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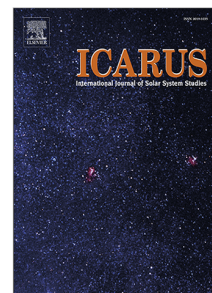
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1 Highlights

2 **On a radiolytic origin of red organics at the surface of the Arrokoth Trans-Neptunian Object**

3 Eric Quirico, Aurore Bacmann, Cédric Wolters, Basile Augé, Laurène Flandinet, Thibault Launois, John F. Cooper, Véronique
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- 7 • The origin of Arrokoth's red surface through methanol ice radiolysis was investigated.
- 8 • Doses and destruction yields of methanol were calculated for Solar and Cosmic-rays ions.
- 9 • Experiments driven by calculations show that abundant red organics materials are synthesized in the first meter
10 of the subsurface.
- 11 • These complex organics are composed of tens of thousands of individual molecules and cover a broad range of
12 weight.
- 13 • A radiolytic origin of Arrokoth's red surface is plausible, provided the lack of major ablation event (e.g. collision
14 in the Kuiper Belt).

On a radiolytic origin of red organics at the surface of the Arrokoth Trans-Neptunian Object

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ABSTRACT

The classical Kuiper Belt Object (KBO) Arrokoth was surveyed by the New Horizons spacecraft on 1st January 2019, revealing a small bilobed object with a red surface, whose spectral slope lies in the average of the whole KBOs population. This red color has been assigned to reddish organic materials, either inherited from the protosolar disk during accretion, or formed through radiolytic processes in the surface due to exposure to solar or interstellar photons, Solar Wind, Solar Energetic Particles or Galactic Cosmic Rays. We report here a study investigating the radiolytic scenario, based on numerical calculations and experimental simulations run with swift heavy ions (74.8 MeV $^{136}\text{Xe}^{19+}$ and 33.06 MeV $^{58}\text{Ni}^{9+}$), and low-energy 105 keV $^{18}\text{O}^{6+}$ ions on CH_3OH ice, the only molecule identified at Arrokoth's surface. Calculations show that sputtering is essentially controlled by Solar Wind (H and He), and that the sputtering rate depends on the nature of the material: erosion thickness over 4.55 Gyr are a few micrometers for amorphous carbon (as an analog of red organics) and a $\sim 240 \mu\text{m}$ to around $\sim 10 \text{mm}$ for H_2O and CO ice, respectively. Chemistry within the subsurface is essentially controlled by Galactic Cosmic rays (H and He), which penetrate deep down to several tens of meters and deliver an electronic dose higher than $1 \text{eV}\cdot\text{atom}^{-1}$ in the first meter. The electronic and elastic doses delivered by Solar Wind ions are limited to the first 10s nm of the top surface, but Solar Energetic Particles deliver high electronic doses in the first 100 μm of the surface (up to 200 $\text{eV}\cdot\text{atom}^{-1}$). Experimental simulations show that irradiating methanol ice with a dose consistent with that in planetary conditions, results in the formation of reddish organic materials made of aliphatic, conjugated and unconjugated olefinic, acetylinic, carbonyl and hydroxyl groups. A similarity with irradiated simple polymers (e.g. polyethyleneglycol) and materials formed through cold plasma experiments (tholins) is observed. There is little dependence with the nature and energy of the ion. The residue recovered at room temperature was analyzed with High Resolution Mass Spectrometry (Orbitrap), revealing a complex composition with around 6596 chemical formulas and likely several tens of thousands of molecules. Altogether, these analyses support active polymerisation mechanisms similar to those observed in irradiated polymers, as bond-breaking, cross-linking or formation of olefinic bonds through recombination of radicals in adjacent carbon atoms. Considering both sputtering and radiolysis, as well as material ablation due to dust bombardment reported in literature, a scenario is taking shape as the production of reddish organics deep in the subsurface, and the settling of an organic crust at the top surface through volatiles removal. The presence of methanol and absence of water, inconsistent with sputtering fractionation, remains unexplained.

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1. Introduction

The Trans-Neptunian Object (TNO) Arrokoth was surveyed by the New Horizons spacecraft on 1st January 2019 (Stern et al., 2019). This small cold classical¹ Kuiper Belt Object (KBO) ~ 33 km across has a bilobed shape, and consists of two rounded icy planetesimals ($r \sim 9.7$ and 7.1 km). Reflectance spectra and spectro-photometric data collected by the LEISA and MVIC components of the Ralph instrument have revealed a reddish surface (Reuter et al., 2008; Grundy et al., 2020), as observed for a large fraction of the whole population of classical KBOs (Cruikshank et al., 2005; Barucci et al., 2005; Doressoundiram et al., 2008; Perna et al., 2010; Brown, 2012; Lacerda et al., 2014). Methanol has been identified, while no other ices were detected. The red material at Arrokoth surface has possibly two origins: (1) a primordial origin, i.e. formed in the proto-solar disk and accreted with the other constituents that form Arrokoth; (2) a radiolytic origin, as the airless Arrokoth is directly exposed to energetic radiations: Solar and interstellar photons, Solar Wind (SW), Solar Energetic Particles (SEPs) and Galactic Cosmic Rays (GCRs). The penetration of UV photons is very shallow (few hundreds of nm), with limited impacts on optical effects. In contrast, ions penetrate deeper in the subsurface, trigger chemistry and sputtering, and several experimental simulations have reported the formation of reddish organic materials from simple ices (Moore et al., 1996; Brunetto et al., 2006; Dartois et al., 2013; Materese et al., 2015; Auge et al., 2016, 2019; Urso et al., 2020b). However, the nature of the organic species formed in these experiments remains poorly known, and the experimental doses are not necessarily in agreement with the actual conditions at the surface and in the subsurface of Arrokoth.

In this study, our objective is to question a radiolytic origin of the red color of Arrokoth through numerical simulations and ion irradiation experiments. We report numerical simulations that estimate the sputtering rate of a surface composed of pure methanol ice, the elastic and electronic doses and the destruction yield of methanol upon depth in the subsurface (section 2). We present in a second step (section 3, 4) the results of ion irradiation of methanol ice that were conducted under conditions that fit with estimates provided by calculations. The organic byproducts were characterized by Visible and IR spectroscopy, and the room temperature residue was investigated by High Resolution Mass Spectrometry (HRMS). These results are finally discussed (section 5) in the general astrophysical context of Arrokoth, leading to the conclusion that reddish materials should be present in Arrokoth conditions through a radiolysis chemistry controlled by GCRs, provided that the first meters of the surface were not removed by dust ablation or collisions within the Kuiper Belt.

2. Energetic particles at Arrokoth's surface

In this section, we provide estimates of (1) the erosion thickness controlled by sputtering and (2) the electronic and nuclear doses deposited versus depth in a methanol putative surface. The electronic and nuclear irradiation doses are a global indicator of the energy made available for chemistry in an irradiated solid, and a simple proxy for comparison with experimental data presented in the next section.

2.1. Sputtering

We first consider the sputtering effect of SW and GCR for species present on a semi-infinite surface. In that case, neglecting radiolysis chemistry during the process, the column density N (molec.cm⁻² or at.cm⁻²) of a molecule or atom sputtered by an ion X with an energy E reads:

$$\frac{dN}{dF} = -Y_X(E) \quad (1)$$

where F is the fluence (ions.cm⁻²) and Y_X (molec.ion⁻¹ or at.ion⁻¹) the sputtering yield. This column density corresponds to the erosion thickness t :

$$t = C \frac{M}{\rho N_a} \Delta t \sum_{i=1}^{92} \int_{E_{min}}^{E_{max}} Y_X^i(E) \left(\frac{dN}{dE} \right)_i dE \quad (2)$$

¹cold classical: small objects on low inclination and low eccentricity orbits, over heliocentric distances between 42 and 47 au.

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where M is the molar mass, Δt the irradiation time, ρ the density, N_a the Avogadro number, i the atomic number of the chemical element, and $\left(\frac{dN}{dE}\right)_i$ the ions differential flux at energy E . The angular dependency of the sputtering yield is neglected and the value at normal incidence is used. The density of crystalline methanol ice $\rho = 1.02 \text{ g.cm}^{-3}$ was taken from Torrie et al. (1989). Our calculations were limited to the most abundant elements H, He, C, N, O, Mg, Si and Fe. In the case of GCR, which is omnidirectional and isotropic, $C=\pi$, resulting from the average over all incidences from 0 to 90° for the co-latitude angle and 0 to 180° for the azimuthal angle.

The case of SW is more complicated and needs assumptions and simplifications. Arrokoth's obliquity is 99° , close to $\pi/2$, which means that the surface is in average uniformly irradiated during half of an orbital period. Therefore, the irradiation time over 4.55 Gyr was taken as 2.225 Gyr. We have assumed that SW is directional and hits a smooth and flat Arrokoth's surface, and only consider the surface perpendicular to the rotation vector. As the angle of the incoming SW with respect to the surface varied between 0 and $\pi/2$, the averaged irradiation flux equals the flux at $\theta=0$ (θ being the incidence angle with respect to the normal vector at the surface) multiplied by the averaged cosine $\cos\theta=2/\pi$. As the flux density is given per steradian, we multiply by π , assuming an isotropic flux density over an hemisphere, which overestimates the actual value. Finally, this leads to $C=2$.

Two SW/SEPs differential fluxes were used. First, we used the He fluence measured at 1 au between 10/97 and 06/00 by Mewaldt et al. (2007), assuming a simple scaling law with the solar abundances of Meyer et al. (1998). The differential flux at 44 au was obtained by applying a $1/44^2$ factor (Fig. 1). This scaling appears consistent with the $\sim 1/R^2$ dependance (R being the heliocentric distance) of the proton density and energy flux (Liu et al., 2021; Adhikari et al., 2015). However, it neglects interstellar pickup ions and cooling of the bulk plasma temperature, which results as a narrowing of the SW peak at $\sim 1 \text{ keV/u}$. In this respect, we used for comparison a differential protons flux modelled from the LECP (Voyager 1 and 2) and PEPSSI (New Horizons) instruments (Fig. 1). The contribution of the slow and fast SW and SEPs ($E > 10 \text{ keV/u}$) are processed as two distinct sources in some publications (Urso et al., 2020a). Here, the differential fluxes used span the range $1 \times 10^{-4} - 30 \text{ MeV/u}$ and include both of them. However, the quiet Sun conditions that prevailed in the period 10/1997 to 06/2000 have been extrapolated to 4.55 Gyr. This assumption does not hold in the first millions of years of the very active young Sun, which could have been 100-1000 times more active in terms of mass loss. Unfortunately, young Sun SW/SEPs fluxes are basically unknown due to the lack of compelling direct detection of stellar wind around solar-type stars, and poorly reliable indirect estimates (Ribas et al., 2005).

The contribution of GCR ions to sputtering was estimated using the differential flux of Webber & Yushak (1983). This differential flux, in $\text{atom.cm}^{-2}.\text{s}^{-1}.\text{sr}^{-1}.\text{(MeV)}^{-1}$, was established for protons in Local Interstellar Medium and is easy to compute using the following parametric equation:

$$\frac{dN}{dE} = \frac{CE^{0.3}}{(E + E_0)^{0.3}} \quad (3)$$

with $C=9.42 \times 10^4$ and E_0 a form parameter related to solar modulation, set to 400 MeV to fit Voyager 1 protons measurements (Stone et al., 2013; Cummings et al., 2016) (Fig. 1). For other chemical elements, a scaling law of the cosmic abundance was applied and the C and the E_0 parameters were tuned to fit Voyager 1 data (Cummings et al., 2016) (Tab. 1). Last, but not least, the GCR flux at 44 au is not similar to that in LISM, due to the heliospheric shielding (Usoskin et al., 2005). Measurements at 40 au are only available for protons (Cooper et al., 2003), therefore sputtering calculations have been run using the LISM differential fluxes to consider separately the contribution of each element, thereby overestimating the erosion thickness.

Arrokoth's surface and subsurface are possibly made of several ices and organic materials, but to date only methanol has been identified by the New Horizons spacecraft (Grundy et al., 2020). In addition, its composition could have evolved along 4.55 Gyr. We therefore focused on three case models for which sputtering yields were available at low energy: (1) CO ice, (2) H₂O ice, as the most and less volatile molecules in the icy component of the surface, and (3) amorphous carbon as a simulant of putative reddish organics dispersed in the surface materials. Note that pure CO ice is not expected to be present at the surface of Arrokoth, due to its surface temperature, and is used here to provide an upper limit of surface sputtering. The case of methanol ice could not be considered, due to the scarcity of sputtering yields available in literature. Amorphous carbons constitute a broad family of disordered solids, which are classified according to their elemental composition (H/C, N/C), sp³/sp² ratio and optical properties (e.g. Tauc or E₀₄ gaps) (Ferrari & Robertson, 2000). As there is a limited number of sputtering yields published to date, we had to

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Table 1

C and E_0 parameters of the Webber and Yushak (1983) parametric equation that fit Voyager 1 data with A_i chemical element abundances.

Element	C	E_0	A_i^1
H	9.42×10^4	400	1
He	5.5×10^5	700	8.14×10^{-2}
C	8.5×10^4	800	1.67×10^{-3}
N	1.3×10^5	850	2.44×10^{-4}
O	1.4×10^5	750	1.57×10^{-3}
Mg	2.0×10^5	600	2.26×10^{-2}
Si	2.0×10^5	600	1.90×10^{-4}
Fe	2.0×10^5	600	1.11×10^{-4}

¹ Cummings et al. (2016)

154 compile data collected on different types of amorphous carbons, and calculate sputtering yields at low energy through
155 Monte-Carlo simulations (SRIM software; <http://www.srim.org/>).

156 **2.1.1. CO ice**

157 The sputtering yield of CO ice Y_{CO} follows a S_e^2 dependence (S_e being the electronic stopping power) for irradiation
158 events dominated by electronic interactions (Brown et al., 1984; Seperuelo Duarte et al., 2010). However, at low
159 energy in the solar wind peak, elastic interactions and cascade recoils significantly contribute to sputtering (Sigmund,
160 1969). Balaji et al. (1995) measured sputtering yields of CO ice irradiated with He^+ , Ne^+ , Ar^+ and Kr^+ ions in the
161 range 1-5 keV. Chrisey et al. (1990) focused on He ions in the range 10-60 keV, and Schou & Pedrys (2001) report
162 sputtering yields of protons in the range 9-60 keV. We observe that in the case of H and He irradiations, dominated
163 by electronic interactions, there is no good match between these studies and values obtained from Brown et al. (1984)
164 and Seperuelo Duarte et al. (2010). Reproducibility is a challenging issue, as sputtering yields are very sensitive to
165 film thickness, surface morphology or sample ageing. Note, for instance, that the data of Chrisey et al. (1990) have
166 been rescaled by Schou & Pedrys (2001), and, here, we have used these rescaled data. H seems a particular case as its
167 sputtering yield seems to follow a $E^{1.3}$ dependency with S_e (Schou & Pedrys, 2001), as observed in the case of H_2O
168 ice by Shi et al. (1995).

169 For our calculations, we have combined the low energy data of Schou & Pedrys (2001) and Balaji et al. (1995) with
170 those from Brown et al. (1984) and Seperuelo Duarte et al. (2010). The sputtering yield value at the high-energy edge of
171 the low-energy data of Schou & Pedrys (2001) and Balaji et al. (1995) was extrapolated at higher energy until it meets
172 the sputtering yield of Seperuelo Duarte et al. (2010). This extrapolation certainly results in an overestimation of the
173 actual sputtering yield in this energy range. In the case of protons, no data exist in the SW energy range, we therefore
174 extrapolated the low energy values of Schou & Pedrys (2001) towards low and high energy, resulting once again in an
175 overestimation of the role of protons. Finally, for estimating the erosion thickness of the C, N, O, Mg, Si and Fe ions,
176 we made the following approximations: $Y_{CO}[C] \approx Y_{CO}[N] \approx Y_{CO}[O] \approx Y_{CO}[Ne]$; $Y_{CO}[Mg] \approx Y_{CO}[Si] \approx Y_{CO}[Ar]$; and
177 $Y_{CO}[Fe] \approx Y_{CO}[Kr]$.

178 Results on SW erosion are tabulated in Table 2. We first observe that the erosion thicknesses calculated with the
179 modelled SW/SEPs flux distribution are lower by around a factor of ten compared to the differential flux extrapolated
180 from the measurements of Mewaldt et al. (2007). We hereafter focus on the results obtained with the modelled
181 differential flux. The most contributing ion to erosion thickness is H (6 mm), followed by O, He and Fe, and the total
182 erosion thickness is ~ 10 mm. This upper limit value is significant, but it is unlikely it was achieved in real conditions.
183 First because CO molecules were likely mixed up with other polar species, lowering their sublimation temperature
184 and thereby their sputtering yield, and second because we have severely overestimated H sputtering yields. For GCR
185 surface erosion, calculations run for H, He and Fe provide erosion thicknesses of 6.8×10^{-3} , 6.9×10^{-3} and $0.55 \mu m$,
186 respectively, for an irradiation time of 4.55×10^9 yr. The actual values are lower, because the GCR density flux is
187 expected lower at 44 au (Cooper et al., 2003). In any case they are very weak, and by far the contribution of GCR to
188 surface sputtering is negligible with respect to SW/SEPs.

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Table 2
Solar Wind erosion thickness of CO, H₂O and a-C surfaces at 44 au over 4.55 Gyr

	Thickness (μm)		H ₂ O ice		a-C	
	CO ice		Mewaldt @ 1au/44 ²	Model	Mewaldt @ 1au/44 ²	Model
H	54889	6216	1400	168	16.1	1.9
He	11712	1261	254	29	9.3	1.1
C	6536	758	85	0.9	0.9	0.10
N	299	35	5	0.5	0.02	0.002
O	8105	939	142	14	0.7	0.09
Mg	1894	222	24	2.6	0.6	0.06
Si	1824	214	22	2.4	0.6	0.07
Fe	3412	402	126	12	0.8	0.1
Total	88671	10047	2058	237	29.0	3.35

¹Using SW/SEPs differential flux from Mewaldt et al. (2007) at 1 au rescaled at 44 au by applying a factor 1/44². ²Using SW/SEPs differential flux estimated from modelling (see Text).

2.1.2. H₂O ice

The sputtering yield of water ice at $E < 50$ keV/u was calculated with the parametric equation of Fama et al. (2008), and at higher energies the sputtering yields of Brown et al. (1984) and Dartois et al. (2015) were used (Fig. 2). There is no good match between the two sets of data, except for H (which is unexpected due the non quadratic dependence with Se). Calculations show that the erosion thickness is 237 μm , and that H is the most contributing ion (168 μm).

2.1.3. Amorphous carbon

In the low energy range, the sputtering yields of amorphous carbon (C atom.ion⁻¹) have been estimated with the SRIM software for the H, He, C, N, O, Mg, Si, Fe elements at 0.5, 1, 5, 10, 50, 10 and 500 keV. The sputtering yield of each ion was then set to the highest of these values, and assumed to be constant up to high energies dominated by electronic interactions. Calculations were run for a H/C=0.5 carbon material, $\rho = 1.5$ g.cm⁻³, displacement energy 5 eV, lattice binding energy 1 eV and surface binding energy 4 eV (values for sp³-rich amorphous carbons, see Ullmann et al. (1993); Vukovic et al. (2018)). SRIM simulations provide values consistent within a factor of 2 with experimental measurements for a tetrahedral amorphous carbon (ta-C) irradiated with 50 keV Ga ions (Stanishevsky, 2001). At higher energies, experimental measurements are available, but display huge variabilities from a few tens to several 10⁶ of C atom.ion⁻¹ (Assmann et al., 1996; Behrisch et al., 1996; Boutard et al., 1989; Dollinger et al., 1996; Ghosh et al., 2002; Khan et al., 2013; Pawlak et al., 1999). H-bearing amorphous carbons seem to have a much higher sputtering yield than pure amorphous carbons, and we have selected the data from Pawlak et al. (1999) on a polymeric hydrogenated amorphous carbon (polymeric a-C:H). This kind of amorphous carbon resembles to the methanol ice residue produced in this study (see below), except for the presence of oxygen. The fit of Pawlak et al. (1999) data leads to $Y = -1303 + 1759S_e$ (S_e in keV.nm⁻¹), which is different from the quadratic dependance observed for ices (for He and heavier ions). Note that irradiation leads to chemical fractionation and structural evolution of the film, and a decrease of sputtering yield over irradiation time. With all this in mind, the upper value of the erosion thickness is 3.35 μm , around 2 order of magnitudes lower than water ice.

2.2. Electronic and nuclear doses

The electronic and nuclear doses (eV.atom⁻¹) deposited in the subsurface at a depth of z can be written as:

$$D_{e,n}^i(z) = C \frac{M}{6\rho N_a} \Delta t \sum_{j=0}^{89} \sum_{i=1}^{92} \int_{E_{min}}^{E_{max}} S_{e,n}^i(z, E) \times A_i \frac{dN}{dE}(d_j, E) dE \quad (4)$$

with z the vertical depth in the surface, d_j the distance between the ion entry point and the point at z where the dose is calculated (the ion incidence angle is $\theta_j = \arccos(z/d_j) = j\pi/180$ and $j \in [0; 89]$), M the molar mass, ρ

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216 the density of methanol ice, N_a the Avogadro number, dN/dE the differential flux (SW or GCR), E_{min} and E_{max} the
 217 edges of the energy range, A_i the solar or LISM abundance of the i^{th} chemical element and Δt the irradiation duration
 218 (4.55 Gyr for GCR, 2.225 Gyr for SW). $C=2$ or π for SW and GCR, respectively. Power law grids were used for the
 219 depth and energy ranges, as $z_i = z_{min}(z_{max}/z_{min})^{i/N}$ ($z_{min}:z_{max}=10^{-4} : 60 \times 10^3$ mm, GCR; $=10^{-5}:5$ mm, SW) and
 220 $E_i = E_{min}(E_{max}/E_{min})^{i/N}$ ($E_{min}:E_{max}=10^{-2}:10^4$ MeV/u, GCR; $=3 \times 10^{-4}:30$ MeV/u, SW). The stopping powers S_e^i
 221 and S_n^i were calculated with the SRIM software for pure methanol ice, and the numerical code was computed with
 222 the software Igor Pro 8.04 (Wavemetrics). We have used the same differential fluxes and chemical elements that were
 223 used for sputtering calculations. **Note the dose is given in eV/atom, i.e. we have calculated the dose for one methanol**
 224 **molecule, and divided it by 6.**

225 The results are displayed in Figure 3 for Galactic Cosmic rays. Using the LISM differential flux, the total dose is
 226 > 10 eV.atom $^{-1}$ until 1 m, and is in the range 1-10 eV.atom $^{-1}$ until 10 m. The main contributors are H and He for
 227 $z < 1$ m, and these two ions are the only ones penetrating above 1 m. At 40 au, we have run a calculation for protons
 228 using the differential flux of Cooper et al. (2003) (Fig. 3). The LISM electronic dose is 4.9-6.3 times larger than that
 229 at 40 au in the first 100 mm, and progressively reaches the 40 au values when increasing depth. We then infer that the
 230 actual total dose at 40 au lies around 10 eV.atom $^{-1}$ in the first 10 mm, is higher than 1 eV.atom $^{-1}$ in the first meter,
 231 and drops above. These calculations also show that the nuclear dose remains below 0.2 eV.atom $^{-1}$. It is worth noting
 232 that the penetration of GCR is much higher than the sputtering thickness **controlled by SW/SEPs (237 μ m for water**
 233 **ice and 3.35 μ m for a-C).**

234 In the case of SW and SEPs, sputtering and dose deposition upon depth need to be computed simultaneously,
 235 because the implantation depth is smaller than the erosion thickness. A time-resolved simulation was run over 2.25
 236 Gyr with an incremental time of 222500 years (Fig. 4). For protons, calculations show that the layer that receives a $>$
 237 10 eV.atom $^{-1}$ nuclear dose is around 30 nm thick. This dose of 10 eV.atom $^{-1}$ is the critical nuclear dose above which
 238 a carbonaceous material transforms into an amorphous carbon (Faure et al., 2021) for details. However, the electronic
 239 dose lies between 10 and 200 eV/atom in the first 100 μ m, which are very high values.

240 3. Experimental methods

241 Experiments were conducted at Grand Accélérateur National d'Ions Lourds (GANIL, Caen, France) on the
 242 IRRSUD and ARIBE beamlines with the IGLIAS setup (Tab. 3; see Auge et al. (2018) for a detailed description).
 243 Infrared spectra were collected with a Bruker Vertex 70v FTIR spectrometer, operating with a MCT-detector and a **4**
 244 **cm $^{-1}$ and 1 cm $^{-1}$ spectral resolution, for E1 and (E2, E3, E4), respectively.** The angle between the spectrometer beam
 245 and the sample surface was **78 °**. Thin films were deposited at normal incidence with a needle placed at around 15 mm
 246 from a MgF $_2$ or a ZnS window. The deposition rate was adjusted to get a good optical quality, and sample thickness
 247 was estimated using the band strengths of Bouilloud et al. (2015). The gaseous species sputtered in the chamber were
 248 detected with a MKS Microvision 2 quadrupole mass-spectrometer (QMS). IGLIAS is also equipped with a Perkin
 249 Elmer Lambda 650 VUV spectrometer, but the rapid degradation of the optical quality of the sample upon irradiation
 250 led to significant scattering that blurred the absorption signal.

251 High Resolution Mass Spectrometry analysis of the final organic residue was performed with an LTQ Orbitrap
 252 XL TM mass spectrometer (Thermo Scientific, Bremen, Germany). This instrument is a hybrid mass spectrometer
 253 that uses an ion trap connected to an Orbitrap cell. The ion production was done with an IonMax TM electrospray (ESI)
 254 source, which consists in a soft ionization achieved by protonation or deprotonation, respectively $[M+H]^+$ or $[M-H]^-$
 255 . All analyses were performed at the maximum instrument resolution (100000 at $m/z = 400$) for a mass accuracy of
 256 ± 2 ppm) using an Automatic Gain Control (AGC) set to 500000 ions storage. For accurate mass calibration, we used
 257 the commercial default LTQ-Orbitrap-XL instrument calibration mixture made of caffeine, Met-Arg-Phe-Ala peptide
 258 (MRFA), and Ultramark 1621 (a mixture of fluorinated phosphazine polymers) in positive mode, and a mixture of
 259 sodium dodecyl sulfate, sodium taurocholate and ultramark 1621 for negative mode.

260 Measurements were run with the following ESI source parameters, in positive and negative mode, respectively: 3.5
 261 and -3.5 kV, Sheath gas at 3 and 10 (arb), capillary temperature at 275 °C and tension on the transfer tube at 40 and
 262 -35 V. Each measurements consisted of 3 scans of 256 microscans. The detailed description of the whole procedure
 263 can be found in Wolters et al. (2020).

264 The organic residue recovered at room temperature was solubilized through five washing with 250 μ L of methanol
 265 (Carlo Erba, UPLC/MS grade) into a petri dish. The solution inside the petri-dish was transferred into a glass vial, and
 266 the petri-dish was washed again by adding 100 μ L of methanol. This fraction was added to the previously recovered

267 solution in the glass vial. A procedural blank was made by washing the cleaned petri-dish with 2 x 250 μL of methanol
 268 and placed into a glass vial. Finally, the optical absorption of this solution was measured in the range 200-800 nm with
 269 a JASCO VUV V-730 spectrometer, and then analyzed by HRMS. Methanol was purchased from Sigma Aldrich (high
 270 purity, HPLC grade) and deuterated methanol was purchased from Eurisotop (purity 99.80 %).

271 4. Experimental results

272 We report a series of experiments on methanol ice run with different ions at different energies (Tab. 3). One
 273 experiment was run on deuterated methanol to easier the identification of simple by-products.

274 4.1. CH_3OH - $^{136}\text{Xe}^{19+}$ at 0.55 MeV/u

275 4.1.1. Spectroscopic monitoring

276 A CH_3OH film was deposited at 10 K and irradiated at normal incidence with 0.55 MeV/u $^{136}\text{Xe}^{19+}$ ions ($E=74.8$
 277 MeV) (Fig. 5). At this temperature, solid methanol is amorphous and its density is sensitive to the deposition conditions
 278 (growing rate, beam collimation, angle with respect to the substrate). Luna et al. (2018) report a value of $0.664 \text{ g}\cdot\text{cm}^{-3}$
 279 for methanol ice deposited at 10 K and $0.636 \text{ g}\cdot\text{cm}^{-3}$ at 20 K, while Hudson et al. (2020) report $0.779 \text{ g}\cdot\text{cm}^{-3}$ at 15 K.
 280 These studies also report different values for crystalline methanol ice: 1.02 against 0.795 at 120 K, for Hudson et al.
 281 (2020) and Luna et al. (2018), respectively. The value of Hudson et al. (2020) is similar to the value determined by
 282 neutron diffraction (Torrie et al., 1989), which would mean that perfectly stacked monocrystalline solids were formed.
 283 However, this is unrealistic and the value of Luna et al. (2018) is more consistent with polycrystalline films hosting a
 284 significant porosity due to voids at grains boundary. Finally, regarding that amorphous films display a range of porosity,
 285 depending on experimental conditions, we used an average of both studies as $0.71 \pm 0.072 \text{ g}\cdot\text{cm}^{-3}$ for calculating the
 286 doses deposited in the sample.

287 The maximum fluence was $8 \times 10^{12} \text{ cm}^{-2}$, corresponding to an electronic dose $D_e=5.9 \text{ eV}\cdot\text{atom}^{-1}$. The column
 288 density and thickness of the film were estimated using the infrared integrated cross-section of the C-O band determined
 289 by Bouilloud et al. (2015) (integrated between 986 and 1070 cm^{-1}) (Tab. 3). The sputtered methanol thickness achieved
 290 for the maximum fluence of $8 \times 10^{12} \text{ cm}^{-2}$ was estimated to be 0.03-0.06 μm (against 10.8 μm for the initial thickness of
 291 the film), using the sputtering yield of Dartois et al. (2019) rescaled to the electronic stopping power of our experiment
 292 (assuming a quadratic dependence with the electronic stopping power). As a result, the radiolytic process mostly
 293 controls the decrease of the methanol ice film and there is no need to model sputtering. For the CO most volatile
 294 by-product, an estimate of the upper value of sputtered thickness lies around 0.4 μm , using the sputtering yield of pure
 295 CO ice from Seperuelo Duarte et al. (2010). The experiment was conducted in two steps: (1) the study of the film
 296 and the gaseous by-products during irradiation, until the maximum fluence of $8 \times 10^{12} \text{ ions}\cdot\text{cm}^{-2}$; (2) and during a
 297 Thermally Programmed Desorption (TPD) using a thermal ramp of $0.05 \text{ K}\cdot\text{min}^{-1}$.

298 The spectra of the film during irradiation are displayed in Fig. 5. CO, CO_2 , CH_4 and H_2CO are detected as the
 299 main simple by-products, consistently with previous studies (Moore et al., 1996; Brunetto et al., 2006). These species
 300 were also detected in the gas phase by the QMS spectrometer, plus H_2 and H_2O . H_2 is also a well known by-product
 301 that points to sample dehydrogenation. H_2O results from methanol radiolysis according to experiments run on CD_3OD
 302 (see below), however, a fraction could be due to contamination from the residual gas in the chamber. The infrared
 303 bands of the CH_3OH molecule decrease and broaden with increasing fluence, and above an electronic dose of 1.45
 304 $\text{eV}\cdot\text{at}^{-1}$, two broad congested organic bands arise between 1700 and 1300 cm^{-1} . At the maximum fluence, the spectrum
 305 of the film displays a slope and an asymmetry in the edges of the large 3500-3000 cm^{-1} OH band (Fig. 6), which
 306 points to significant scattering. Accordingly, we have considered that VUV absorption measurements collected during
 307 irradiation were blurred by significant and unquantified scattering.

308 During the TPD sequence, the film was progressively stripped from volatile species, until the formation of a
 309 refractory reddish organic residue at room temperature (Fig. 6). CO starts sublimating around 25 K and a large fraction
 310 is expelled from the film before 65 K. However, a few CO molecules remain until 130 K, pointing to CO binding
 311 interactions with polar hydroxyl groups (Kouchi, 1990). CH_4 and H_2CO are fully sublimated at 130 K, while CO_2
 312 fully vanishes around 150 K. The organic bands in the region 1800-1200 cm^{-1} are almost unchanged below 130 K,
 313 and then progressively decrease until room temperature by a factor ranging from 2 to 6.5 (Fig. 6). Between 175 and
 314 210 K, the shape of the OH band changes and displays 3 components that point to the presence of crystalline water
 315 ice, and the lack of C-O band around 1000 cm^{-1} shows that all CH_3OH has gone. These observations are confirmed
 316 by QMS measurements, which show, in addition, that methanol essentially sublimates between 125 and 155 K, H_2O

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Table 3
Irradiation experiments parameters.

Experiment	T	Ion	E	F max	D _e max	S _e	D _n max	S _n	t	N	PR
	K		MeV	ions.cm ⁻²	eV.atom ⁻¹	keV. μm ⁻¹	eV.atom ⁻¹	keV. μm ⁻¹	nm	mol.cm ⁻²	nm
E ₁ CH ₃ OH	10	¹³⁶ Xe ¹⁹⁺	74.8	8 × 10 ¹²	5.9	5934	0.047	49.5	10872	1.43 × 10 ¹⁹	25875
E ₂ CD ₃ OD	10	⁵⁸ Ni ⁹⁺	33.1	1 × 10 ¹³	4.4	3574	0.016	12.5	1270	1.70 × 10 ¹⁸	21630
E ₃ CH ₃ OH	40	¹⁸ O ⁶⁺	0.105	1.38 × 10 ¹⁵	16.1	132	5.7	46.3	898	1.20 × 10 ¹⁸	520
E ₄ CH ₃ OH											
layer 1	40	¹⁸ O ⁶⁺	0.105	6.12 × 10 ¹⁴	10.1	132	3.54	46.3	1512	2.00 × 10 ¹⁸	
layer 2			0.105	1.57 × 10 ¹⁵	25.9		9.07		1488		
layer 3			0.105	1.65 × 10 ¹⁵	27.2		9.53		1335		
layer 4			0.105	1.70 × 10 ¹⁵	28.0		9.82		1276		

T: temperature. E: total energy of the ion. F max: maximum fluence. D_e max: maximum electronic dose. S_e: electronic stopping power. D_n: maximum nuclear dose. S_n: nuclear stopping power. t: thickness. N: CH₃OH column density. PR: projected range (penetration depth of the ion). The relative uncertainty on thickness and column density is estimated to 10 %. S_e and S_n were calculated with SRIM for a density of 0.71 g.cm⁻³ for CH₃OH, and 0.80 g.cm⁻³ for CD₃OD. **Note that for E1, there is a factor of 2 between the dose at the entry and exit of the sample, and the dose indicated in the table is therefore the dose accumulated in the uppermost layers of the sample. For experiments E3 and E4, the thickness is > PR, and ions implant into the sample. To optimize the thickness of the final irradiation residue, the sample was deposited in 4 steps, each consisting in depositing a layer followed by irradiation. Due to sputtering and to avoid further irradiation of the underlying film, the thickness of each film was larger than PR.**

317 between 155 and 210 K, and that H₂CO has a narrow sublimation surge around 30 K (See Appendix B). Above 210
318 K, no peaks with significant intensity were detected, all ices have vanished and the infrared spectra are dominated by
319 organic materials (Fig 7). Their spectra display:

- 320 (i) a broad feature between 2900 and 3600 cm⁻¹, due to the OH chemical group (B_{OH});
- 321 (ii) an aliphatic band between 2800 and 3000 cm⁻¹ with peaks at 2958, 2933 and 2879 cm⁻¹, due to the symmetric
322 and anti-symmetric stretching modes of CH₃ and CH₂ modes, the C-H stretching mode and complex vibrational
323 interactions including Fermi resonance with the overtones of bending modes (MacPhail et al., 1984) (B_{CH_x}^s);
- 324 (iii) an asymmetric broad band between 1800 and 1500 cm⁻¹ (B_{C=O,C}), which comprises the stretching modes of
325 C=O and C=C;
- 326 (iv) a broad band between 1500 and 1300 cm⁻¹ (B_{CH_x}^b), resulting from different vibration modes of CH_x groups,
327 including bending.

328 We observe a global drop of band intensities when increasing temperature, i.e. a broad range of volatilities and
329 of molecular weight. In spectra normalized at 1700 cm⁻¹, B_{OH}, B_{CH_x}^s and B_{CH_x}^b drop with increasing temperature,
330 showing a decrease of the H/C and O/C elemental ratio, and thereby an increase of unsaturation. By the way, this
331 confirms that B_{CH_x}^b is essentially controlled by CH_x groups. The B_{C=O,C} band is a very congested feature. It is
332 controlled by the stretching modes of the carbonyl (C=O) and olefinic (C=C) chemical groups (Fig. 8). The C=O
333 stretching component lies between 1670 and 1800 cm⁻¹ and that of C=C between 1670 and 1600 cm⁻¹ (Lin-Vien,
334 1991). Unconjugated C=C bonds, which do not lead to π-π* transitions in the visible (no colouring effect), lie between
335 1650-1670 cm⁻¹. C=C bonds conjugated with C=O lie between 1650 and 1600 cm⁻¹, and C=C/C=C conjugation lie
336 in the range 1640-1600 cm⁻¹. C=C conjugation also leads to a splitting of the stretching mode into symmetric and anti-
337 symmetric components. Figure 8 shows a tentative spectral decomposition of the spectrum of the refractory residue.
338 Regarding the lack of constraints on the actual number and position of the components, other solutions are possible
339 and no unambiguous spectral decomposition can be achieved. Complicating the picture, the band strength of olefinic
340 bonds or aromatic C=C are very sensitive to the molecular environment, in particular to the C=O group that has a
341 strong dipolar moment (Painter et al., 1981).

342 The composition of the film after irradiation was estimated using the integrated absorption cross-sections from
343 Bouilloud et al. (2015). The following column densities were found: N_{CO₂} = 1.59 × 10¹⁷; N_{CO} = 2.10 × 10¹⁸; N_{CH₃OH} =

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344 2.68×10^{18} ; $N_{CH_4} = 3.20 \times 10^{17}$; $N_{H_2CO} = 7.49 \times 10^{17}$ molec.cm⁻². The column density of CH₂+CH₃ groups was
 345 calculated using the band strengths of the antisymmetric stretching bands (Dartois et al., 2007), and was found to be 4.1
 346 $\times 10^{17}$ molec.cm⁻² for the spectra collected at 210 K during the TPD. The fraction of alkyl groups that sublimated
 347 below 210 K cannot be directly estimated because they are blurred by other bands, in particular the broad OH band. As
 348 a consequence, it was roughly estimated through the intensity of the ($B_{CH_x}^b$) band, which decreases by a factor of 2.7
 349 between 40 and 210 K. Using the initial column density of CH₃OH $N_{CH_3OH} = 1.43 \times 10^{19}$ molec.cm⁻², we estimate
 350 these species account for 50% of the starting carbon atoms, and CH₂+CH₃ groups represent 18% of these detected
 351 carbon atoms. However, we have not estimated the contribution of carbonyl and olefinic groups, due to the strong
 352 spectral congestion. In addition, aliphatic CH and non-protonated C have not been estimated. We then only estimate
 353 a lower value of ~ 10% for initial carbon atoms incorporated in organic molecules. Beside the lack of detection of
 354 olefinic, carbonyl, non-protonated and C-H aliphatics, some small volatile species may have been undetected by FTIR
 355 (due to the lack of IR active vibrations) and by QMS data, due to a lack of precision in peak intensities and reference
 356 spectra. Another explanation is the quite large uncertainty on band strengths. Usually a relative error of 30% is given,
 357 but they can also be blurred by systematic errors (e.g. lack of knowledge about density). Last, spectral congestion and
 358 baseline correction are always an issue, and can lead to very significant systematic errors (i.e. H₂CO).

359 The residue recovered at room temperature was dissolved in methanol for analysis by VUV absorption spectroscopy
 360 (Fig. 9). The transmission spectrum of the solution shows an absorption continuum from the UV to ~ 500 nm, consistent
 361 with the reddish colour observed by the naked eye. This information is semi-quantitative, as the nature of the species
 362 and their concentrations are unknown in the detail.

363 4.1.2. Molecular complexity of room-T residues

364 Mass spectra of the residue solubilized in methanol were collected along the procedure described in section 3. These
 365 spectra are complex in terms of peak numbers (several thousands). We have used here a homemade software developed
 366 at IPAG with the IGOR Pro software (Wavemetrics) (Orthous-Daunay et al., 2019). The data description was achieved
 367 in three successive steps: (1) the description of the mass spectrum, (2) the analysis of the apparent diversity and (3)
 368 the description of the attributed stoichiometric formulas. A mass spectrum contains much information simply derived
 369 from the mass and intensity of the peaks, such as intensity patterns and profiles, or systematic mass differences. Once
 370 the general data structure has been described, the stoichiometric diversity is analyzed through dedicated mathematical
 371 processing, which are allowed by the high precision and mass resolution of the Orbitrap spectrometer. Several data
 372 representations, based on all the attributed formulas, can eventually be used for comparison to reference samples.

373 Fig. 10 displays the mass spectrum of the sample collected in ESI positive mode between 150 and 800 Da. The
 374 intensity profile, with a maximum intensity around 320 Da, shares similarities with those of N-rich tholins acquired
 375 in similar analytical conditions (Vuitton et al., 2021; Moran et al., 2020; Maillard et al., 2018; Jovanovic et al., 2020).
 376 However, the intensity profile decreases more slowly, with less than one decade of intensity between 320 and 800 Da.
 377 Repetitive intensity patterns are observed in the spectrum, similarly to the abovementioned tholins. They are usually
 378 described as a signature of polymerization, the mass difference between two consecutive maxima being an averaged
 379 value of several monomers. Here, the value of 14.016 Da shows that the polymerization growth is dominated by the
 380 addition of CH₂ molecular groups. Similar observations can be achieved from the ESI negative mode mass spectrum.

381 A standardized process was used to assign a unique molecular formula to ions peaks over the entire mass range
 382 ($m/z=150-800$ Da) (Vuitton et al., 2021). A unique formula is first assigned to a peak at low mass, and peaks at
 383 heavier mass are then identified through the addition of CH₂ (alkylation) or other building groups (C, O, NH). Overall,
 384 the nature of the building blocks appear in a Mass defect-versus-Mass (MDvM) diagram, where the mass defect is
 385 the difference between the exact mass and the closest nominal mass (Fig. 11). The MDvM plot allows direct visual
 386 recognition of point alignments representing monomers that separate repetitive molecular groups. Trends due to CH₂,
 387 O and H₂ groups are displayed in Figure 11.

388 The full assignment led to 6596 exact stoichiometric formulae, which represents several tens or hundred thousands
 389 of individual compounds due to the large number of isomers for each mass. The unsaturation was estimated through
 390 the double-bound equivalents (DBE), defined as the number of rings plus the number of double and triple bonds in a
 391 neutral molecule. It was calculated from each stoichiometric formula $C_cH_hO_oN_n$ as:

$$DBE(C_cH_hO_oN_n) = c - \frac{h}{2} + \frac{n}{2} + 1 \quad (5)$$

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Even if oxygen is known to create double bounds like in ketones or carboxylic acids, it does not control unsaturation (as the number of double bonds and rings, and a triple bond corresponding to 2 double bonds). As our sample is essentially made of C, H and O atoms, unsaturation is only achieved by carbon and hydrogen. Figure 12 displays two representations of stoichiometric diversity of the residue. On the left, O/C value is plotted against mass for varying number of oxygen atoms. For a given oxygen value, data points appear as a hyperbolic distribution, consistent with other sample analyses (Maillard et al., 2018; Moran et al., 2020). This representation is a way to assess the attribution quality, as any misattribution will appear on the wrong hyperbolic line. This diagram also shows that the radiolytic process populates all oxygen levels. Hence, we are not only observing O₁-bearing molecules that could refer to alcohol, phenol, or epoxy chemical functions, or O₂-bearing molecules that could refer to carboxylic acids, but a broad diversity of molecular structures that contain several oxygenated groups. This points to the complexity of the compounds and the lack of selectivity of the radiolytic chemical process. Figure 12 also reports the DBE value plotted against mass peak. As expected, the DBE values are not very high, as they are controlled only by carbon and hydrogen. In the case of N-rich tholins, the DBE distributions show values up to 40 due to the ability of nitrogen to promote unsaturation (Maillard et al., 2018). At a given number of oxygens, almost all DBE values are observed, indicating that the polymerisation process responsible for the unsaturation is weakly or not sensitive to the oxygen functionality. Note however that, due to the analytical technique, especially using the electrospray source as ionisation method, we are only sensitive to polar molecules. This means that this study does not investigate pure hydrocarbon diversity, i.e. when the number of oxygen is equal to zero.

Finally, the elemental ratio of the polar fraction of the residue were calculated from both ESI positive and negative modes by using the stoichiometric composition of mass peaks ponderated by peak intensities. We found H/C=1.50 ± 0.08 and O/C=0.4 ± 0.02. These estimates must be considered with care, because the ionisation yield is controlled by the molecular structure, which must promote protons exchange with the solvent.

4.2. CD₃OD - ⁵⁸Ni⁹⁺ at 33.1 MeV

The irradiation of CD₃OD with ⁵⁸Ni⁹⁺ ions resulted in the production of similar simple by-products as CO, CO₂ and D₂CO and HDCO, detected by FTIR spectroscopy and MS/QMS (Fig. 13). CD₄ could not be detected because the position of its bands was coincident with broad features of methanol. Interestingly, we observed the formation of D₂O molecules, demonstrating that water is also a by-product of methanol irradiation. This confirms that the water signatures in the infrared spectra collected during the TPD sequence are not controlled by contamination from the residual vacuum in the chamber.

We have estimated the band strengths of several vibration modes of pure CD₃OD from experiments run at IPAG at 20 K, using a He-Ne laser for determining the film thickness (Appendix A). We then determined the radiolytic destruction cross-section of deuterated methanol, by fitting the first derivative of the column density with the following relationship:

$$-\frac{dN}{dF} = \sigma_d N + Y \quad (6)$$

The fit led to $\sigma_d = (1.5 \pm 0.6) \times 10^{-13} \text{ cm}^2 \cdot \text{ion}^{-1}$. We have compared this value to the data of de Barros et al. (2011) and Dartois et al. (2019) (Fig. 14). The reanalysis of earlier data by Dartois et al. (2019) led to a destruction cross-section of methanol of $(4.14 \pm 2.0) \times 10^{-17} S_e^{1.11 \pm 0.11}$. However, one cross-section from de Barros et al. (2011) was not reported correctly, and the error estimated by these authors ($\pm 5\%$) was clearly underestimated. We run again this fit with more realistic errors ($\pm 25\%$) and got $\sigma_d = (5.5 \pm 3.0) \times 10^{-17} S_e^{1.06 \pm 0.08}$. The destruction cross-section derived for CD₃OD in this study lies at the edge of the 95% confidence area, and is consistent with CH₃OH data. As it is based on the destruction of the C-O bond, the effect of D atoms appears weak or negligible.

4.3. CH₃OH - ¹⁸O⁶⁺ at 105 keV

The conditions of CH₃OH ice irradiation with low energy ¹⁸O⁶⁺ ions are different from the two previous experiments run with swift heavy ions. The penetration depth is lower than the thickness of the film, ions eventually implant and the deposited dose varies upon depth. Moreover, there is a significant contribution of elastic interactions (See S_n versus S_e in Tab. 3). Even though those conditions are different, we observe qualitatively a similar evolution of methanol ice: formation of CO, CO₂, H₂CO and CH₄ as simple byproducts, and similar bands assigned to organics (C=O, C=C, CH_x groups) (Fig. 13). After the sublimation of ices, a residue was recovered at room temperature, which

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439 shares similarities with those recovered in experiment E₁. In details, we observe slight differences in the shape of the
 440 B_{C=O,C} band that ranges from 1500 to 1800 cm⁻¹. This experiment shows that, at least qualitatively, the final organic
 441 material does not depend significantly on the ion energy over 4 orders of magnitudes. The same mechanisms seem to
 442 be at play, which is consistent with observations on simple polymers that do not contain aromatic species (Faure et al.,
 443 2021). Interestingly, the presence of elastic interactions does not modify the main composition of the organics.

444 5. Discussion

445 5.1. Organic by-products: chemical routes and composition

446 Our experiments show that complex organics are formed from pure methanol ice for electronic doses consistent
 447 with those at Arrokoth surface, down to 1 m deep. These complex organics are a mixture of molecules spanning a broad
 448 range of weight, from a few to several hundred C atoms. The most refractory fraction recovered at room temperature is
 449 essentially soluble in polar solvents. The similarity of the infrared features in the region 1800-1200 cm⁻¹ across 40-300
 450 K points to a continuum, i.e. species bearing similar chemical groups as OH, CH, CH₂, CH₃, olefinic C=C and, in
 451 weaker abundance, C≡C. The molecular complexity is high, with 6596 molecular formulas and several hundred of
 452 thousands of molecules. The formation mechanisms includes bond breaking, radical recombination and sputtering of
 453 atoms and molecules in the gas phase. The large H₂ signal in the QMS spectra reveals a large dehydrogenation, turning
 454 the initial H/C ratio from 4 to 1.5 in the refractory residue collected at room temperature. The formation of olefinic and
 455 acetylinic bonds results from the recombination of adjacent carbon radicals (Balanzat et al., 1995; Steckenreiter et al.,
 456 1999; Severin et al., 2010). Interestingly, the chemical evolution of methanol ice shares similarities with the irradiation
 457 of simple oxygenated polymers, e.g. poly-ethylene-glycol (PEG) (Faure et al., 2021). The infrared spectra of irradiated
 458 PEG display similar features in the range 1800-1200 cm⁻¹, CO and CO₂ as simple by-product, and overall the spectral
 459 evolution looks similar between the two materials. Noteworthy is the abundance of OH groups, very weak or negligible
 460 in irradiated PEG compared to irradiated methanol. A large fraction of the initial hydroxyl groups in methanol are then
 461 preserved during the irradiation of methanol ice. The profile of the band B_{CH_x}^s points to a significant proportion of
 462 methylene versus methyl groups (n_{CH₂}/n_{CH₃} around 1 at 210 K and 0.83 at 300 K), which supports short alkyl chains
 463 and significant cross-linking.

464 Irradiated methanol also shares similarities with organic solids produced from cold plasma vapor deposition (e.g.
 465 Phan et al. (2021)). The HCO tholin from that study is made of C=O, C=C, CH_x and OH groups, and accordingly the
 466 infrared spectra are fairly similar. The relative abundances of these chemical groups are, however, not strictly similar
 467 to those of the methanol residue, which result from the initial composition of the gas mixture injected in the plasma
 468 reactor and/or the physical conditions in the plasma. This points to similarities between the physical processes at play
 469 in a cold plasma experiment and in an irradiated solid. Structural and chemical effects triggered by swift heavy ions
 470 in solids can be accounted for by the thermal spike model (Toulemonde et al., 1993). In this model, incoming ions
 471 interact with electrons, which are locally released and leave ionized tracks (diameter ~ 1 nm). The interactions of these
 472 electrons with atoms generate electronic cascades and a plasma with high-temperature electrons, which eventually
 473 transfer kinetic energy to the atomic lattice and trigger a temperature surge of several thousands of degrees for atoms
 474 in the lattice. This temperature surge is responsible of sputtering in the vicinity of the sample surface. The whole
 475 sequence of these processes is shorter than 1 ns, i.e. it is an ultra-fast pyrolysis that is very difficult to simulate in
 476 the laboratory, even by means of femto-second laser (Toulemonde et al., 1993). The thermal degradation of organic
 477 material through fast pyrolysis (~ 1 s) leads to aromatic-rich residues (Cui et al., 2016), which are very different from
 478 irradiated methanol or oxygenated polymer (Faure et al., 2021). The similarities between irradiated and cold plasma
 479 materials support the view that temperature is not the main physical parameter that controls chemistry. Estimates of the
 480 atomic peak temperature by the thermal spike model are usually around 2000-3000 K, but they decrease very rapidly
 481 across the track. Furthermore, the very short heating duration probably largely inhibits the aromatization process.
 482 Finally, bond breaking and recombination during electronic cascades would dominate irradiation chemistry, which are
 483 the conditions that prevail in cold plasmas. Altogether, this suggests that cold plasma materials formed in the laboratory
 484 (tholins) should be considered as fair analogs of irradiated solid materials.

485 The absorption properties of the organic material are controlled by conjugated olefinic groups. They are responsible
 486 for π → π* electronic transitions that control absorption at short wavelength in the visible, thereby providing a reddish
 487 color. The abundance of conjugated bonds could not be determined, due to the spectral congestion of the B_{C=O,C} band.
 488 The DBE provided by HRMS analysis provides insights into saturation, but includes ring with no unsaturated bonds.

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489 In addition, only conjugated olefinic bonds lead to visible absorption. In this respect, linking the chemical composition
490 to the absorption properties is not suitable with our set of data.

491 5.2. Relevance to planetary conditions

492 The irradiation experiment E₁ was run with a ¹³⁶Xe¹⁹⁺ ion, while calculations show that H and He are the
493 main contributor of the dose deposited in Arrokoth's surface. According to de Barros et al. (2011), the destruction
494 cross section of methanol ice is written as AS_e^n , with A is a pre-exponential factor and n ranges between 1
495 and 1.5. Our reevaluation of this cross section leads to an exponent n between 0.98 and 1.14. Because $n \neq 1$,
496 ¹³⁶Xe¹⁹⁺ achieve faster methanol ice destruction than H at the same equivalent dose, and we overestimate the
497 rate of chemical evolution in planetary conditions. Taking electronic stopping powers at 0.55 MeV/u, the ratio of
498 $[S_e^n(136Xe)/S_e^n(H)]/[S_e(136Xe)/S_e(H)]$ is equal to 2.1, 4 and 525 for $n = 1.14, 1.25$ and 1.5, respectively. These
499 values span a broad range and show that the exponent is a critical parameter. But with an upper value of 1.14, the impact
500 is quite limited. H irradiation of methanol ice and methanol:water mixtures by Moore et al. (1996) were achieved with
501 a dose of 34 eV/molecule (against ~ 36 eV/molecule in our experiment). The organic residue from that study measured
502 at 220 K (spectrum (a) in Fig. 4) displays the same bands B_{OH}, B_{CH_x}^s, B_{C=O,C} and B_{CH_x}^b displayed by our sample
503 at the same temperature, pointing to similarities in the chemical routes. The shape of B_{C=O,C} appears however more
504 similar to that in our low energy experiments E3 and E4. We also note the presence of the 1041 cm⁻¹ band, due to
505 the C-O bond, which may be more difficult to break with protons. In the case of He, the second contributor to the
506 electronic dose in Arrokoth's subsurface, the ratio $[S_e^n(136Xe)/S_e^n(He)]/[S_e(136Xe)/S_e(He)]$ is equal to 1.7, 2.5
507 and 6.4 for $n = 1.14, 2.5$ and 6.5, respectively. In this respect, the ¹³⁶Xe¹⁹⁺ ion fits better the contribution of He, but
508 further experiments are necessary to get an appraisal of chemical similarities and differences of the final by-product.
509 For C, N, O, Mg, Si and Fe, which probe the depth 1-1000 mm, we infer that the ¹³⁶Xe¹⁹⁺ ion experiments are more
510 representative of the planetary conditions. Another point to address is the presence of a thermally-activated chemistry
511 during TPD. Molecular diffusion, radical recombination and other chemical reactions happen in the sample during
512 warming up. However, these chemical reactions do not lead to a major evolution of the organics. The characteristic
513 features B_{C=O,C} and B_{CH_x}^b are present from 10 K to room temperature, showing that aliphatic, olefinic and carbonyl
514 groups are the main chemical groups composing the organics.

515 At the surface of Arrokoth, CH₃OH may be, or may have been mixed with other molecules, e.g. H₂O. A
516 concentration effect can then be expected. Moore et al. (1996) have investigated mixtures with the H₂O:CH₃OH = 1:0.6
517 composition, and mixtures dominated by methanol. For these concentrations, any methanol molecules is surrounded
518 by other methanol molecules, therefore polymerization and chemical growth are expected. Their spectra collected at
519 220 K show similar organic features. At 10% concentration, calculations of Behringer (1958) run for crystalline cubic
520 solids, show that 30-50% of molecules should be present as monomer, 20% as dimers, and the rest as multimers. At
521 1% concentration, the abundance of monomers is around 90%, which decreases the abundance of chromophores by
522 one order of magnitude. This conclusion holds if the surrounding matrix is devoid of C atoms, not in the case of other
523 species like H₂CO, CO₂ or CH₄, which would react with methanol.

524 Last, the actual conditions in the subsurface may lead to hypervolatile (H₂ or CO) trapping at some depth,
525 either in the water lattice or as bubble. In thin films experiments, volatiles can escape more easily. These trapped
526 molecules would react further, changing the chemistry, for instance through mitigating dehydrogenation. In addition,
527 our calculations do not include secondary reactions at high energy that generate gamma radiation, and contribute to
528 the total dose. To get an appraisal of this contribution, we have run simulations on a crystalline water ice surface in
529 the same physical conditions as Loeffler et al. (2020), who considered these secondary reactions using the GEANT4
530 software. Comparing our results with theirs shows that our calculation underestimates the dose by a factor ranging 2-7
531 in the first meter of the subsurface.

532 5.3. A reddening scenario for Arrokoth's surface

533 A reddening scenario of Arrokoth's surface is taking place based on the above results (Fig. 15). Our calculations
534 show that sputtering is essentially controlled by SW and SEPs (Tab. 2). The erosion of organics (formed by radiolysis)
535 is the lowest over 4.55 Gyr, compared to ices. Above ~ 10 mm, the effect of sputtering disappears. Because materials
536 display very different responses to sputtering, a chemical fractionation is expected in the first millimeters of the surface,
537 which corresponds to the depth probed by the MVIC and LEISA spectrometers. Hyper-volatiles (e.g. CO) and volatiles
538 (CO₂, CH₄, H₂CO) will get less and less abundant, and even water ice may become a weak component with respect to
539 organic species. We may infer that eventually sputtering could generate an organic crust, covering a more icy material.

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540 Accordingly, the detection of buried icy species would be difficult. However, the detection of methanol at the surface
 541 of Arrokoth along with the non detection of water ice raises questions, as the sputtering yield of methanol is higher
 542 than that of water ice. In the case of Centaur Pholus (Cruikshank et al., 1998), TNO (55638), TNO 2002 VE₉₅ and
 543 TNO (120348) 2004 TY364, water ice could be present as mixed with methanol (Merlin et al., 2012).

544 The contribution of SW to ice radiolysis is weak. The nuclear dose lies above $10 \text{ eV}\cdot\text{atom}^{-1}$ in the first 30 nm, and
 545 organics formed from ice radiolysis should be transformed into dark amorphous carbons (Faure et al., 2021). However,
 546 its presence at the very top of the surface during 4.55 Gyr is unlikely, due to burying and mixing processes triggered
 547 by regolith gardening. GCRs leave high electronic doses in the range 50-200 eV/atom in the first 100 μm . Experiments
 548 on polymers show that their evolution upon increasing doses includes two stages (Calcagno et al., 1992). The first
 549 consists in scission, cross-linking and bond creation within chains. The respective contribution of these processes
 550 depend on the nature of the polymer, i.e. linear or reticulated structure, molecular weight of chains, composition of
 551 monomers. PTFE (Polytetrafluoroethylene) is for instance very sensitive to chain scission and show a significant
 552 sputtering yield, while PE (polyethylene) or PS (polystyrene) are very resistant and promote instead cross-linking.
 553 PMMA (Poly(methyl methacrylate)) and PEG (polyethylene glycol) that contain tetrahedral carbons are somewhere in-
 554 between (Calcagno et al., 1992; Balanzat et al., 1995; Faure et al., 2021). In a second stage, further irradiation promotes
 555 extensive dehydrogenation and sp^2 carbon, forming material that share similarities with hydrogenated amorphous
 556 carbons. According to (Calcagno et al., 1992), the end of the first stage is a material whose composition and structure
 557 are irrespective of the starting polymer, and whose subsequent evolution is essentially controlled by the dose. However,
 558 the nature of the dose (elastic versus electronic) is a key factor and several precursors evolve towards amorphous carbon
 559 even at low electronic dose, if the elastic dose is higher than $10^{+10}_{-7} \text{ eV}\cdot\text{atom}^{-1}$. In addition, the presence of radio-resistant
 560 aromatic species in the polymer tend to form polyaromatic by-products after extensive electronic irradiation (Costantini
 561 et al., 2002, 2005). In the case of methanol ice, a cross-linked organic macromolecular compound is achieved at
 562 electronic doses in the range 5-20 $\text{eV}\cdot\text{atom}^{-1}$. Following Calcagno et al. (1992), we expect a progressive H loss and
 563 sp^2/sp^3 increase, and finally a range of hydrogenated amorphous carbons with varying Tauc gap and optical absorptions.
 564 Experiments run until a $200 \text{ eV}\cdot\text{atom}^{-1}$ electronic dose are here necessary to quantify the absorption properties of this
 565 family of hydrogenated amorphous carbons.

566 In contrast to Solar ions, Galactic cosmic-rays control methanol ice radiolysis as deep as several meters in
 567 Arrokoth's subsurface. The electronic dose is significant in the first meter ($> 1 \text{ eV}/\text{atom}$), and we expect a significant
 568 abundance of reddish organics. The main contributing ions to radiolysis are H and He. Other ions provide a dose
 569 lower by \sim one order of magnitude and only within the first meter. The destruction yield calculated with a revised
 570 destruction cross-section from de Barros et al. (2011) also meets this conclusion (Fig. 3), as we obtain, for protons at
 571 44 au, a destruction yield $> 10\%$. The deep penetration of H and He ions mitigate the effect of regolith turn-over that
 572 tends to lower the actual irradiation time.

573 However, other processes control the surface evolution of Kuiper Belt objects (Stern, 2003). The surface of
 574 Arrokoth has been exposed to interplanetary dust particles (IDPs) and interstellar grains (ISG) fluxes, leading to
 575 surface ablation and regolith gardening (Poppe, 2015, 2016; Szalay et al., 2018). Poppe (2015) has estimated the
 576 mass ejecta rate at the Pluto system using the IDP and ISG fluxes derived from dust models and the crater yield
 577 determined from laboratory simulations (Koschny & Grun, 2001). If we take the average value of these estimates that
 578 vary during the Pluto year, we obtain an ablation rate of $\sim 30 \mu\text{m}\cdot\text{Myr}^{-1}$ for water ice, i.e. $\sim 14 \text{ cm}$. The analysis of
 579 the data collected by the Student Dust Counter aboard New Horizons spacecraft led to higher estimates between 30
 580 and $300 \mu\text{m}\cdot\text{Myr}^{-1}$ (Bernardoni et al., 2022). However, these values are likely overestimated, in particular because the
 581 experimental conditions of Koschny & Grun (2001) do not strictly fit planetary conditions (ice temperature was 250
 582 K against 40 K, projectiles were glass particles against fragile chondritic porous assemblages). In addition, organic
 583 materials are more resistant to hypervelocity impact. Shock experiments in the laboratory show that Titan's tholins
 584 are carbonized and transformed into a polyaromatic residue, with a moderate mass loss (Quirico et al., 2019). Last,
 585 impacting particles or their fragments may remain stuck at the surface, thereby contributing to the spectral properties
 586 of Arrokoth's surface.

587 Other processes that possibly mitigate a radiolytic origin of red organics are catastrophic surface ablation events
 588 triggered by (i) crossing Giant Molecular Clouds, (ii) passing stars or supernovae heating and (iii) collisions (Stern,
 589 2003). Crossing giant molecular clouds would enhance the flux of ISGs at the surface, thereby increasing the ablation
 590 rate of ice. It is however difficult to constrain the frequency and intensity dust surges that happened in the past.
 591 Heating by passing stars or supernovae may have been significant in the Kuiper belt at the early stages of Solar System
 592 formation, but no later than 2 Myr, which means a lack of thermal destabilisation during almost 4.55 Gyr (Pfalzner,

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2013). Collisions between KBOs are in contrast a frequent process that shaped the present size distribution of KBOs (Abedin et al., 2021). Low-sized KBOs (< 10-20 km) would be collisionally evolved, and most collisions would have likely happened within the main classical belt at low collisional speed (< km.s⁻¹). Recent fragmentation would have delivered fragments with fresh and weakly irradiated surface. It is however unclear whether Arrokoth has experienced a recent collision. In the case of small impactors, the physics of collision of icy porous bodies, and consequently effects on optical and chemical properties of an impacted surface remain poorly known (Leinhardt et al., 2007).

Finally, the formation of reddish organic materials is supported by calculations and experimental simulations. The deep penetration of GCRs generate organics deep enough to escape ablation processes such as sputtering and dust bombardment. This provides evidence that Arrokoth's red surface has not a primordial origin, but is a direct consequence of space weathering. Future studies should focus on the optical properties of the radiolytic organic byproducts, as there is yet no direct evidence that these materials fit MVIC and LEISA observations. The determination of the absorption properties of irradiated methanol is tricky due to the contribution of scattering, but a way to circumvent this problem could be to produce analogs in cold plasma reactors. The room-temperature residue could also be tentatively characterized by combined FTIR and VUV measurements after dissolution in different solvents, suitable with both spectral ranges.

6. Conclusions

The main conclusions of this study are the following:

1. SW control the sputtering rate of Arrokoth's surface. This erosion thickness is estimated at ~ 240 μm in the case of water ice, and at a few μm for organic materials. Sputtering tends to favor the formation of a pure organic crust at the surface.
2. SEPs generate a nuclear dose greater than the critical dose 10⁺¹⁰₋₇ eV/atom and a significant electronic dose (until 200 eV.atom⁻¹) in the first tens of nm of the surface. A range of hydrogenated amorphous carbons may form there, with varying optical properties depending on the dose.
3. Extrapolating the differential flux of SW and SEPs measured at 1 au at high heliocentric distance leads to an overestimate of sputtering yields by one order of magnitude. Dedicated models need to be used.
4. GCRs dominate radiolysis in the first meter of the subsurface, and generate macromolecular reddish organic compounds. This deep chemistry mitigates the effect of regolithic turnover that tends to limit the actual irradiation time of grains.
5. Macromolecular organics formed from pure methanol ice are a complex mixture of tens or hundreds thousands of compounds. The main functional groups are CH_x, carbonyl C=O, olefinic C=C and -OH. Optical absorption through π → π* is controlled by conjugated C=C bonds.
6. Tholins, which are polymeric amorphous macromolecular solids formed in cold plasma reactors, appear as fair analogues of irradiation by-products, and could be helpful to determine their optical properties.
7. According to these numerical and experimental results, the formation of reddish organics at Arrokoth's surface from methanol-rich ices by GCRs radiolysis (and to a lesser extent SEPs) appears plausible. This holds in the lack of ancient events (interplanetary and interstellar dust impacts, collisions) that would have ablated several meters of the surface.

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Table 4
Band strengths of CD₃OD.

Vibration mode	Band strength (cm/molec)	Integration range (cm ⁻¹)
γ CD ₃	$4.0 \pm 0.2 \times 10^{-19}$	889-913
δ CD ₃ as	$1.5 \pm 0.1 \times 10^{-18}$	1050-1075
δ CD ₃ s	$7.2 \pm 0.4 \times 10^{-18}$	1079-1166
ν CD ₃ as	$7.5 \pm 0.4 \times 10^{-18}$	2196-2263
ν CD ₃ s	$4.4 \pm 0.3 \times 10^{-18}$	2054-2104
ν CO as	$8.3 \pm 0.5 \times 10^{-18}$	941-1005

as=antisymmetric. s=symmetric.

A. Measurements of the band strengths of CD₃OD ice

Experiments were run at IPAG with a Bruker Vertex70v spectrometer, equipped with a DTGS detector, a KBr beamsplitter and a Globar source. The spectral resolution was 1 cm⁻¹. Thin films were produced in a chamber maintained under secondary vacuum (typically, 5 x 10⁻⁷ mbar), by condensation onto a KBr window at 24 K. The film growth was monitored with a He-Ne laser at an incidence angle of 45°. Interference fringes were used to determine the sample thickness, using the refractive index of liquid methanol n=1.33 (Bouilloud et al., 2015). The density of solid CD₃OD has not been determined experimentally. We have used the value 0.796 g.cm⁻³, calculated by scaling the density of amorphous CH₃OH (0.71 g.cm⁻³) with the density of liquid CH₃OH and CD₃OD. The band strengths of 6 vibration modes were then determined (Tab. 4).

B. Measurements of gaseous products by QMS

Gas by-products produced during irradiation and the Thermally Programmed Desorption (TPD) sequence were analyzed by means of a MKS Microvision 2 quadrupole mass-spectrometer (QMS). Masses from 1 to 100 were scanned continuously during the experiment (one full scan ~ 7s). The main volatile by-products were targeted (i.e. CH₃OH, H₂CO, CO, CO₂, CH₄, H₂ and H). No signal was detected above m/z=45, in particular organic species released after 210 K were not detected, while the corresponding IR spectra showed their disappearance from the solid sample. Fig. 16 displays the mass spectrum of pure methanol (during injection) and one spectrum collected during the TPD sequence. We clearly observe an intense peak at m/z=2, due to H₂, which points to dehydrogenation. Excesses over the methanol peak at m/z=28, 29 and 31 essentially report the production of CO and H₂CO. m/z=18 points to the presence of H₂O, while m/z at 13, 14 and 15 point to the presence of CH₄. Fig. 17 reports the evolution of the intensity of the peak at m/z=2, 18, 28 and 32. During irradiation, H₂ and CO are the main by-products, while CO₂ was hardly detected at m/z=44. During TPD (Fig. 18), H₂ is essentially expelled at low temperature (<40 K). CO is essentially sublimated before 50 K, but sublimation continues until 120 K. At low temperature, H₂CO and O₂ (contamination from vacuum and produced from H₂O radiolysis) are expelled around 30 K. Methanol is sublimated between 130 and 155 K, and water has fully sublimated at 210 K. Note that this QMS monitoring is at best semi-quantitative: the data were not corrected from the electron-impact ionization cross-sections of the molecules, and we did not collect at the time of the experiment the fragmentation pattern of the by-products. In the case of methanol, the fragmentation pattern measured in our experiment and that provided by the NIST database were significantly different.

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Reddish Organics at Arrokoth's surface

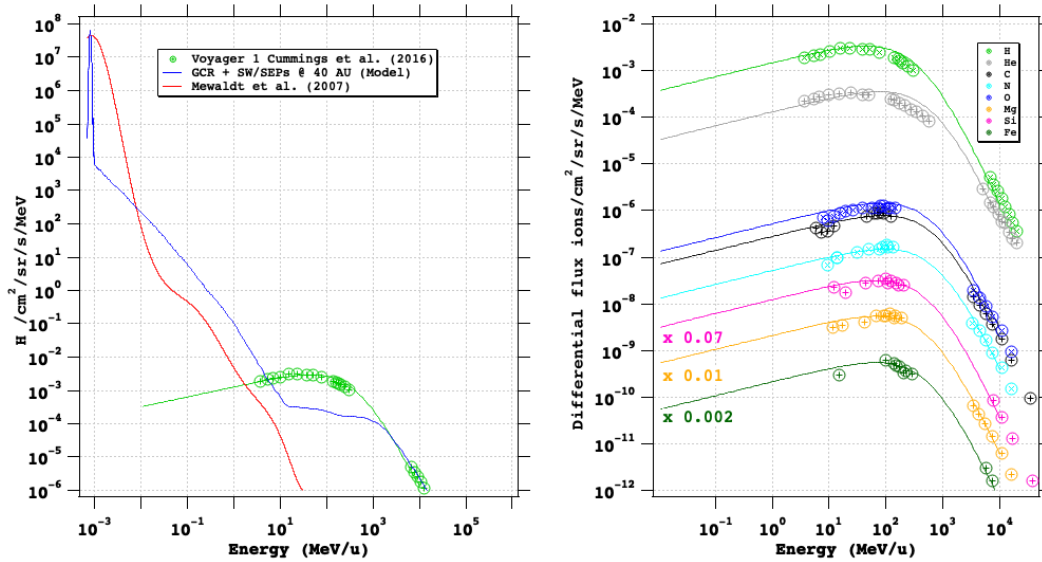


Figure 1: Left: The differential spectra of Solar Wind, Solar Energetic Particles and Galactic Cosmic Ray used in sputtering and doses calculations. Right: Voyager 1 data compared with the parametric law of Webber and Yushak (2003) calculated with C and E_0 values from Table 1 and the chemical abundances derived from Voyager 1 data at 80 MeV/u.

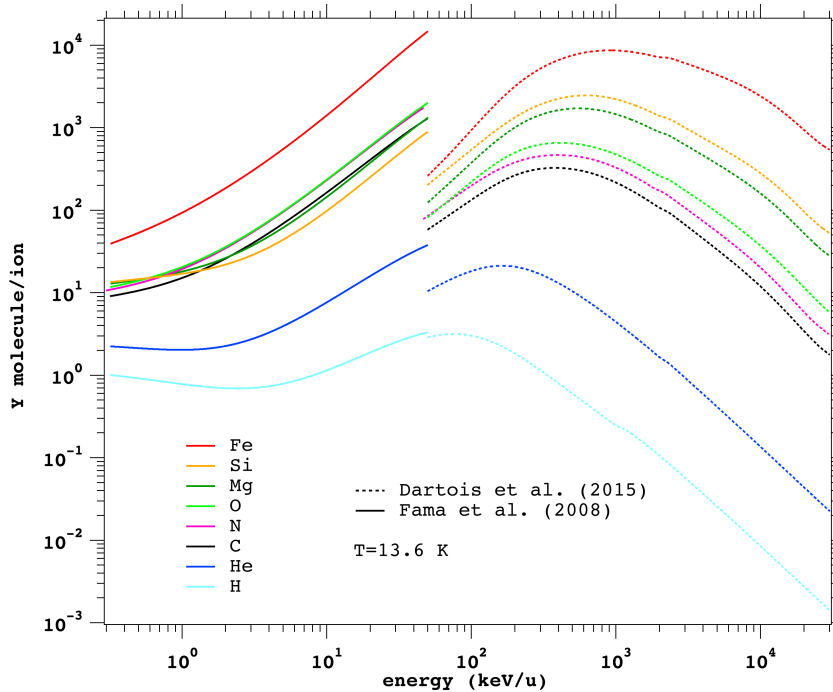


Figure 2: The sputtering yield of water ice calculated from Fama et al. (2008) at 13.6 K, compared with measurements from Brown et al. (1984) and Dartois et al. (2015). Note the mismatch at 50 keV/u, which likely points to an overestimation in the low energy range. At 50 keV/u and above, $S_e \gg S_n$.

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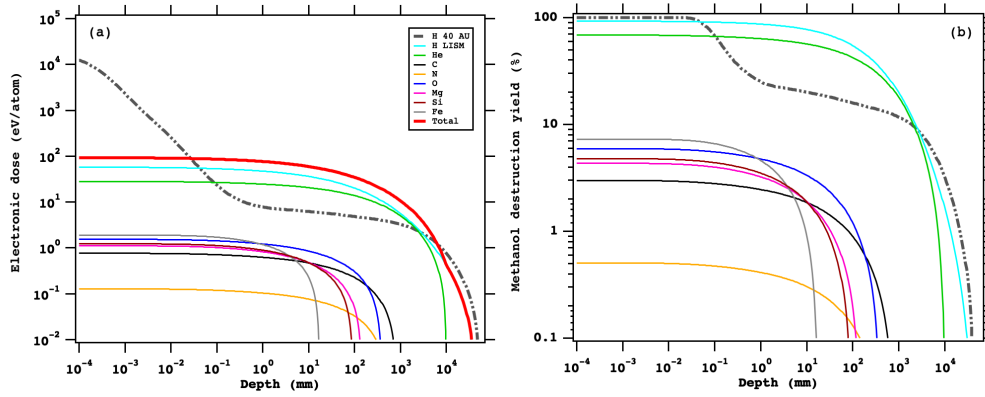


Figure 3: (a): Electronic dose deposited in Arrokoth's surface upon depth, for a LISM differential flux (solid lines) and a protons differential flux at 40 au (mixed dotted line). (b): Destruction (breaking of the C-O bond) yield of methanol molecules (i.e., number of destroyed molecules divided by the initial number of molecules, multiplied by 100) using a revised destruction cross-section from de Barros et al. (2011). H and He are the main contributors to the dose, in term of intensity and depth.

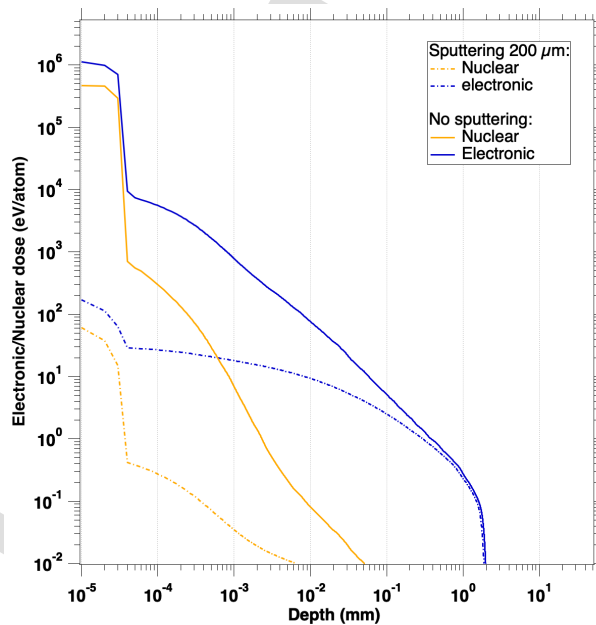


Figure 4: Electronic and nuclear doses deposited by Solar Wind ions at 44 au. Calculations were run without and with sputtering. The dose is significant in the first hundred of nm.

Reddish Organics at Arrokoth's surface

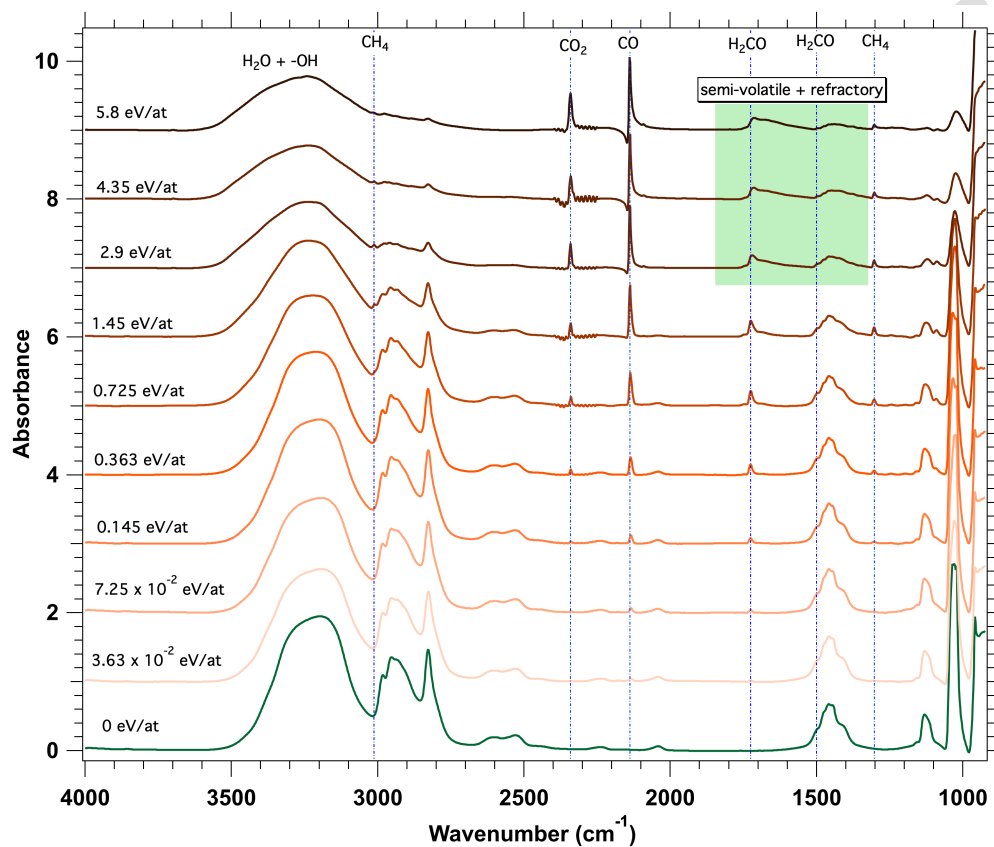


Figure 5: The evolution of methanol ice in experiment E₁. Signatures of organics appear around 1.45 eV·atom⁻¹.

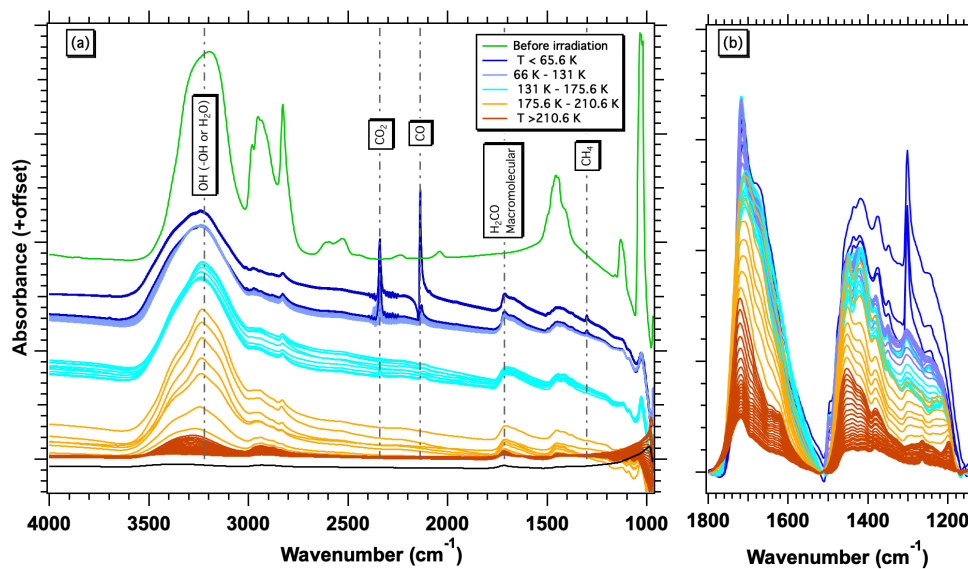


Figure 6: (a): Raw spectra of irradiated methanol film during thermal programmed desorption (experiment E₁). (b): zoom on the organic bands with baseline correction.

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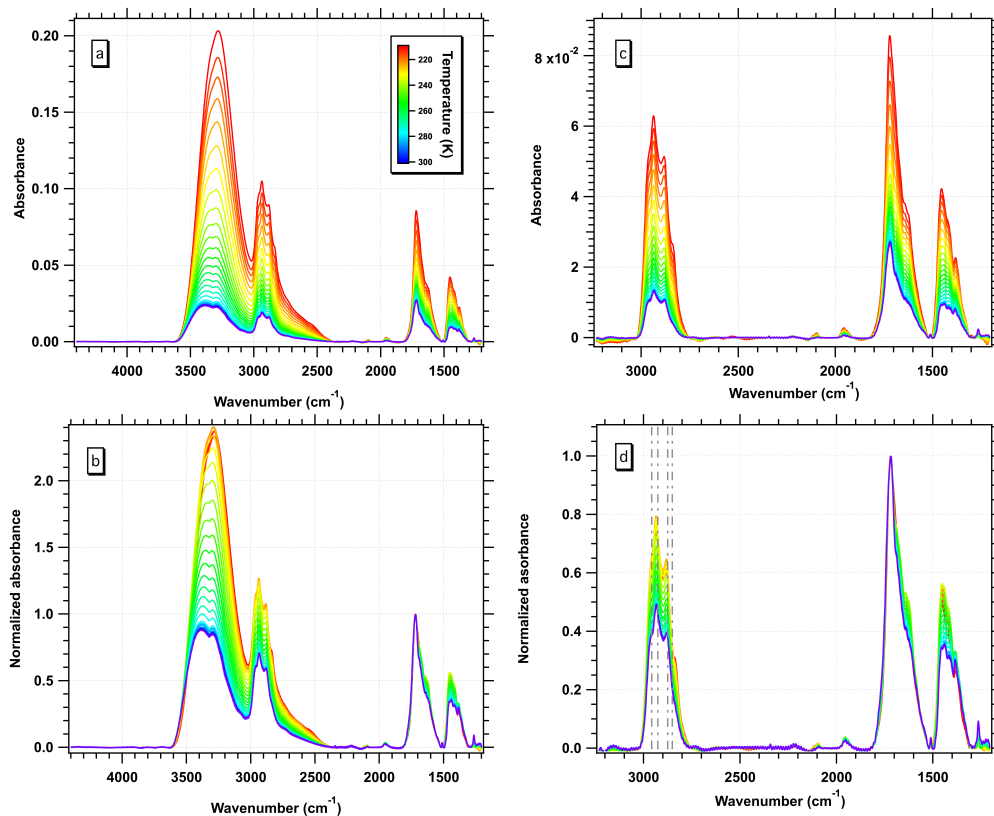


Figure 7: (a): Infrared spectra of organics during the Thermally Programmed Desorption sequence between 210 and 300 K. (b) Same with absorbance normalization at 1750 cm^{-1} . (c) Infrared spectra with a baseline correction in the region of the aliphatic band in the range $2800\text{--}3000\text{ cm}^{-1}$. (d): Same with absorbance normalization at 1750 cm^{-1} .

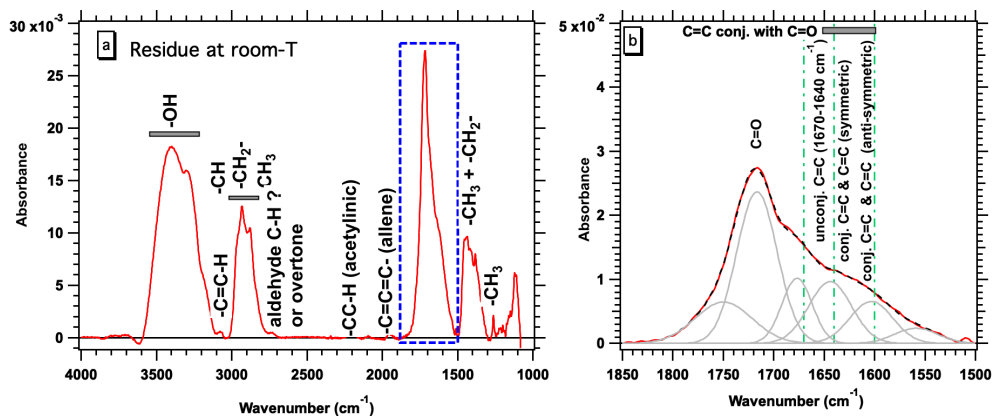


Figure 8: Bands assignment of the spectrum of the room temperature residue. (a): Full spectral range. (b): Blow out on the $1850\text{--}1500\text{ cm}^{-1}$, which contains signatures of olefinic groups that control the absorption properties in the visible range.

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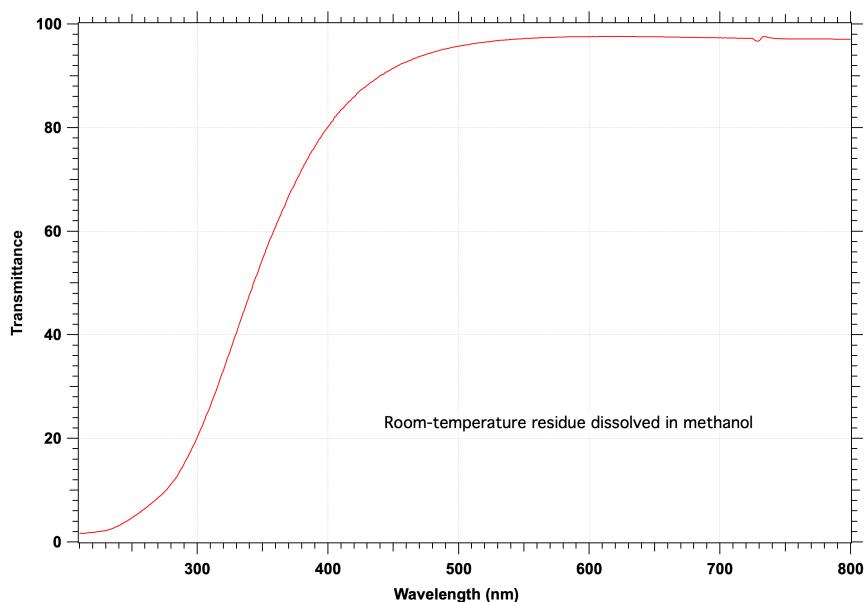


Figure 9: VUV absorption spectrum of the room temperature residue dissolved in methanol.

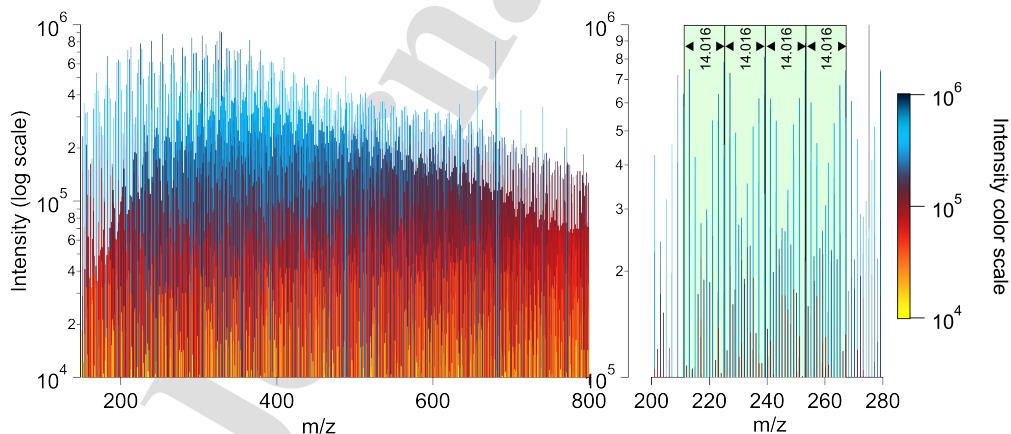


Figure 10: ESI mass spectra, with intensity color code in log scale. The right spectrum is a zoom between 200 and 280 Da as well as between 10^5 and 10^6 intensities. The large number of mass peaks at each nominal mass reflects the complexity of the sample.

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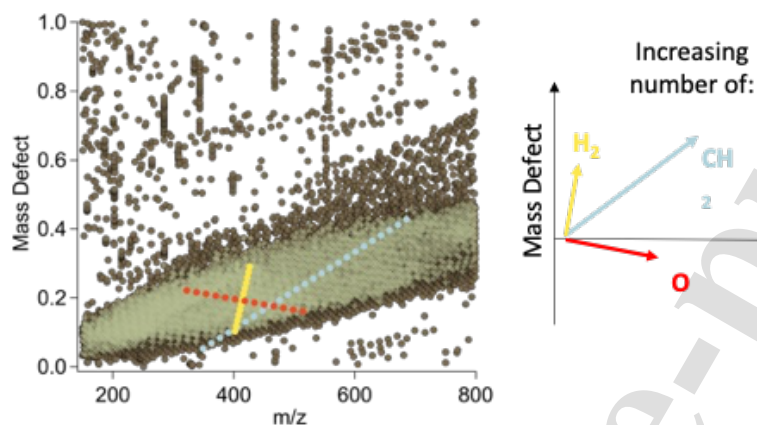


Figure 11: Mass defect versus mass diagram with three main directions being represented. The purple data points represent the final points assigned a stoichiometric formula. Other points are artifacts, as radiofrequency signals contamination (e.g. red area) or electronic noise (e.g. light blue area). The contribution of multicharged ions is negligible.

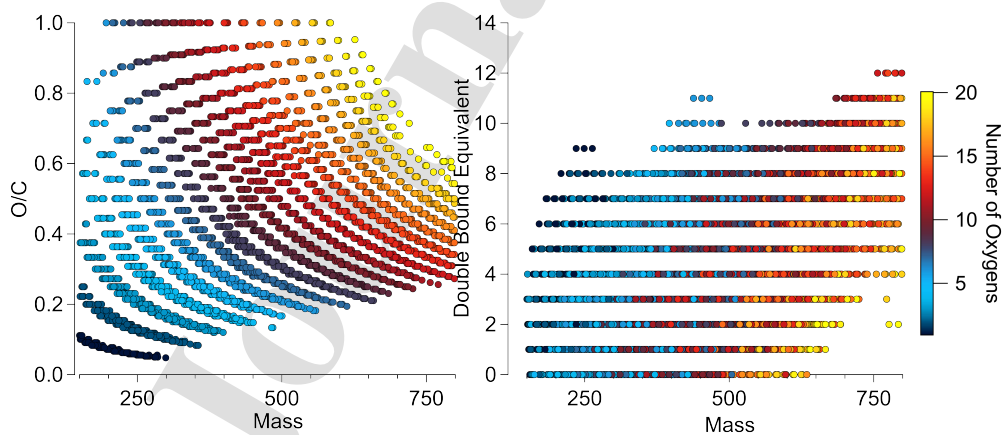


Figure 12: O/C and DBE versus mass representations, with the number of oxygens as colour code

Reddish Organics at Arrokoth's surface

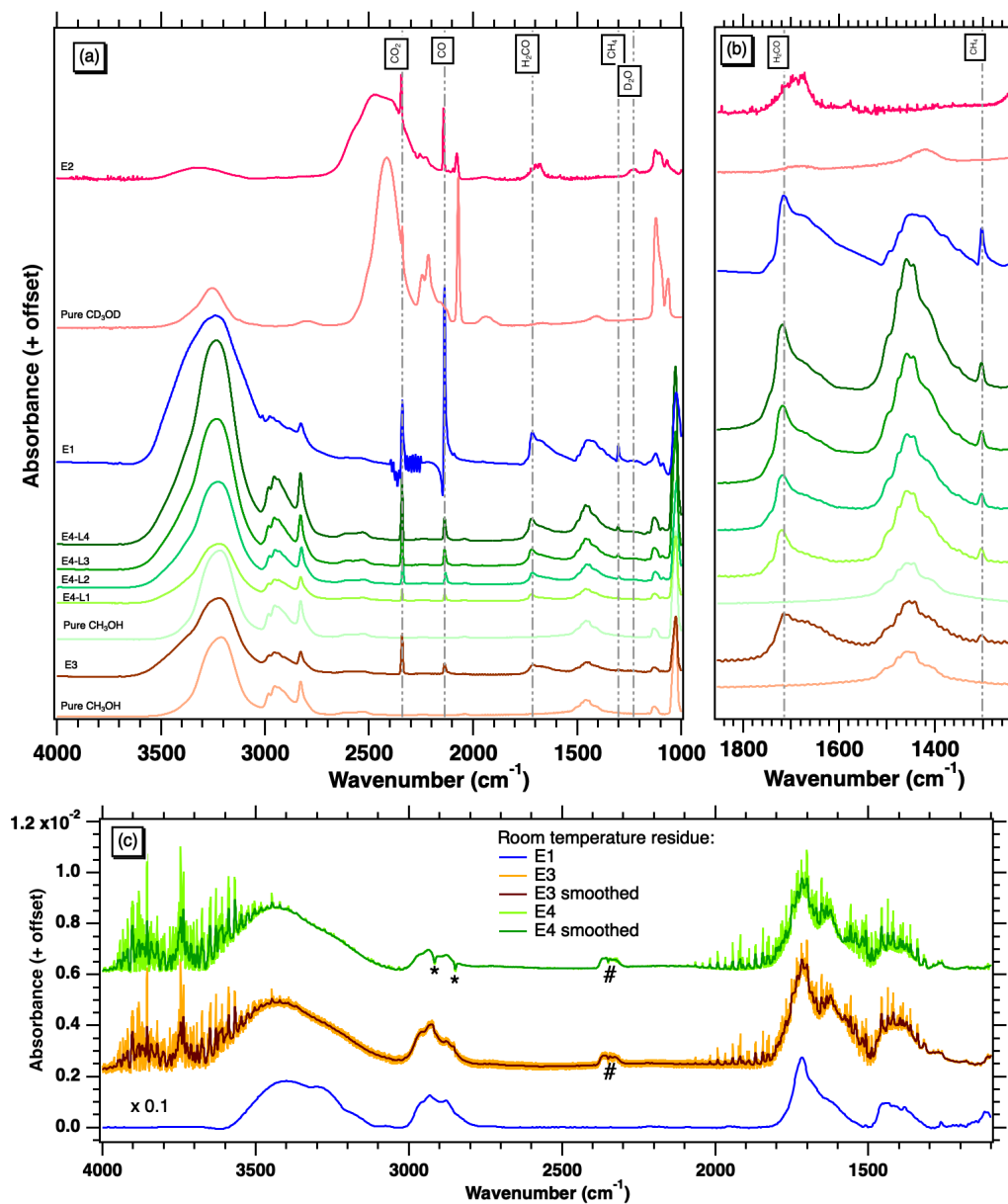


Figure 13: (a): Spectra of methanol films after irradiation for experiments E2, E3 and E4. The Li label refers to the layers from $i=1$ to 4 in experiment E4. (b): Blow up in the region of the organic bands. (c): Room temperature residues. *: artifact due to window pollution and background subtraction. #: incomplete correction of atmospheric CO₂.

Reddish Organics at Arrokoth's surface

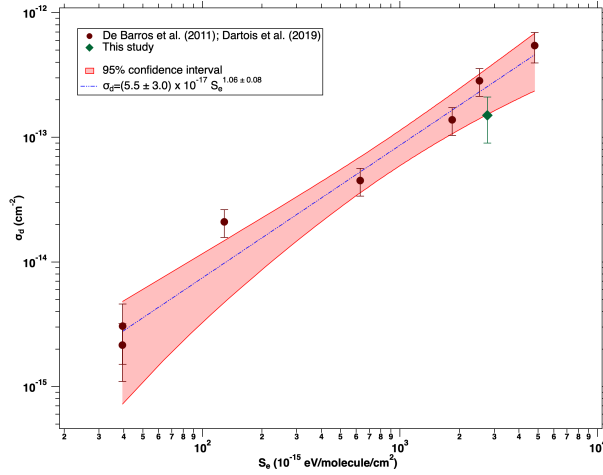


Figure 14: The destruction cross-section for CD_3OD derived from experiment E_2 , compared with experimental data of earlier studies.

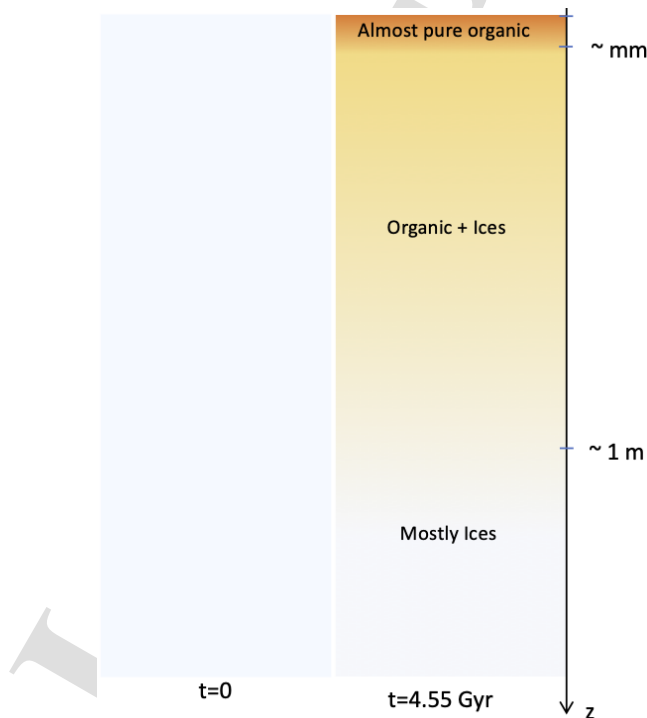


Figure 15: Distribution of organic radiolytic byproducts upon depth. The uppermost region of the surface is an almost pure organic crust, due to volatile removal by sputtering. The first meter region, where electronic dose is $> \sim 2 \text{ eV}\cdot\text{atom}^{-1}$, contains a significant abundance of organics. GCR protons goes down to several tens of meters, but produce there much less organic due to the lower dose.

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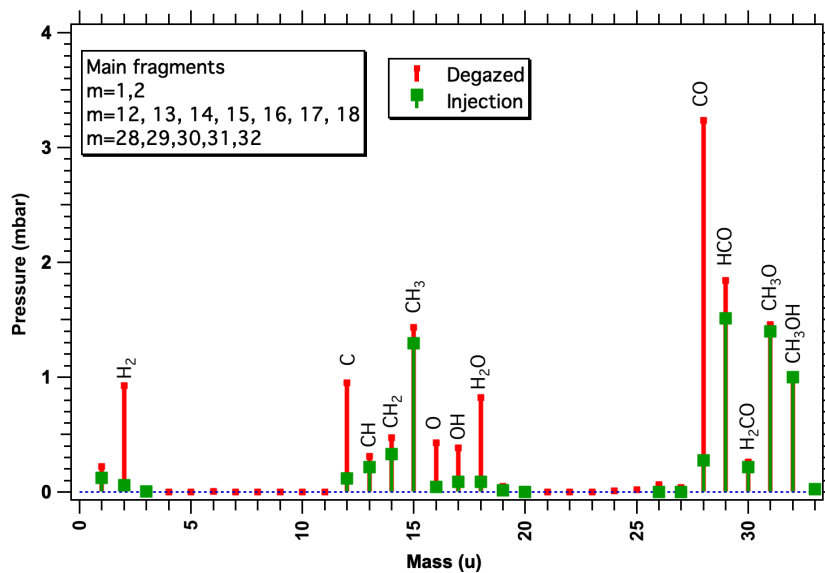


Figure 16: QMS spectra collected during injection (pure methanol) and during TPD.

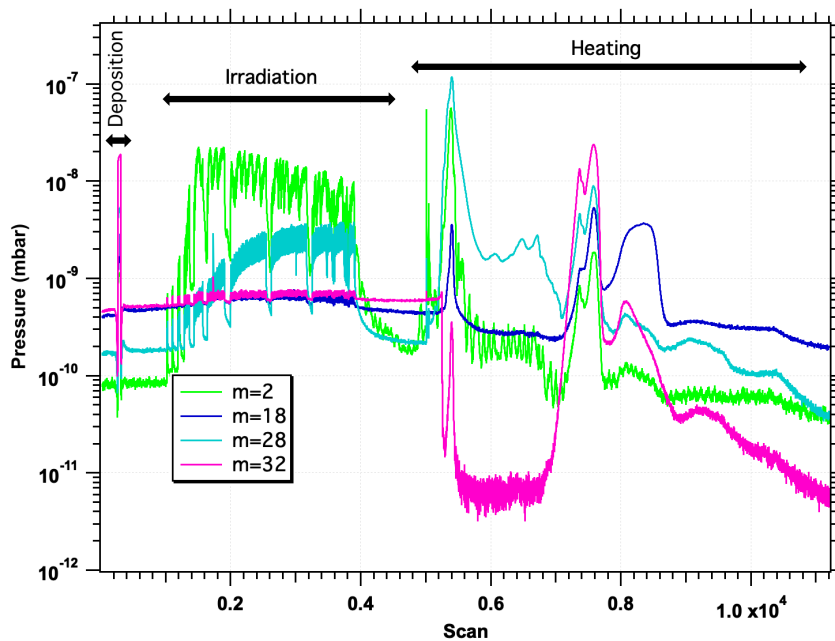


Figure 17: Peak intensity at $m/z=2, 18, 28$ and 32 during injection, irradiation and TPD.

Reddish Organics at Arrokoth's surface

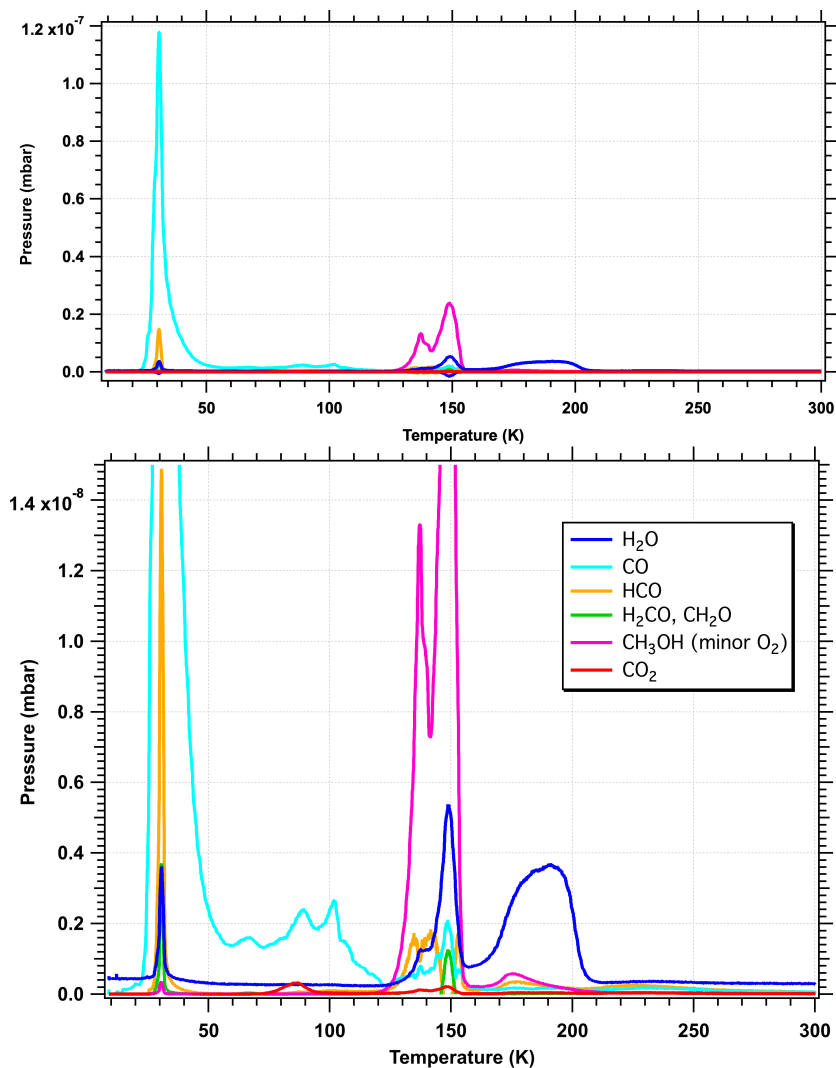


Figure 18: Top: The peak intensity of the main gaseous by-product after correction from CH₃OH contribution in the mass spectra, plotted against temperature. Bottom: same with magnification. No correction of the electron-impact cross sections and of the fragmentation patterns of the by-products were applied to the data.