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Sublimation of ice–tholins mixtures: A morphological and spectro-photometric study

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ABSTRACT

Sublimation, the direct transition from solid to gas phase, is a process responsible for shaping and changing the reflectance properties of many Solar System surfaces. In this study, we have characterized the evolution of the structure/texture and of the visible and near-infrared (VIS–NIR) spectral reflectance of surfaces made of water ice mixed with analogues of complex extraterrestrial organic matter, named *tholins*, under low temperature (<−70 °C) and pressure (10^{-5} mbar) conditions. The experiments were carried out in the SCITEAS simulation setup recently built as part of the Laboratory for Outflow Studies of Sublimating Materials (LOSSy) at the University of Bern (Pommerol, A. et al. [2015a]. Planet. Space Sci. 109–110, 106–122). As the water ice sublimated, we observed *in situ* the formation of a sublimation lag deposit made of a water-free porous (>90% porosity) network of organic filaments on top of the ice. The temporal evolution of the tholins and water ice spectral features (reflectance at the absorption bands wavelengths, red slope, from 0.40 to 1.90 μm) are analyzed throughout the sublimation of the samples. We studied how different mixtures of tholins with water (0.1 wt.% tholins as coating or inclusions within the water particles), and different ice particle sizes (4.5 ± 2.5 or 67 ± 31 μm) influence the morphological and spectral evolutions of the samples. The sublimation of the ice below the mantle produces a gas flow responsible for the ejection of mm to cm-sized fragments of the deposit in outbursts-like events. The results show remarkable differences between these samples in term of mantle structure, speed of mantle building, rates and surface area of mantle ejections. These data provide useful references for interpreting remote-sensing observations of icy Solar System surfaces, in particular the activity of comet nuclei where sublimation of organic-rich ices and deposition of organic-dust particles likely play a major role. Consequently, the data presented here could be of high interest for the interpretation of Rosetta, and also New Horizons, observations.

1. Introduction

The surfaces of many objects in the Solar System comprise substantial quantities of water ice either in pure form or mixed with mineral and/or organic molecules. Missions exploring these objects usually carry imaging systems and spectrometers which require a good knowledge of the spectro-photometric properties of ice to allow appropriate interpretation. Both numerical models and laboratory experiments are used to overcome this challenge. This paper presents laboratory experiments focusing on the evolution of the optical properties of surfaces composed of water ice and complex organic matter during the sublimation of the water ice.

Water ice is found associated with organics in many objects of the Solar System. Comets are probably the most striking examples, because they possess a high mass ratio of organics compared to ice, estimated from 0.1 to 1 (Fomenkova, 1999; Huebner, 2003; Jessberger et al., 1989; Kuppers et al., 2005; Marboeuf et al., 2014; Weiler et al., 2004). Recent observations of Comet 67P/Churyumov–Gerasimenko by the Rosetta spacecraft suggest a surface dominated by organic materials with water ice near the surface (Altwegg et al., 2015; Thomas et al., 2015). The icy satellites of Jupiter (Europa, Ganymede, Callisto) and Saturn (Titan, Iapetus) (Moore et al., 2009), as well as the Trans-neptunian Objects (TNOs) (including Kuiper belt objects, KBOs) and Centaurs (Duffard et al., 2014) also probably have a surface consisting of ice mixed with

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organics, but at a lower mass ratio than comets. The surface of the Saturn's moon Titan contains a large amount of organics and possibly some water ice, but there is no definitive spectral evidence for water ice exposed at the surface (see Neish et al., 2015 and references herein). Finally, even very close to the Sun, the ice deposits on Mercury have been hypothesized to be locally covered by organic matter partly because of their probable cometary origin (Paige et al., 2013). The complex organic matter present in those different environments has been synthesized (endogenously or exogenously) from smaller molecules in the gas or solid phase.

In the gas phase, solid macromolecular carbonaceous products are efficiently formed after the irradiation of a reduced or neutral gas mixture composed of CH_4, N_2, CO, etc. The breakdown of these simple molecules by energetic particles (VUV/UV photons, electrons, ions) followed by the recombination of their fragments lead to the production of increasingly heavy organic molecules, and finally to solid aerosols. This process has only been observed in the laboratory experiments and in Titan's atmosphere, but it probably occurs on other planetary bodies having thin atmospheres, such as Triton and Pluto (Cruikshank, 2005; Cruikshank et al., 2015; McDonald et al., 1994). The analogue solid organic residues produced after irradiation of a gas mixture composed of simple molecules in the laboratory have been named "*tholins*" by Sagan and Khare (1979). It is derived from the Greek θόλος meaning "muddy", in reference to the orange-brownish color of the material.

In the solid phase, such solid organic residues can also be produced via energetic processing of ice mixtures (such as VUV/UV photons, cosmic rays and thermal processes), although less efficiently than in the gas phase. Similarly as in the gas phase, the irradiation of simple molecules (H_2O, CO, CH_4, NH_3, CH_3OH, etc.) in the form of ices can produce radicals that recombine within the ice to form higher mass molecules, up to macromolecular substances which are called organic refractory matter. Many laboratory experiments performed since 1961 have proved that virtually any carbon-containing ice produces organics upon irradiation (Berger, 1961; Thompson et al., 1987 and references herein). As the irradiation doses or energies are increased, more refractory and darker carbonaceous compounds can be formed (Andronico et al., 1987; Thompson et al., 1987). The thermal processing of the ices also contributes to the production of complex refractory organics. Icy dust particles that formed the pre-solar nebula underwent such irradiation and thermal processing before being incorporated to comets and planetesimals (Herbst and Van Dishoeck, 2009). Solid phase synthesis of complex organic matter may also occur currently on the surfaces of TNOs, comets and icy satellites.

The color of these organic residues (from pale yellow, orange, brown to dark) originate from electronic transitions in the molecular orbitals of the molecules present in the residues. Electrons engaged in bonding σ, π or non-bonding n molecular orbitals can be promoted to anti-bonding orbitals σ^* or π^* by the absorption of photons in the UV–visible range. These transitions occur in specific chemical groups called chromophores. Transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ occurring in π-bonds are very efficient in absorbing visible light if the molecule possesses an extended chain of π-bonds (—C=C—, —C=N—, etc.), called a conjugated system (such molecule is called an "aromatic" molecule). Other transitions such as $n \rightarrow \sigma^*$, most often centered in the ultraviolet, can also efficiently cause absorption in the visible range (Mahjoub et al., 2012; Quirico et al., 2008). These organic residues are made of a mixture of diverse molecules having different structures and chromophores able to absorb light in the UV–visible range. The reflectance spectra of such complex mixtures are characterized by a spectral red slope that can extend from 0.2 to 1.0 μm, with low reflectance values in the ultraviolet and higher values as we go to the near infrared. Heavily irradiated mixtures of organics tend to preferentially lose their H, O and N heteroatoms, extend their conjugated systems and consequently become darker, a process called carbonization (Andronico et al., 1987; Thompson et al., 1987). The dense and highly branched carbon network resulting from this carbonization is very dark from the UV to the infrared and its spectral red slope is significantly reduced (Moroz et al., 2004).

Many surfaces of primitive objects such as asteroids, comets or TNOs appear dark, with a red or neutral spectral slope, possibly because of the presence of complex organic matter at diverse stages of irradiation (Cruikshank, 2005; Cruikshank et al., 2015, 2005). However, the "reddish" color of some Solar System objects could also be explained by the presence of minerals such as iron-oxides (Singer et al., 1979), sulfur polymorphs (Geissler et al., 1999) or nanophase reduced iron (Clark et al., 2012; Bennett et al., 2013), which also exhibit such red slopes in the visible part of the spectrum. But overall, the association of ices and complex organics appears widespread and is an important aspect of many surfaces in the Solar System.

On all these objects, except Titan,[1] sublimation, the direct transition from solid to gas phase, can occur, changing their surfaces and reflectance properties. It is thus essential to characterize the spectrophotometric properties of such surfaces of ices and organics when they undergo sublimation. Sublimation and the subsequent lag deposit are particularly important in the case of comets, because these ice-rich bodies approach the Sun periodically and a huge amount of ice sublimes at each of their perihelion passages. Since the closest approach of Comet 1P/Halley in 1986, it is assumed that the surface of comet nuclei are mostly covered with an ice-free extremely dark mantle made of complex organic material (Hartmann et al., 1987; Johnson et al., 1988). Only areas representing a small fraction of the cometary surface are actively outgassing (Sekanina, 1991). The dark organic mantle covering most of the surface could be a result of sublimation process (sublimation lag deposit, or dust layer formed by re-deposition of dust lifted by cometary activity), and/or a product of the irradiation of ices by cosmic rays and solar energetic particles. Therefore, studying the building and evolution of organic sublimation lag deposits may help to understand the properties of cometary surfaces.

The formation and consequences of these sublimation mantles have been the subjects of many studies, particularly in the 80s and 90s with the Comet Simulation (KOSI) project carried out at the German Aeronautic and Space Organization (DLR) (see Sears et al. (1999) for a review). A comet analogue of 300 mm diameter and 150 mm thick was produced by spraying suspensions of minerals in water into liquid nitrogen. Black carbon and frozen carbon dioxide were also added to this mixture. The sample was left to evolve at around 10^{-6} mbar and 210 K in a large vacuum simulation chamber, and was illuminated by Xenon-arc lamps to simulate the Sun (Grün et al., 1991; Sears et al., 1999). As the ices sublimed, ejection of mineral grains and ice particles was observed, followed by the build-up of an ice-free mantle made of the dust accumulating at the surface of the sample. During or after the simulations, numerous analyses were performed on the thermal conductivity of the sample, the gas emission, the observation of particles ejections and their imaging by microscopy, etc. Reflectance spectra of the samples surface were also acquired before and after the simulations (from 0.5 to 2.5 μm), revealing the darkening of the sample and the decrease of the water and carbon dioxide absorptions (Oehler and Neukum, 1991). However, no measurement was performed *in situ*, during the simulation, and the ex situ analyses suffered from water frost contamination.

[1] Sublimation process is expected to be insignificant on Titan because of the high surface pressure of 1.4 atm (Fulchignoni et al., 2005) and the extremely low surface temperatures.