A Radiolytic Origin of Red Organics at the Surface of the Arrokoth Trans-Neptunian Object

Eric Quirico, Basile Augé, Aurore Bacmann, Cédric Wolters, Véronique Vuitton, Thomas Gautier, Laurène Flandinet, Thibault Launois, Lora Jovanovic, Philippe Boduch, et al.

A RADIOLYTIC ORIGIN OF RED ORGANICS AT THE SURFACE OF THE ARROKOTH TRANS-NEPTUNIAN OBJECTS. E. Quirico[1](eric.quirico@univ-grenoble-alpes.fr), A. Bacmann[1], B. Auge[1], C. Wolters[1], V. Vuitton[1], T. Gautier[2], L. Flandinet[1], T. Launois[1], L. Jovanovic[2], P. Boduch[3], H. Rothard[3], L. Desage[1], A. Faure[1], B. Schmitt[1], O. Poch[1], W. Grundy[4], S. Protopapa[5], S. Fornasier[6], J. F. CooperAlan Stern[5] and the New Horizons Team. [1]Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, CNRS CNES, (Grenoble, France). [2]LATMOS University Versaille St Quentin France. [3]CIMAP-CIRIL-GANIL, Normandie Universite, ENSICAEN, UNICAEN, CEA, CNRS, 14000 Caen, France. [4] Lowell Obs.; Northern Arizona Univ.,USA. [5]Southwest Research Institute, Boulder, CO 80302, USA. [6]LESIA, Observatoire de Paris, CNRS, UPMC Univ Paris 06, Univ. Paris-Diderot, 5 Place J. Janssen, 92195 Meudon Cedex, France.[7]NASA Goddard Space Flight Center (Emeritus)

Introduction: Arrokoth was surveyed by the New Horizons spacecraft on 1st January 2019 [1]. This small cold classical Kuiper Belt Object (KBO) ~ 33 km across has a bilobed shape, and consists of two rounded icy planetesimals (r ~ 9.7 and 7.1 km). Reflectance spectra and spectro-photometric data collected by the LEISA and MVIC instruments have revealed a reddish surface [2]. Methanol has been tentatively identified, while no other ices were detected. The red material at Arrokoth's surface has possibly two origins: (1) a primordial origin, i.e. formed in the proto-solar disk; (2) a radiolytic origin. Different energetic particles can produce organics from ices: Solar or interstellar UV photons, Solar wind (SW) and Solar Energetic Particles (SEPs), and Galactic Cosmic rays. The penetration of UV photons is very shallow (few hundreds of nm), with limited impacts on optical effects. Here, we question the contribution of SW, SEPs and GCR ions that penetrate deeper.

Sputtering and doses: The differential flux of SW and SEPs was calculated from the He fluences of [3], and extended to the most abundant elements (H, He, C, N, O, Mg, Si, Fe) using the solar abundances of [4]. The differential flux of GCR was calculated with the parametric equation of [5] and using Voyager1's measurements [6]. We calculated the sputtered thickness for 3 end-member materials: (1) CO ice and (2) H_2O ice, which are the most and least volatile ice, respectively, and (3) amorphous carbon (hereafter a-C), as an analog of putative organic solids present on Arrokoth surface. We have used sputtering yields earlier published [7,8] and calculated with the SRIM software. Calculations show that the sputtered thicknesses over 4.55 Gyr are 13.9 cm, 3.2 mm and 46 µm for CO ice, H_2O ice and a-C, respectively. The main contributors to sputtering are H and He. The electronic and nuclear doses deposited in the surface have been calculated for a putative methanol surface with stopping powers provided by SRIM (http://www.srim.org/). The omnidirectional nature of the GCR source was taken into account. For GCR, we have also calculated the destruction yield of methanol using the destruction cross-section of [9]. SW and SEPs penetrate at ~ 1.5 mm at the deepest, therefore sputtering erosion has been taken into account in the numerical code. Calculations show that a dose of 1 eV/atom is achieved in the first ~ 100 nm thickness, and that the critical nuclear dose > 10 eV/atom is restricted to a depth of 80 nm. This critical dose is a threshold above which a carbonaceous-material is transformed into amorphous carbon [10]. These results show that the contribution of SW and SEPs ions is weak or negligible in terms of contribution to MVIC and LEISA spectra.

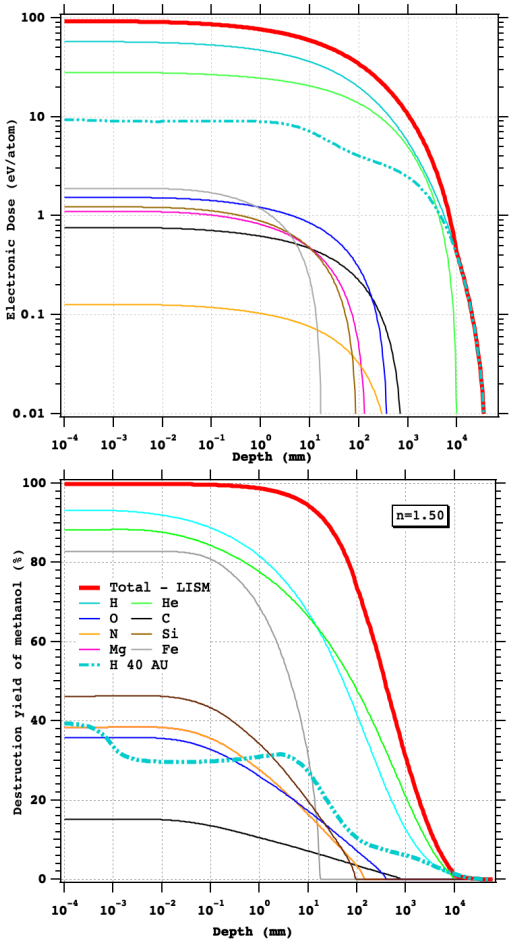

Figure 1: Top-Electronic dose deposited by GCR ions versus depth. Bottom: Destruction yield of methanol molecules.

The penetration depth of GCR ions is much larger, up to 20 m in the case of H (Fig. 1). H and He are the main contributors in terms of dose and depth.

However, dose is just a first crude estimator of chemistry. Using the destruction cross-section of methanol expressed as power law of the electronic power S_e ($\sigma = \alpha.S_e^n$ with n~ 1.5), we observe that other ions (e.g. Fe) have a significant contribution at low depth (< 1 mm). These calculations have been run using the GCR distribution of Local Interstellar Medium, but at 40 AU the GCR distribution flux is modified by solar activity. Calculations were then conducted for protons using the data from [11]. The electronic dose remains close to 10 eV/atom at depth < 1 mm, and between 1 and 10 at depth < 1 m, while the destruction yield of methanol lies around 30% at depth < 1 mm, and around 10-20 % between 1 mm and 1 m. The nuclear dose, in contrast, is smaller than 0.2 eV/atom and elastic interactions can be neglected. *To sum up: (1) sputtering is controlled by SW and SEPs; (2) ices are depleted more efficiently than organic materials; (3) radiolysis is controlled by GCR, and a significant electronic dose, and thereby chemistry, is expected down to at least 1 m.*

Irradiation experiments: Three experiments were conducted on pure methanol ice (10-40 K) at the Grand Accelerateur National d'Ions Lourds (GANIL, Caen – France). (1) CH_3OH – $^{136}Xe^{19+}$ 0.55 MeV/u; (2) CD_3OD – $^{58}Ni^{9+}$ 0.7 MeV/u and (3) CH_3OH – $^{18}O^{6+}$ 105 keV. The composition of irradiated methanol film was monitored by FTIR spectroscopy and gaseous products generated by sputtering were analyzed with a QMS spectrometer. The maximal electronic doses were 5.8 and 3.8 eV/atom for experiments (1) and (2), while experiment (3) included significant elastic interactions with electronic doses ranging from 10 to 30 and nuclear doses ranging from 3 to 10 eV/atom. Upon irradiation, FTIR spectra show the appearance of two main bands in the range 1800-1500 and 1500-1200 cm^{-1}, corresponding to organic species containing C=O and C=C, and aliphatic CH, CH_2, CH_3 chemical groups, respectively. Other features point to the presence of organic OH and C≡C, and simple molecular byproducts as CO, CO_2, H_2CO, CH_4 and H_2O. Upon heating from 40 K up to room temperature (TPD sequence), ices sublimate and we observe the progressive decrease of the abovementioned organic bands. At room temperature, a reddish organic residue was recovered, dissolved in liquid methanol and analyzed by VUV spectroscopy. The spectra show an absorption continuum with an increasing absorption towards short wavelengths, consistent with the reddish color observed with the naked eye. The carriers of this absorption are likely conjugated olefinic C=C groups, which contribute to the BI band.Mass spectra in the range 150-400 m/z were collected with a LTQ-Orbitrap spectrometer operating in ESI positive and negative modes. Around 4000 formulae were identified, likely corresponding to several hundreds of thousands of molecules. Several repetitive molecular patterns were observed, pointing to polymeric processes during radiolysis. Average H/C and O/C ratios have been estimated as 1 and 0.2, respectively. That H/C drops from 4 (pure methanol) to 1 is consistent with the intense H and H_2 peaks in QMS spectra collected during the TPD sequence due to dehydrogenation.

Discussion: The evolution of methanol ice upon radiolysis share similarities with that of simple polymers devoid of aromatic groups, e.g. polyethyleneglycol [10, 12]. We observe the typical evolution scheme as dehydrogenation, formation of olefinic and acetylenic unsaturated bonds and cross-linking. Interestingly, irradiated methanol residues also share similarities with organic solids formed in plasma reactor (often named *tholins*) [13]. Radiolytic chemistry triggered by swift ions is described with the thermal spike model: electrons generated by collisions with the incident ion trigger electronic cascade and deliver energy to the lattice, resulting in the formation of a plasma and a temperature surge of several thousands of degrees. This ultrafast pyrolysis (~ns) does not produce aromatic species as observed with usual fast pyrolysis (~s) in the laboratory, and the chemical routes are best accounted by plasma reactions. *Overall, our calculations and experiments demonstrate that reddish organic materials are produced from methanol ice under conditions acting at the surface of Arrokoth. These organics should be produced in the first meter by GCR ions, thereby detectable by VNIR spectroscopy and deep enough to survive surface erosion by SW sputtering and dust impacting* [14]. *Sputtering could efficiently wipe ices out from the surface, resulting in an almost pure organic crust. This might explain the scarcity of ice features at the surface of Arrokoth, and of TNOs in general.*

References: [1] Stern A. et al. (2019) *Science.* [2] Grundy W. M. et al. (2020) *Science.* [3] Mewaldt R. A. et al. (2007) *Space Sci. Rev, 130*, 323-308. [4] Meyer et al. (1998) Von Rosenvinge (Eds.), Dordrecht: Springer Netherlands, 179-201. [5] Webber, W. R., & Yushak, S. M. (1983). *ApJ*, *275*, 391. [6] Cummings A. C. (2016) ApJ., 831:18. [7] Schou, J., & Pedrys, R. (2001). *J. Geophys. Res.*, *106*, 33309–33314. [8] Famą, M. et al. (2008). *Surface Science*, *602*, 156–161. [9] deBarros A. L. F. et al. (2011) Mon. Not. R. Astronom. Soc. 418, 1363-1374. [10] Faure M. et al. (2021) Icarus, 364, 114462. [11] Cooper J. F. et al. (2003) *Earth, Moon Planets,* **92,** 261–277. [12] Balanzat, E. et al. (1995). *NIMPR B*, *105*, 46–54. [13] Phan V. et al. (2021) Spec. Acta Part A: 259 119853 . [14] Poppe A. R. et al. (2016) Icarus, Volume 264, p. 369-386.