D.C., Versteeg, M.H., Greathouse, T.K.,
727 Retherford, K.D., Throop, H.B., Cunningham, N.J., Woods, W.W., Singer, K.N., Tsang,
728 C.C.C., Schindhelm, E., Lisse, C.M., Wong, M.L., Yung, Y.L., Zhu, X., Curdt, W.,
729 Lavvas, P., Young, E.F., Tyler, G.L., 2016. The atmosphere of Pluto as observed by New
730 Horizons. *Science* (80-.). 351.
- 731 Gladstone, G.R., Young, L.A., 2019. New Horizons Observations of the Atmosphere of Pluto.
732 *Annu. Rev. Earth Planet. Sci.* 47, 119–140. [https://doi.org/10.1146/annurev-earth-](https://doi.org/10.1146/annurev-earth-053018-060128)
733 [053018-060128](https://doi.org/10.1146/annurev-earth-053018-060128)
- 734 Grundy, W.M., Binzel, R.P., Buratti, B.J., Cook, J.C., Cruikshank, D.P., Dalle Ore, C.M.,
735 Earle, A.M., Ennico, K.A., Howett, C.J.A., Lunsford, A.W., Olkin, C.B., Parker, A.H.,
736 Philippe, S., Protopapa, S., Quirico, E., Reuter, D.C., Schmitt, B., Singer, K.N.,
737 Verbiscer, A.J., Beyer, R.A., Buie, M.W., Cheng, A.F., Jennings, D.E., Linscott, I.R.,
738 Parker, J.W., Schenk, P.M., Spencer, J.R., Stansberry, J.A., Stern, S.A., Throop, H.B.,
739 Tsang, C.C.C., Weaver, H.A., Weigle, G.E., Young, L.A., 2016. Surface compositions
740 across Pluto and Charon. *Science* (80-.). 351.
- 741 He, C., Hörst, S.M., Lewis, N.K., Yu, X., Moses, J.I., Kempton, E.M.-R., Marley, M.S.,
742 McGuiggan, P., Morley, C. V., Valenti, J.A., Vuitton, V., 2018a. Photochemical Haze
743 Formation in the Atmospheres of Super-Earths and Mini-Neptunes. *Astron. J.* 156, 38.
744 <https://doi.org/10.3847/1538-3881/aac883>
- 745 He, C., Hörst, S.M., Lewis, N.K., Yu, X., Moses, J.I., Kempton, E.M.-R., McGuiggan, P.,
746 Morley, C. V., Valenti, J.A., Vuitton, V., 2018b. Laboratory Simulations of Haze
747 Formation in the Atmospheres of Super-Earths and Mini-Neptunes: Particle Color and
748 Size Distribution. *Astrophys. J.* 856, L3. <https://doi.org/10.3847/2041-8213/aab42b>
- 749 He, C., Hörst, S.M., Riemer, S., Sebree, J.A., Pauley, N., Vuitton, V., 2017. Carbon
750 Monoxide Affecting Planetary Atmospheric Chemistry. *Astrophys. J.* 841, L31.
751 <https://doi.org/10.3847/2041-8213/aa74cc>
- 752 He, C., Smith, M.A., 2014. Identification of nitrogenous organic species in Titan aerosols
753 analogs: Implication for prebiotic chemistry on Titan and early Earth. *Icarus* 238, 86–92.
754 <https://doi.org/https://doi.org/10.1016/j.icarus.2014.05.012>
- 755 He, C., Smith, M.A., 2013. Identification of nitrogenous organic species in Titan aerosols
756 analogs: Nitrogen fixation routes in early atmospheres. *Icarus* 226, 33–40.
757 <https://doi.org/https://doi.org/10.1016/j.icarus.2013.05.013>

- 758 Hinson, D.P., Linscott, I.R., Young, L.A., Tyler, G.L., Stern, S.A., Beyer, R.A., Bird, M.K.,
759 Ennico, K.A., Gladstone, G.R., Olkin, C.B., Pätzold, M., Schenk, P.M., Strobel, D.F.,
760 Summers, M.E., Weaver, H.A., Woods, W.W., 2017. Radio occultation measurements of
761 Pluto's neutral atmosphere with New Horizons. *Icarus* 290, 96–111.
762 <https://doi.org/https://doi.org/10.1016/j.icarus.2017.02.031>
- 763 Hörst, S.M., He, C., Lewis, N.K., Kempton, E.M.-R., Marley, M.S., Morley, C. V., Moses,
764 J.I., Valenti, J.A., Vuitton, V., 2018a. Haze production rates in super-Earth and mini-
765 Neptune atmosphere experiments. *Nat. Astron.* 2, 303–306.
766 <https://doi.org/10.1038/s41550-018-0397-0>
- 767 Hörst, S.M., Tolbert, M.A., 2014. The Effect of Carbon Monoxide on Planetary Haze
768 Formation. *Astrophys. J.* 781, 53. <https://doi.org/10.1088/0004-637x/781/1/53>
- 769 Hörst, S.M., Yelle, R. V., Buch, A., Carrasco, N., Cernogora, G., Dutuit, O., Quirico, E.,
770 Sciamma-O'Brien, E., Smith, M.A., Somogyi, Á., Szopa, C., Thissen, R., Vuitton, V.,
771 2012. Formation of Amino Acids and Nucleotide Bases in a Titan Atmosphere
772 Simulation Experiment. *Astrobiology* 12, 809–817.
773 <https://doi.org/10.1089/ast.2011.0623>
- 774 Hörst, S.M., Yoon, Y.H., Ugelow, M.S., Parker, A.H., Li, R., de Gouw, J.A., Tolbert, M.A.,
775 2018b. Laboratory investigations of Titan haze formation: In situ measurement of gas
776 and particle composition. *Icarus* 301, 136–151.
777 <https://doi.org/https://doi.org/10.1016/j.icarus.2017.09.039>
- 778 Hubbard, W.B., Hunten, D.M., Dieters, S.W.B., Hill, K.M., Watson, R.D., 1988. Occultation
779 evidence for an atmosphere on Pluto. *Nature* 336, 452.
- 780 Imanaka, H., Khare, B.N., Elsila, J.E., Bakes, E.L.O., McKay, C.P., Cruikshank, D.P., Sugita,
781 S., Matsui, T., Zare, R.N., 2004. Laboratory experiments of Titan tholin formed in cold
782 plasma at various pressures: Implications for nitrogen-containing polycyclic aromatic
783 compounds in Titan haze. *Icarus* 168, 344–366.
784 <https://doi.org/https://doi.org/10.1016/j.icarus.2003.12.014>
- 785 Imanaka, H., Smith, M.A., 2010. Formation of nitrogenated organic aerosols in the Titan
786 upper atmosphere. *Proc. Natl. Acad. Sci. U. S. A.* 107, 12423–12428.
787 <https://doi.org/10.1073/pnas.0913353107>
- 788 Imanaka, H., Smith, M.A., 2009. EUV Photochemical Production of Unsaturated
789 Hydrocarbons: Implications to EUV Photochemistry in Titan and Jovian Planets. *J. Phys.*
790 *Chem. A* 113, 11187–11194. <https://doi.org/10.1021/jp9041952>
- 791 Khare, B.N., Sagan, C., Thompson, W.R., Arakawa, E.T., Suits, F., Callcott, T.A., Williams,
792 M.W., Shrader, S., Ogino, H., Willingham, T.O., Nagy, B., 1984. The organic aerosols
793 of Titan. *Adv. Sp. Res.* 4, 59–68. [https://doi.org/https://doi.org/10.1016/0273-](https://doi.org/https://doi.org/10.1016/0273-1177(84)90545-3)
794 [1177\(84\)90545-3](https://doi.org/https://doi.org/10.1016/0273-1177(84)90545-3)
- 795 Kim, S., Kramer, R.W., Hatcher, P.G., 2003. Graphical Method for Analysis of Ultrahigh-
796 Resolution Broadband Mass Spectra of Natural Organic Matter, the Van Krevelen

797 Diagram. *Anal. Chem.* 75, 5336–5344. <https://doi.org/10.1021/ac034415p>

798 Konopacky, Q.M., Barman, T.S., Macintosh, B.A., Marois, C., 2013. Detection of Carbon
799 Monoxide and Water Absorption Lines in an Exoplanet Atmosphere. *Science* (80-.).
800 339, 1398–1401. <https://doi.org/10.1126/science.1232003>

801 Krasnopolsky, V.A., 2020. A photochemical model of Pluto’s atmosphere and ionosphere.
802 *Icarus* 335, 113374. <https://doi.org/https://doi.org/10.1016/j.icarus.2019.07.008>

803 Krasnopolsky, V.A., Cruikshank, D.P., 1999. Photochemistry of Pluto’s atmosphere and
804 ionosphere near perihelion. *J. Geophys. Res. Planets* 104, 21979–21996.
805 <https://doi.org/10.1029/1999JE001038>

806 Kumar, P.P., Broekhuizen, K.E., Abbatt, J.P.D., 2003. Organic acids as cloud condensation
807 nuclei: Laboratory studies of highly soluble and insoluble species. *Atmos. Chem. Phys.*
808 3, 509–520. <https://doi.org/10.5194/acp-3-509-2003>

809 Lara, L.M., Ip, W., Rodrigo, R., 1997. Photochemical Models of Pluto’s Atmosphere. *Icarus*
810 130, 16–35. <https://doi.org/https://doi.org/10.1006/icar.1997.5798>

811 Lavvas, P., Strobel, D.F., Lellouch, E., Gurwell, M.A., Cheng, A.F., Summers, M., Gladstone,
812 G.R., 2016. Photochemical aerosol formation in planetary atmospheres: A comparison
813 between Pluto and Titan, in: *AAS/Division for Planetary Sciences Meeting Abstracts*
814 #48. p. 224.06.

815 Lellouch, E., 1994. The Thermal Structure of Pluto’s Atmosphere: Clear vs. Hazy Models.
816 *Icarus* 108, 255–264. <https://doi.org/https://doi.org/10.1006/icar.1994.1060>

817 Lellouch, E., Gurwell, M.A., Butler, B.J., Fouchet, T., Lavvas, P., Strobel, D.F., Sicardy, B.,
818 Moullet, A., Moreno, R., Bockelée-Morvan, D., Biver, N., Young, L.A., Lis, D.C.,
819 Stansberry, J.A., Stern, S.A., Weaver, H.A., Young, E.F., Zhu, X., Boissier, J., 2017.
820 Detection of CO and HCN in Pluto’s atmosphere with ALMA. *Icarus* 286, 289–307.
821 <https://doi.org/https://doi.org/10.1016/j.icarus.2016.10.013>

822 Ligon, S.C., Husár, B., Wutzel, H., Holman, R., Liska, R., 2014. Strategies to Reduce Oxygen
823 Inhibition in Photoinduced Polymerization. *Chem. Rev.* 114, 557–589.
824 <https://doi.org/10.1021/cr3005197>

825 Luspay-Kuti, A., Mandt, K., Jessup, K.L., Kammer, J., Hue, V., Hamel, M., Filwett, R., 2017.
826 Photochemistry on Pluto: Part I. Hydrocarbons and aerosols. *Mon. Not. R. Astron. Soc.*
827 472, 104–117. <https://doi.org/10.1093/mnras/stx1362>

828 Maillard, J., Carrasco, N., Schmitz-Afonso, I., Gautier, T., Afonso, C., 2018. Comparison of
829 soluble and insoluble organic matter in analogues of Titan’s aerosols. *Earth Planet. Sci.*
830 *Lett.* 495, 185–191. <https://doi.org/https://doi.org/10.1016/j.epsl.2018.05.014>

831 Makarov, A., Denisov, E., Kholomeev, A., Balschun, W., Lange, O., Strupat, K., Horning, S.,
832 2006. Performance Evaluation of a Hybrid Linear Ion Trap/Orbitrap Mass Spectrometer.
833 *Anal. Chem.* 78, 2113–2120. <https://doi.org/10.1021/ac0518811>

- 834 Mandt, K., Luspay-Kuti, A., Hamel, M., Jessup, K.-L., Hue, V., Kammer, J.A., Filwett, R.,
835 2017. Photochemistry on Pluto: Part II. HCN and nitrogen isotope fractionation. *Mon.*
836 *Not. R. Astron. Soc.* 472, 118–128. <https://doi.org/10.1093/mnras/stx1587>
- 837 Marshall, A.G., Rodgers, R.P., 2008. Petroleomics: Chemistry of the underworld. *Proc. Natl.*
838 *Acad. Sci.* 105, 18090–18095. <https://doi.org/10.1073/pnas.0805069105>
- 839 McDonald, G.D., Thompson, W.R., Heinrich, M., Khare, B.N., Sagan, C., 1994. Chemical
840 Investigation of Titan and Triton Tholins. *Icarus* 108, 137–145.
841 <https://doi.org/https://doi.org/10.1006/icar.1994.1046>
- 842 Molnárné Guricza, L., Schrader, W., 2015. Electrospray ionization for determination of non-
843 polar polyaromatic hydrocarbons and polyaromatic heterocycles in heavy crude oil
844 asphaltenes. *J. Mass Spectrom.* 50, 549–557. <https://doi.org/10.1002/jms.3561>
- 845 Morisson, M., Szopa, C., Carrasco, N., Buch, A., Gautier, T., 2016. Titan’s organic aerosols:
846 Molecular composition and structure of laboratory analogues inferred from pyrolysis gas
847 chromatography mass spectrometry analysis. *Icarus* 277, 442–454.
848 <https://doi.org/https://doi.org/10.1016/j.icarus.2016.05.038>
- 849 Orthous-Daunay, F.-R., Piani, L., Flandinet, L., Thissen, R., Wolters, W., Vuitton, V., Poch,
850 O., Moynier, F., Sugawara, I., Naraoka, H., Tachibana, S., 2019. Ultraviolet-photon
851 fingerprints on chondritic large organic molecules. *Geochem. J.* 53, 21–32.
- 852 Owen, T.C., Roush, T.L., Cruikshank, D.P., Elliot, J.L., Young, L.A., de Bergh, C., Schmitt,
853 B., Geballe, T.R., Brown, R.H., Bartholomew, M.J., 1993. Surface Ices and the
854 Atmospheric Composition of Pluto. *Science* (80-.). 261, 745 LP – 748.
- 855 Pernot, P., Carrasco, N., Thissen, R., Schmitz-Afonso, I., 2010. Tholinomics - Chemical
856 Analysis of Nitrogen-Rich Polymers. *Anal. Chem.* 82, 1371–1380.
857 <https://doi.org/10.1021/ac902458q>
- 858 Perry, R.H., Cooks, R.G., Noll, R.J., 2008. Orbitrap mass spectrometry: Instrumentation, ion
859 motion and applications. *Mass Spectrom. Rev.* 27, 661–699.
860 <https://doi.org/10.1002/mas.20186>
- 861 Pont, F.J., Sing, D.K., Gibson, N.P., Aigrain, S., Henry, G.W., Husnoo, N., 2013. The
862 prevalence of dust on the exoplanet HD 189733b from Hubble and Spitzer observations.
863 *Mon. Not. R. Astron. Soc.* 432, 2917–2944. <https://doi.org/10.1093/mnras/stt651>
- 864 Rodgers, R.P., Schaub, T.M., Marshall, A.G., 2005. Petroleomics: MS Returns to Its Roots.
865 *Anal. Chem.* 77, 20–27. <https://doi.org/10.1021/ac053302y>
- 866 Sarker, N., Somogyi, Á., Lunine, J.I., Smith, M.A., 2003. Titan Aerosol Analogues: Analysis
867 of the Nonvolatile Tholins. *Astrobiology* 3, 719–726.
868 <https://doi.org/10.1089/153110703322736042>
- 869 Sciamma-O’Brien, E., Carrasco, N., Szopa, C., Buch, A., Cernogora, G., 2010. Titan’s
870 atmosphere: An optimal gas mixture for aerosol production? *Icarus* 209, 704–714.
871 <https://doi.org/https://doi.org/10.1016/j.icarus.2010.04.009>

- 872 Sciamma-O'Brien, E., Upton, K.T., Salama, F., 2017. The Titan Haze Simulation (THS)
873 experiment on COSmIC. Part II. Ex-situ analysis of aerosols produced at low
874 temperature. *Icarus* 289, 214–226.
875 <https://doi.org/https://doi.org/10.1016/j.icarus.2017.02.004>
- 876 Sebree, J.A., Roach, M.C., Shipley, E.R., He, C., Hörst, S.M., 2018. Detection of Prebiotic
877 Molecules in Plasma and Photochemical Aerosol Analogs Using GC/MS/MS
878 Techniques. *Astrophys. J.* 865, 133. <https://doi.org/10.3847/1538-4357/aadba1>
- 879 Sekine, Y., Lebonnois, S., Imanaka, H., Matsui, T., Bakes, E.L.O., McKay, C.P., Khare, B.N.,
880 Sugita, S., 2008. The role of organic haze in Titan's atmospheric chemistry: II. Effect of
881 heterogeneous reaction to the hydrogen budget and chemical composition of the
882 atmosphere. *Icarus* 194, 201–211.
883 <https://doi.org/https://doi.org/10.1016/j.icarus.2007.08.030>
- 884 Somogyi, Á., Oh, C.-H., Smith, M.A., Lunine, J.I., 2005. Organic environments on Saturn's
885 moon, Titan: Simulating chemical reactions and analyzing products by FT-ICR and ion-
886 trap mass spectrometry. *J. Am. Soc. Mass Spectrom.* 16, 850–859.
887 <https://doi.org/10.1016/j.jasms.2005.01.027>
- 888 Somogyi, Á., Smith, M.A., Vuitton, V., Thissen, R., Komáromi, I., 2012. Chemical ionization
889 in the atmosphere? A model study on negatively charged “exotic” ions generated from
890 Titan's tholins by ultrahigh resolution MS and MS/MS. *Int. J. Mass Spectrom.* 316–318,
891 157–163. <https://doi.org/https://doi.org/10.1016/j.ijms.2012.02.026>
- 892 Somogyi, Á., Thissen, R., Orthous-Daunay, F.-R., Vuitton, V., 2016. The Role of Ultrahigh
893 Resolution Fourier Transform Mass Spectrometry (FT-MS) in Astrobiology-Related
894 Research: Analysis of Meteorites and Tholins. *Int. J. Mol. Sci.*
895 <https://doi.org/10.3390/ijms17040439>
- 896 Stansberry, J.A., Lunine, J.I., Tomasko, M.G., 1989. Upper limits on possible photochemical
897 hazes on Pluto. *Geophys. Res. Lett.* 16, 1221–1224.
898 <https://doi.org/10.1029/GL016i011p01221>
- 899 Stern, S.A., Bagenal, F., Ennico, K.A., Gladstone, G.R., Grundy, W.M., McKinnon, W.B.,
900 Moore, J.M., Olkin, C.B., Spencer, J.R., Weaver, H.A., Young, L.A., Andert, T.,
901 Andrews, J., Banks, M., Bauer, B., Bauman, J., Barnouin, O.S., Bedini, P., Beisser, K.,
902 Beyer, R.A., Bhaskaran, S., Binzel, R.P., Birath, E., Bird, M.K., Bogan, D.J., Bowman,
903 A., Bray, V.J., Brozović, M., Bryan, C., Buckley, M.R., Buie, M.W., Buratti, B.J.,
904 Bushman, S.S., Calloway, A., Carcich, B., Cheng, A.F., Conard, S.J., Conrad, C.A.,
905 Cook, J.C., Cruikshank, D.P., Custodio, O.S., Dalle Ore, C.M., Deboy, C., Dischner,
906 Z.J.B., Dumont, P., Earle, A.M., Elliott, H.A., Ercol, J., Ernst, C.M., Finley, T.,
907 Flanigan, S.H., Fountain, G., Freeze, M.J., Greathouse, T., Green, J.L., Guo, Y., Hahn,
908 M., Hamilton, D.P., Hamilton, S.A., Hanley, J., Harch, A., Hart, H.M., Hersman, C.B.,
909 Hill, A., Hill, M.E., Hinson, D.P., Holdridge, M.E., Horányi, M., Howard, A.D., Howett,
910 C.J.A., Jackman, C., Jacobson, R.A., Jennings, D.E., Kammer, J.A., Kang, H.K.,
911 Kaufmann, D.E., Kollmann, P., Krimigis, S.M., Kusnierkiewicz, D., Lauer, T.R., Lee,

912 J.E., Lindstrom, K.L., Linscott, I.R., Lisse, C.M., Lunsford, A.W., Mallder, V.A.,
913 Martin, N., McComas, D.J., McNutt, R.L., Mehoke, D., Mehoke, T., Melin, E.D.,
914 Mutchler, M., Nelson, D., Nimmo, F., Nunez, J.I., Ocampo, A., Owen, W.M., Paetzold,
915 M., Page, B., Parker, A.H., Parker, J.W., Pelletier, F., Peterson, J., Pinkine, N., Piquette,
916 M., Porter, S.B., Protopapa, S., Redfern, J., Reitsema, H.J., Reuter, D.C., Roberts, J.H.,
917 Robbins, S.J., Rogers, G., Rose, D., Runyon, K.D., Retherford, K.D., Ryschkewitsch,
918 M.G., Schenk, P.M., Schindhelm, E., Sepan, B., Showalter, M.R., Singer, K.N., Soluri,
919 M., Stanbridge, D., Steffl, A.J., Strobel, D.F., Stryk, T., Summers, M.E., Szalay, J.R.,
920 Tapley, M., Taylor, A., Taylor, H.W., Throop, H.B., Tsang, C.C.C., Tyler, G.L.,
921 Umurhan, O.M., Verbiscer, A.J., Versteeg, M.H., Vincent, M., Webbert, R., Weidner, S.,
922 Weigle, G.E., White, O.L., Whittenburg, K., Williams, B.G., Williams, K., Williams, S.,
923 Woods, W.W., Zangari, A.M., Zirnstein, E.J., 2015. The Pluto system: Initial results
924 from its exploration by New Horizons. *Science* (80-). 350.

925 Stern, S.A., Kammer, J.A., Barth, E.L., Singer, K.N., Lauer, T.R., Hofgartner, J.D., Weaver,
926 H.A., Ennico, K.A., Olkin, C.B., Young, L.A., 2017. Evidence for Possible Clouds in
927 Pluto's Present-day Atmosphere. *Astron. J.* 154, 43. [https://doi.org/10.3847/1538-](https://doi.org/10.3847/1538-3881/aa78ec)
928 [3881/aa78ec](https://doi.org/10.3847/1538-3881/aa78ec)

929 Szopa, C., Cernogora, G., Boufendi, L., Correia, J.-J., Coll, P., 2006. PAMPRE: A dusty
930 plasma experiment for Titan's tholins production and study. *Planet. Space Sci.* 54, 394–
931 404. <https://doi.org/https://doi.org/10.1016/j.pss.2005.12.012>

932 Trainer, M.G., Jimenez, J.L., Yung, Y.L., Toon, O.B., Tolbert, M.A., 2012. Nitrogen
933 Incorporation in CH₄-N₂ Photochemical Aerosol Produced by Far Ultraviolet
934 Irradiation. *Astrobiology* 12, 315–326. <https://doi.org/10.1089/ast.2011.0754>

935 Tziotis, D., Hertkorn, N., Schmitt-Kopplin, P., 2011. Kendrick-Analogous Network
936 Visualisation of Ion Cyclotron Resonance Fourier Transform Mass Spectra: Improved
937 Options for the Assignment of Elemental Compositions and the Classification of Organic
938 Molecular Complexity. *Eur. J. Mass Spectrom.* 17, 415–421.
939 <https://doi.org/10.1255/ejms.1135>

940 Vuitton, V., Bonnet, J.-Y., Frisari, M., Thissen, R., Quirico, E., Dutuit, O., Schmitt, B., Le
941 Roy, L., Fray, N., Cottin, H., Sciamma-O'Brien, E., Carrasco, N., Szopa, C., 2010. Very
942 high resolution mass spectrometry of HCN polymers and tholins. *Faraday Discuss.* 147,
943 495–508. <https://doi.org/10.1039/C003758C>

944 Wong, M.L., Fan, S., Gao, P., Liang, M.-C., Shia, R.-L., Yung, Y.L., Kammer, J.A.,
945 Summers, M.E., Gladstone, G.R., Young, L.A., Olkin, C.B., Ennico, K.A., Weaver,
946 H.A., Stern, S.A., 2017. The photochemistry of Pluto's atmosphere as illuminated by
947 New Horizons. *Icarus* 287, 110–115.
948 <https://doi.org/https://doi.org/10.1016/j.icarus.2016.09.028>

949 Wu, Z., Rodgers, R.P., Marshall, A.G., 2004. Two- and Three-Dimensional van Krevelen
950 Diagrams: A Graphical Analysis Complementary to the Kendrick Mass Plot for Sorting
951 Elemental Compositions of Complex Organic Mixtures Based on Ultrahigh-Resolution

952 Broadband Fourier Transform Ion Cyclotron Resonance. *Anal. Chem.* 76, 2511–2516.
953 <https://doi.org/10.1021/ac0355449>

954 Yamashita, M., Fenn, J.B., 1984. Electrospray ion source. Another variation on the free-jet
955 theme. *J. Phys. Chem.* 88, 4451–4459. <https://doi.org/10.1021/j150664a002>

956 Young, L.A., Kammer, J.A., Steffl, A.J., Gladstone, G.R., Summers, M.E., Strobel, D.F.,
957 Hinson, D.P., Stern, S.A., Weaver, H.A., Olkin, C.B., Ennico, K.A., McComas, D.J.,
958 Cheng, A.F., Gao, P., Lavvas, P., Linscott, I.R., Wong, M.L., Yung, Y.L., Cunningham,
959 N., Davis, M., Parker, J.W., Schindhelm, E., Siegmund, O.H.W., Stone, J., Retherford,
960 K.D., Versteeg, M.H., 2018. Structure and composition of Pluto’s atmosphere from the
961 New Horizons solar ultraviolet occultation. *Icarus* 300, 174–199.
962 <https://doi.org/https://doi.org/10.1016/j.icarus.2017.09.006>

963 Young, L.A., Stern, S.A., Weaver, H.A., Bagenal, F., Binzel, R.P., Buratti, B.J., Cheng, A.F.,
964 Cruikshank, D.P., Gladstone, G.R., Grundy, W.M., Hinson, D.P., Horányi, M., Jennings,
965 D.E., Linscott, I.R., McComas, D.J., McKinnon, W.B., McNutt, R.L., Moore, J.M.,
966 Murchie, S., Olkin, C.B., Porco, C.C., Reitsema, H.J., Reuter, D.C., Spencer, J.R., Slater,
967 D.C., Strobel, D.F., Summers, M.E., Tyler, G.L., 2008. New Horizons: Anticipated
968 Scientific Investigations at the Pluto System. *Space Sci. Rev.* 140, 93–127.
969 <https://doi.org/10.1007/s11214-008-9462-9>

970 Zhang, X., Strobel, D.F., Imanaka, H., 2017. Haze heats Pluto’s atmosphere yet explains its
971 cold temperature. *Nature* 551, 352.

972 Zhu, X., Strobel, D.F., Erwin, J.T., 2014. The density and thermal structure of Pluto’s
973 atmosphere and associated escape processes and rates. *Icarus* 228, 301–314.
974 <https://doi.org/https://doi.org/10.1016/j.icarus.2013.10.011>

975