Research Article

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Organic Molecules in the Icy Bodies of Planetary Systems – Accepted Notions and New Ideas

<https://doi.org/10.1515/astro-2018-0038>

Received Feb 26, 2018; accepted Jun 01, 2018

Abstract: Cometary bodies are acknowledged to contain some of the most pristine matter in the Solar System, including ices and minerals. Certain number of previously unidentified spectral emission features detected in comets can be explained as emission by hydrocarbon molecules enclosed in a Shpol'skii matrix and forming frozen hydrocarbon particles. UV-induced photoluminescence spectra of several self-organized molecules exhibit emission lines coincident with unidentified cometary lines, and open the possibility of the presence of this complex organic as components of the pristine organic inventory of comets. Complex organic was detected also in three satellites of Saturn. We describe in this paper results of our investigation of complex organic of the small bodies and present new approaches and hypotheses.

Keywords: comets, planets, ice, organic matter, prebiotic evolution

1 Introduction

The icy halos of comets, which include minerals, consist of shells of micro and nano grains are responsible for the scattering of solar electromagnetic radiation. A complex mixture of gas and dust around cometary nuclei gives rise to the gaseous emissions and the scattering of sunlight. Taken all together, this constitutes the atmosphere of a comet. The spectra of comets also contain series of unknown emissions. These unidentified emissions have been found in the spectra of many comets (Brown et al. 1996; Cochran and Cochran 2002; Cremonese et al. 2007; Kobayashi and Kawakita 2009; Dello Russo et al. 2013), for example, 109P/Swift-Tuttle. These emissions are assigned to multiple ionized molecules (Wyckoff et al. 1999; Cochran and Cochran 2002; Kawakita and Watanabe 2002). A new theory by Simonia (2004, 2007, 2011a,b, 2013) suggests that the luminescence nature of unidentified emissions result of photoluminescence by frozen hydrocarbon particles (FHPs) of cometary atmospheres. Roughly 14% of the previously unidentified emissions have been identified as photoluminescence of cometary FHP. However 86% of the mentioned emissions remained as unidentified (Simonia 2011b). Comets are known to

be rich in complex organic materials (Ehrenfreund and Charnley 2000; Clairemidi et al. 2004; Crovisier and Bockelee-Morvan 2007; Li 2009; Kobayashi and Kawakita 2009). In this paper, in accord with other investigators, we consider cometary nuclei as the reservoirs of relict organic matter, that is, primitive material that has survived largely unaltered from an earlier time. The surfaces of icy satellites and Trans-Neptunian Objects (TNO's) scatter solar radiation, resulting in the appearance of solar-similar spectra but with different peculiarities (e.g., specific slopes, absorption bands) reflective of the chemical-mineralogical composition of a particular surface. The presence of complex organics in cometary or planetary ices is characterized by specific colors of surfaces in integrated light or by the appearance of the specific emissions and absorptions in the spectral profiles of these bodies. In this paper, we will discuss similarities and differences of complex organic properties for different classes of icy bodies in the Solar System. The complexity of the organic components, the color and other properties will be the focus of our interest, as well as possible methods for revealing potential prebiotics in the icy bodies.

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2 Frozen hydrocarbon matter as a compressed snow – the methodological approach

An important key to the interpretation of comet spectra is derived from the work of Shpolskii (1959, 1960, 1962), who described a matrix with the form of frozen polycrystalline mixtures of polycyclic aromatic hydrocarbons in n-alkanes. Quasilinear photoluminescence spectra of these matrix have been investigated in detailed. Physical properties and the exact chemical composition of polycrystalline mixtures were measured and analyzed. The results of Shpolskii's work could have astrochemical and astrobiological significance. We enumerate here experimental results of the mentioned works in the context of the investigation of comets and other icy bodies of the planetary systems. 1) Solid solutions of polycyclic aromatic hydrocarbons (PAH's) and n-alkanes (from pentane to decane) at $4 < T < 77$ K demonstrate photoluminescence spectra in the form of a series of very narrow emission lines. In such mixtures, aromatic hydrocarbons are guest substances and n-alkanes host substances – solvents, or the so-called matrix. In the referenced works, the matrix (host substance) was in the form of straight chains of n-alkanes. An aromatic compound (ring) substituted in the n-alkane matrix is frozen as a rarefied "oriented gas". Freezing of the solvents as crystallized masses, that is as microcrystals, results in the formation of discrete luminescence spectra when excited by ultraviolet radiation in the range 2500 - 3900 Å; 2) frozen mixtures of polycyclic aromatic hydrocarbons and n-alkanes (pentane, hexane, heptane, etc.) in the form of microcrystals similar to fine-grain snow, have specific luminescence and absorption spectra, appearing as a series of narrow lines. In the case of larger sizes of n-alkane molecules narrow luminescence emission lines transform into diffuse bands; 3) luminescence spectra of complex crystalline organic substances in certain cases have an anomalous character, resulting in the formation of wide structureless bands. Dimers (which consist of two identical monomers) are characterized by such spectra.

Simonia and Simonia (2013) proposed that comets nuclei are rich with frozen organics as snow-like microcrystals of polycyclic aromatic hydrocarbons in n-alkanes. Clusters of numerous snow-like microcrystals congregate in specific zones irregularly distributed in different layers of the cometary nuclei. These zones may constitute the principal sources of hydrocarbons. In this view, flat snow-like microcrystals consist of aromatic molecules fixed in an aliphatic matrix. Hydrocarbons' sources of comets are

rich with various aromatic and aliphatic molecules. The hydrocarbons sequestered in the inner layers or centers of cometary nuclei may be relict material inherited directly from the solar nebula without ever having been processed by the solar electromagnetic radiation or the solar wind.

Cometary relicts are the witness of the Solar System formation, resulting from condensation processes, while the building blocks of complex cometary organic in the form of molecular rings or chains have a presolar origin. This means that cometary relicts convey the physical properties and chemical composition of pristine matter of the solar nebula. Cometary nuclei might be rich in frozen hydrocarbons in the form of compressed snow. Physical conditions of the formation process of each specific cometary nucleus, the local chemical composition of the solar nebula and other parameters have conditioned the density, colors, and other characteristics of frozen hydrocarbon matter in the cometary nucleus. The cometary organic material in the form of frozen hydrocarbons as a compressed snow is probably a dense but rather fragile substance. It may be that, layers of frozen hydrocarbons in the form of molecularly dispersed substance or substitutional solid solutions carry information on physical processes of the evolution of the solar nebula.

When comets approach the Sun, processes of thermal destruction and sublimation of their ices begin. Micro fragments of nucleus ices form the spherical halo, which becomes larger at shorter heliocentric distances. Shells of frozen hydrocarbon particles (FHPs) are the sources of cometary hydrocarbons that are released from the nucleus to form the coma (Simonia 2004). Each FHP is characterized by an inherent size, shape, and color. FHPs with substitutional solid solution structures have nano dimensions, but molecularly dispersed FHPs have micro dimensions. The shape of each FHP depend on structural peculiarity of icy grain. FHP with substitutional structures may be flat, but molecular dispersed grains might be bulky and irregular in shape.

Solar UV radiation of 2400 – 3950 Å excites photoluminescence of frozen hydrocarbon particles in the coma in the wavelength range 3990 – 9000 Å (Simonia 2004, 2007). The chemical compositions of cometary FHPs and the physical peculiarities of Shpolskii microcrystals have specific properties of their photoluminescence spectra including the positions and profiles of emission lines. Photoluminescence spectra of the cometary FHPs at low temperature ($T < 80$ K) have the standard quasiline shapes – a series of multiple narrow emission lines with average line width $\Delta\lambda \leq 1$ Å. Laboratory analogs of such spectra are called quasilinear photoluminescence spectra of the Shpolskii matrix (Figures 1, 2). Photoluminescence spec-

tra of the cometary frozen hydrocarbons could also show wide, featureless bands (the case of resonance dimmers). Such featureless bands may be observed as a quasicon-
tinuum. A similar phenomenon was reported by Churyumov and Kleshchenok (1999) and Churyumov et al. (2013). The width of emissions and general character of luminescence spectra of a Shpolskii matrix depends also on the temperature of the polycrystalline mixtures. Microcrystals of aliphatic (linear chains) matrix provides a quasilinear nature of the luminescence spectrum of PAHs frozen in this matrix (Shpolskii 1959). For a glass-like (the certain derivatives – for example acphols) matrix, the same PAHs demonstrate featureless luminescence emissions. For comets, it probably means that quasi-continuum luminescence emissions belong to amorphous mixtures of hydrocarbons. Narrow luminescence emissions indicate PAHs in an n-alkane matrix, that is, crystalline FHPs. The detection of luminescence emissions can be a qualitative tool for determination of the state of hydrocarbons in cometary substance. The materials constituting the deep inner parts of comets nuclei, including hydrocarbons, that have never been processed by solar radiation have primordial properties. These unaltered materials can be called cometary relicts. We note, however, that energetic cosmic rays penetrate comet nuclei to a depth of a few meters, causing changes in the structure and chemistry of the ices and minerals. Properties of cometary relict substance are: 1) low temperature; 2) complex matter with pristine structural features; 3) absence of ionized and implanted compounds; 4) possible presence of prebiotics; 5) isotopic ratios for principal elements with characteristic for the Solar System (Simonia and Simonia 2013, 2014). The *in situ* investigation of comet 67P/CG by Rosetta demonstrated that some of the outer layers of the nucleus were removed when the comet was close to the Sun. Both solid particles and gas ejected from deeper layers contain prebiotic molecules (Altwegg et al. 2016) and numerous other volatile molecules and refractory organics (Le Roy et al. 2015; Quirico et al. 2016).

Cometary relicts, including frozen hydrocarbons, lying deep inside the nucleus have never been illuminated by solar radiation, and the nucleus is too small to have been heated significantly either by gravitational compression or by the inclusion of large quantities of radiogenic elements. Comets with long orbital periods are the principal reservoirs of the relict substance of the Solar System. In time of active cometary processes, including outbursts, fragments of relict hydrocarbon-rich material may be delivered into the coma. Incident solar radiations could excite photoluminescence and cathodoluminescence of the relict organics newly delivered from the depths of the nu-

Figure 1. The spectra of quasilinear photoluminescence of perylene in n-hexane (Nakhimovsky et al. 1989).

Figure 2. The spectrum of quasilinear photoluminescence of naphthalene in n-nonane (Nakhimovsky et al. 1989).

cleus. Depending on the chemical composition and the physical properties of the concrete relicts, such luminescence can be in the form of featureless bands or structured quasilinear spectra. The duration of the luminescence of relicts may be short, because the intense luminescence emissions may be quenched by solar infrared radiation. Complex molecules of such relict matter may be dissociated into daughter molecules by exposure to the solar UV. Taking into account the high quantum yield of hydrocarbon luminescence it seems clear that ground-based observations for the detection of relict organic luminescence must be made at the times of outbursts or immediately after afterward. Radiative unprocessed cometary relicts may be characterized with high luminescence quantum yield and the specific spectral features of such a luminescence. Laboratory investigations of luminescence of frozen organics demonstrated, that quantum yield of luminescence of such substance varies from 90% to 100% (Gudipati et al. 2003). In case of low albedo of cometary frozen organic relicts ground-based detection of such a phenomena may be possible. Organics of comets in the form of shells of icy grains may be quickly processed by solar radiation. It means that, within 6-8 hours after outburst the luminescence properties of the relict material will be lost or changed. Outburst spectra of comets have shown

Figure 3. Spectra of photoluminescence of Pyrene and 3-4 Benzopyrene (Shpolskii 1962).

featureless emissions in range 3990–5800 Å (Cochran et al. 1980). Polycrystalline mixtures may demonstrate the luminescence bump at the similar spectral range (figure 3). The presence of complex organics in cometary ice may cause the specific colors of cometary nuclei (e.g. Hartman et al. 1987). The ices of inner layers of icy satellites and certain TNO's may have a similar chemical composition and structural peculiarities to that of compressed snow with PAHs in n-alkanes. The presence of frozen hydrocarbon matter in icy satellites might be confirmed in measurements of the colors of the surfaces of planetary satellites, as well as Centaurs and Kuiper Belt objects. Indeed, the colors of Pluto and some planetary satellites are most likely caused by the processing of hydrocarbons (notably CH_4) by solar ultraviolet and charged particles. This processing erases the intrinsic signatures of the hydrocarbons, leaving a refractory macromolecular material termed “tholin”, as described in a later section of the present paper.

3 Frozen organics of comets - results of comparative analysis

Frozen hydrocarbon particles as constituent of icy halos of comets may photoluminesce in the field of solar ultraviolet radiation. Numerous narrow unknown emission lines of the spectra of comets may have such photoluminescence nature – 4623.31 Å, 4769.04 Å, 4874.10 Å, 5028.42 Å, 5197.20 Å, 5318.22 Å, 5615.20 Å, 6134.99 Å, 6638.21 Å (Simonia 2007). Aromatic and aliphatic hydrocarbons are principal components of FHP substance. At the same time, complex molecules in the form of rings and their structures, may compile the principal elements or bases for self organized substance of FHP. The field of solar radiation may provide energy for transformations or evolution

of such self-organized substance of cometary relicts. Interaction: solar electromagnetic, corpuscular radiation – cometary relicts, may have high significance within process of formation of potential prebiotics in cometary substance. Bombardment of cometary relicts by the solar electrons and protons may stimulate certain processes in self-organized substance of such relicts. The important conditions for self-assembled processes in cometary relicts might be: 1) penetration of solar radiation in the inner layer of comet nuclei substance. 2) Possibility of absorbed energy accumulation by the cometary relict ices (Simonia 2016). 3) Charges transmission and sharing electrons pairs appearance in molecular systems of cometary relict ices in conditions of low temperatures ($T < 80$ K). 4) Presence of aromatic compounds in cometary relicts. For different comets (for example long periodic) on the different heliocentric distances interaction: solar radiation-cometary substance might be different in characteristics. Therefore, self-assembled processes in molecules of cometary relicts may have different peculiarities.

Possible cometary prebiotics and self-organized substance search remains significance task. Following on the recent results of the Rosetta investigation of 67P/Churyumov-Gerasimenko (Altwegg et al. 2016) it is expected that the nuclei of most, and perhaps all comets contain prebiotic compounds, possibly including certain types of self-organized matter such as heterocycles, proteins, etc. Photoluminescence of self-organized matter might be excited by solar ultraviolet. FHPs of comets with prebiotic compounds may luminesce in the optical range in the form of quasilinear spectra (Simonia and Simonia 2013, 2014; Gudipati et al. 2015). We have compared spectral positions of the cometary unidentified emissions with luminescence emissions of enzymes, pigments and proteins (Simonia and Simonia 2014). Results are given in Table 1.

On the basis of our comparative analysis, we suggest a new hypothesis that chlorophyll-like, porphyrin-like, and photoprotein-like molecules might be present in relict ice throughout the Galaxy, including cometary relict ices both of Solar System comets and exo-comets as well. Our hypothesis suggests that cometary ices, especially frozen organic relicts, could contain the structural analogs of prebiotics, self-organized matter. The example of such an analogy might be the possible presence of the phthalocyanine molecule in the cometary ice. Phthalocyanine is the structural analog of the porphyrin molecule (Kadish et al. 2010). Oxygen atoms provide excitation of luminescence of prebiotics, including proteins and pigments. Photoluminescence of the structural analogs (phthalocyanine) is excited by UV photons and solar UV could excite photolumines-

Figure 4. Fluorescence spectrum of chlorophyll “b” in n-undecane at 4.2 K. (Personov et al. 1974).

Figure 5. Fluorescence spectrum of Zn-phthalocyanine in paraffin oil at 4.2 K. (Personov et al. 1974).

cence of frozen phthalocyanine in the cometary material.

In many cases luminescence emissions of various prebiotics have a featureless character, appearing as rather wide bands (at room temperature). However, the results of several experiments demonstrate that different heterocycles, pigments, and prebiotic molecules dissolved in an organic matrix ($T < 80$ K) have standard quasilinear luminescence spectra (Platenkamp and Canters 1981; Avarmaa and Rebane 1988) Figure 4, 5, 6, 7. In other words, a Shpolskii matrix in the form of frozen polycrystalline mixture (heterocycles, prebiotics in n-alkanes) luminesces as a series of very narrow emission lines. In this case, luminescence of such mixtures is excited by ultraviolet radiation. This suggests that series of very narrow unidentified emission lines found in cometary spectra might represent lumi-

Figure 6. Fluorescence (upper trace) and phosphorescence (lower trace) of Cd-tetrabenzoporphyrines in n-octane at 4.2 K. (Platenkamp and Canters 1981).

Figure 7. Fluorescence spectra of chlorophyll-a in toluene at 4.2 K. (Avarmaa and Rebane 1988).

nescence of FHPs with possible prebiotic compounds (Simonia and Simonia 2014).

Table 1. Unidentified cometary emissions and bioluminescence maxima of the terrestrial prebiotics, heterocycles, and pigments. Possible inventory of organics for exo-comets. The first column of the table – comets names; second column – unidentified emissions of comets (angstrom); third column – maxima of luminescence emissions of various substance; the fourth – specific materials' type; fifth column – references for luminescence data.

Comets	λ unid	λ Bioluminescence	Substance	Reference
De Vico	5380.88	5380	luciferase	Ugarova and Brovko 2002
	5459.97	5460	luciferase	Ugarova and Brovko 2002
	5509.39	5510	luciferase	Viviani et al. 2007
	5520.97	5520	luciferase	Viviani et al. 2007
	5620.68	5620	luciferase	Ugarova and Brovko 2002
	5649.117	5650	luciferase	Viviani et al. 2007
	5710.11	5710	luciferase	Ugarova and Brovko 2002
	5719.24	5720	luciferase	Viviani et al. 2007
	5730.57	5730	luciferase	Viviani et al. 2007
	5759.36	5760	luciferase	Ugarova and Brovko 2002
	5780.54	5780	luciferase	Ugarova and Brovko 2002
	5790.49	5790	luciferase	Ugarova and Brovko 2002
	5800.10	5800	luciferase	Ugarova and Brovko 2002
	5819.92	5820	luciferase	Ugarova and Brovko 2002
	5820.33	5820	luciferase	Ugarova and Brovko 2002
	5840.66	5840	luciferase	Ugarova and Brovko 2002
	5860.56	5860	luciferase	Ugarova and Brovko 2002
	5879.77	5880	luciferase	Viviani et al. 2007
	5920.13	5920	luciferase	Viviani et al. 2007
	5930.60	5930	luciferase	Ugarova and Brovko 2002
	5940.52	5940	luciferase	Ugarova and Brovko 2002
	5950.72	5950	luciferase	Viviani et al. 2007
	6040.77	6040	luciferase	Viviani et al. 2007
	6060.32	6060	luciferase	Ugarova and Brovko 2002
	6070.22	6070	luciferase	Ugarova and Brovko 2002
	6079.27	6080	luciferase	Ugarova and Brovko 2002
	6099.35	6100	luciferase	Viviani et al. 2007
	6109.27	6110	luciferase	Viviani et al. 2007
	6122.39	6123	luciferase	Ugarova and Brovko 2002
	6130.63	6130	H ₂ Porphirin	Ugarova and Brovko 2002
	6135.00	6135	luciferase	Osad'ko 1979
	6146.14	6146	H ₂ Porphirin	Osad'ko 1979

Continued on next page

Table 1. ...continued

Comets	λ unid	λ Bioluminescence	Substance	Reference
Ikeya-Zhang	6148.20	6149	H ₂ Porphirin	Osad'ko 1979
	6159.73	6160	luciferase	Viviani et al. 2007
	6180.91	6180	luciferase	Ugarova and Brovko 2002
	6210.04	6210	luciferase	Viviani et al. 2007
	6219.91	6220	luciferase	Ugarova and Brovko 2002
	6818.02	6818	Chlorophyll	Jovanić and Dramićanin 2003
	6859.33	6860	Chlorophyll a	Erokhina et al. 2002
	7350.53	7350	Chlorophyll	Jovanić and Dramićanin 2003
	4630.153	4630	luciferin	Shimomura 2006
	4630.388	4630	luciferin	Shimomura 2006
	4649.478	4650	Aequorin+Ca ²⁺ (photoprotein)	Shimomura 2006
	4649.917	4650	Aequorin+Ca ²⁺ (photoprotein)	Shimomura 2006
	4750.938	4750	Obelin+Ca ²⁺ (photoprotein)	Shimomura 2006
	4800.920	4800	Luciferin	Shimomura 2006
	4850.474	4850	Photoprotein+Ca ²⁺	Shimomura 2006
	4850.680	4850	Photoprotein+Ca ²⁺	Shimomura 2006
	4899.811	4900	luciferin	Shimomura 2006
	4900.788	4900	luciferin	Shimomura 2006
	4949.918	4950	luciferase-oxyluciferin	Shimomura 2006
	4969.310	4970	Green Fluorescent Protein	Shimomura 2006
	4979.702	4980	Green Fluorescent Protein	Shimomura 2006
	5030.540	5030	luciferine	Shimomura 2006
	5230.606	5230	Obelin+Ca ²⁺ (photoprotein)	Shimomura 2006
	5280.241	5280	Isothiocyanate	Shimomura 2006
	5339.280	5340	luciferase	Shimomura 2006
	5339.477	5340	luciferase	Shimomura 2006
	5339.741	5340	luciferase	Shimomura 2006
	5340.130	5340	luciferin	Ugarova and Brovko 2002
	5350.441	5350	luciferin	Ugarova and Brovko 2002
	5350.771	5350	luciferin	Ugarova and Brovko 2002
	5350.875	5350	luciferin	Shimomura 2006
	5359.122	5360	luciferin	Shimomura 2006
	5359.250	5360	luciferin	Shimomura 2006
	5360.295	5360	luciferin	Shimomura 2006

Continued on next page

Table 1. ...continued

Comets	λ unid	λ Bioluminescence	Substance	Reference
	5369.835	5370	luciferin	Ugarova and Brovko 2002
	5370.734	5370	luciferin	Ugarova and Brovko 2002
	5379.364	5380	Green Fluorescent Protein	Shimomura 2006
	5379.480	5380	Green Fluorescent Protein	Shimomura 2006
	5379.770	5380	Green Fluorescent Protein	Shimomura 2006
	5380.892	5380	Green Fluorescent Protein	Shimomura 2006
	5401.419	5400	luciferin	Shimomura 2006
	5450.064	5450	luciferase	Shimomura 2006
	5459.960	5460	luciferase	Ugarova and Brovko 2002
	5520.942	5520	luciferase	Ugarova and Brovko 2002
	5620.727	5620	Luciferase-oxyluciferin	Shimomura 2006
	5649.117	5650	luciferase	Ugarova and Brovko 2002
	5790.830	5790	luciferase	Shimomura 2006
	5800.090	5800	luciferase	Ugarova and Brovko 2002
	5819.947	5820	luciferase	Ugarova and Brovko 2002
	5830.	5830	Green Fluorescent Protein	Shimomura 2006
	5839.545	5840	luciferase	Ugarova and Brovko 2002
	5860.572	5860	luciferase	Ugarova and Brovko 2002
	5879.810	5880	luciferase	Ugarova and Brovko 2002
	5940.515	5940	luciferase	Shimomura 2006
	5950.720	5950	luciferase	Shimomura 2006
	6040.752	6040	luciferase	Shimomura 2006
	6060.306	6060	luciferase	Shimomura 2006
	6070.963	6070	luciferase	Shimomura 2006
	6130.630	6130	luciferin	Shimomura 2006
	6150.958	6150	luciferase	Shimomura 2006
	6239.300	6240	luciferase	Shimomura 2006
	6818.013	6818	Chlorophyll	Jovanić and Dramićanin 2003
	7336.250	7336	Chlorophyll	Jovanić and Dramićanin 2003
Hale-Bopp	5800.90	5800	luciferase	Ugarova and Brovko 2002
	6818.85	6818	Chlorophyll	Jovanić and Dramićanin 2003

Concluded

We have investigated the spectra of several comets in search of possible prebiotic emissions of compounds of similar structure. We studied optical cometary spectra in the range of 3900 – 8000 Å. We could not find any prebiotic emissions in the spectra of comets Ikeya-Zhang, and de Vico (Cochran and Cochran 2002; Cremonese et al. 2007). At the same time, we found possible prebiotic emissions in the spectrum of comet C/2004 Q2 Machholz (Figure 8). In particular, two earlier unidentified emissions in the spectrum of this comet are correlated in spectral positions and profiles with fluorescence emissions of Cd-tetrabenzoporphyrine (Figure 6). It will be useful to obtain integral images of cometary coma in these bands.

We do not consider the results we have obtained so far to be the final identification of unknown cometary emissions. Instead, our results show the possibilities of the presence of prebiotic materials and their structural analogs in the cometary ices. At the same time the organic material noted here, including prebiotics, may exist in icy planetary satellites and TNO's in the outer Solar System. The next part of this paper explores some aspects of the presence of primitive organic matter on three of Saturn's icy satellites.

4 Refractory organics on planets and planetary satellites – data analysis

The detection of organic complexes, both the soluble and the insoluble fractions, in the carbonaceous meteorites (e.g. Alexander et al. 2008), and CHON (carbon, hydrogen, oxygen, nitrogen) particles detected in comets (e.g. Jenniskens et al. 1991; Lawler and Brownlee 1992; Fomenkova 1999; Briani et al. 2012) reinforces the view that organic solids occur throughout the Solar System, and that they were incorporated into solid bodies at the time of their formation. Flynn et al. (2003) have presented evidence from the analysis of interplanetary dust particles that the bulk of the prebiotic organic matter in the Solar System did not form by aqueous processing, but had already achieved its structure at the time of its origin in the interstellar medium, in the solar nebula, or both. The organic matter in the carbonaceous meteorites does, however, show evidence of chemical alteration by the presence of liquid water (e.g. Pizzarello and Shock 2010), a condition that is unlikely to occur in comet nuclei and on the surfaces of most planetary satellites. At the same time, most of the carbon compounds found in meteorites carry isotopic compo-

sitions that date their formation to the presolar space environment (Wopenka et al. 2013). The ancient organics in comets can also be expected to bear isotopic signatures of ancient origin.

We consider here the organic solid material that occurs on the surfaces of some planetary satellites, and speculate on its origin from the same feedstock as that from which the comets condensed in the solar nebula. Small particles of complex organic matter produced by photochemical processing of gases occur in the upper atmospheres of several planetary bodies, such as Titan, Triton, Saturn, and Pluto, primarily as a consequence of ultraviolet processing of methane gas. In certain cases, nitrogen is also a key component, and oxygen also contributes to the resulting chemical composition. The occurrence of refractory macromolecular organic material on the surfaces of many planetary satellites in the outer Solar System (distance from the Sun >5 astronomical units) is inferred from the colors of these bodies (i.e. Phoebe, some Centaurs, etc). The spectroscopic signatures of this material are primarily found in a region of the infrared spectrum where groundbased astronomical observations of small outer Solar System bodies are not possible. Macromolecular organic solids produced in the laboratory under conditions that reasonably simulate the space environment acting on native materials on planetary surfaces and in their atmospheres, are distinctively colored, usually in a range from yellow to red-orange and brown. The measurement of closely similar colors on planetary bodies leads in several cases to the logical inference that those surfaces contain a macromolecular organic component (e.g. Cruikshank et al. 2005; Kargel 2007; Waite et al. 2009; Scipioni et al. 2014), even if diagnostic spectral bands cannot be detected.

Macromolecular organic solids produced in the laboratory by the energetic processing (by ultraviolet, electrons, protons, cold-cathode discharges, etc.) of gases and ices that include CH₄ and other simple molecules are called tholins (Khare et al. 1984). Most of the production and analysis of tholin has been undertaken in the gas phase in the context of the photochemical haze in the atmosphere of Titan, known to have an atmosphere primarily of N₂ and CH₄, but with other molecules in small concentrations (e.g. Coll et al. 1999; Imanaka et al. 2004). There are many recent papers on Titan tholins, but a complete review is beyond the scope of the present paper.

Colored refractory residues called ice tholins are produced by the UV photolysis or charged-particle radiolysis of pure or mixed ices (e.g. McDonald et al. 1996). The analysis of these residues, for example from processing of a mixture of N₂, CH₄, and CO ices, reveals the presence of carboxylic acids, urea, HCN and other nitriles, alcohols, ke-

Figure 8. Fragment of the spectrum of comet Machholz (C/2004Q2). We found that 6289.88 Å and 6290.64 Å unidentified emissions (red arrows) are correlates in positions and profiles with fluorescence emissions of Cd-tetrabenzoporphyrine (Figure 6, red arrows). The spectrum of comet Machholz was obtained by Sung-Won et al. (2009).

tones, aldehydes, and amines, with other unidentified materials of high molecular weight (several hundred Da) (e.g. Materese et al. 2014, 2015). These materials are expected to be present and to provide coloration to the surfaces of Neptune's satellite Triton, and Pluto, where N_2 , CH_4 , and CO ices are known to be present (Cruikshank et al. 1993; Owen et al. 1993).

Colors in macromolecular solids originate from electronic transitions when σ or π bonding and n non-bonding orbitals are promoted to anti-bonding orbitals σ^* or π^* by the absorption of UV photons. Chromophores thus produced are efficient in absorbing visible light, especially when conjugated molecules (unsaturated compounds with alternating single and double bonds) are present. In general, the longer the conjugated chain, the farther into the visible spectral region the absorption extends, thus producing a range of colors from yellow to red, and a significant decrease in the overall reflectance (albedo, in astronomical terms). The absorption in solids arising in this manner does not occur at narrow or discrete wavelength intervals, and is therefore not directly diagnostic of specific molecules.

Clearly, colored organic material currently or recently formed in planetary atmospheres or by radiation-induced chemical reactions on planetary surfaces is not relict material, but a special case found in the Saturn system may be relevant to the discussion of ancient organics in comets.

A new perspective on the organic content of material either created in situ or deposited on planetary surfaces comes from a study of the satellites of Saturn accomplished with the *Cassini* spacecraft. Iapetus is the outermost large satellite of Saturn (diameter 1492 km), and it has long been known that the hemisphere facing the

direction of its orbital motion around Saturn has a deep red color and very low reflectivity. This unusual property is attributed to the sweeping up of dust particles as the body moves through space, and its color properties suggest that these particles are organic-rich. Prior to the *Cassini* mission, the spectral characteristics of the dark red material did not reveal diagnostic bands that would identify its composition, nor could the source of the dust particles accumulating on Iapetus' leading hemisphere be reliably established (Tosi et al. 2010; Cruikshank et al. 2014).

The source of the dust encountered by Iapetus in its orbital path is Saturn's more distant satellite, Phoebe, which, because of its irregular orbit, is widely presumed to have originated elsewhere in the Solar System (beyond 30 AU) and was subsequently captured into its current orbit around the planet (e.g. Johnson and Lunine 2005). Dust and other debris ejected from Phoebe by the impact of another (unknown) asteroidal or cometary body is dispersed in an enormous ring centered on Saturn and filling the orbit of Phoebe (Verbiscer et al. 2009). Small particles ($\sim <10$ μm), spiral inward toward Saturn and encounter Iapetus on route, where they accumulate to a depth of a few tens of centimeters (measured by the *Cassini* radar experiment) primarily on the leading hemisphere (Tamayo et al. 2011). The dark red debris from Phoebe is apparently accumulating in the present epoch because the ring, is clearly evident from its infrared thermal signature, and the dust layer on Iapetus is very young, judged from the paucity of craters left by penetrating meteoroid impacts.

The imaging spectrometer on the *Cassini* spacecraft obtained spectral images of Iapetus in the range 0.3-5.1 μm of surface units as small as a few kilometers in size. The spectrum of the dark red material shows a broad absorp-

tion band centered near $3.0\text{ }\mu\text{m}$ attributed to H_2O ice and OH in the surface materials. Additionally, there are two absorption band complexes centered at 3.28 and $3.4\text{ }\mu\text{m}$ attributed, respectively, to aromatic and aliphatic hydrocarbons in the solid material covering the surface (Cruikshank et al. 2008, 2014; Dalle Ore et al. 2012). The spectral evidence is insufficient to permit the identification of specific molecular species, but the relative abundances of the aromatic and aliphatic components can be estimated from the measured band widths and optical thickness, and the relative abundances of $-\text{CH}_3$ and $-\text{CH}_2-$ aliphatic moieties can be determined. Both of these parameters can be compared quantitatively to laboratory compositional studies of interplanetary dust particles (from asteroids and comets), dust particles from comet 81P/ Wild returned to Earth from the *Stardust* spacecraft, and meteorites, and also to astronomical results for the interstellar medium in our galaxy and other galaxies.

The suite of aromatic molecules that can contribute to the unresolved absorption envelope in the Iapetus spectrum includes a suite of neutral polycyclic aromatic hydrocarbons for which theoretical calculations have been made by Bauschlicher et al. 2008, 2009, and Ricca et al. 2012. Aromatic molecular structures revealed by their peripheral CH or CH_n bands can be arbitrarily large in size, because only those peripheral bonds with hydrogen produce detectable bands in the $\sim 3.28\text{-}\mu\text{m}$ region. Consequently, the total molecular mass of aromatics can be large, as it seen with interplanetary dust particles, comets samples, meteorites, and micrometeorites. In the spectra of astronomical objects that can be observed only in limited wavelength regions, a large amount of carbon remains unseen. The absorption envelope centered at $\sim 3.45\text{ }\mu\text{m}$ is characteristic of $-\text{CH}_2-$ and $-\text{CH}_3$ symmetric and asymmetric overtones in aliphatic molecules; these four bands are found in absorption in galactic interstellar dust (e.g. Pendleton et al. 1994) and in some external galaxies (Dartois et al. 2004). Other molecular materials that may be contributing to the absorption on Iapetus include CH in cycloalkane, olefinic CH and CH_2 , CH_3OH ice, and CH_3 +lone pair electrons in N and O (Cruikshank et al. 2014).

While some extraterrestrial materials studied in the laboratory are found to contain aromatic molecular material, the remote spectroscopic study with telescopes and spacecraft is the only available technique for the majority of Solar System bodies. The detection of organic molecules is thus limited to those with spectroscopically active modes that lie within the observable spectral ranges. In this respect, many extraterrestrial materials (comet particles, micrometeorites, interplanetary dust particles, etc.) are known to contain aromatic material,

but it is very weakly seen or absent in spectra in the $3.3\text{-}\mu\text{m}$ region. Consequently, the appearance of the aromatic spectral band on Iapetus indicates a high relative abundance of this material, of order eight to ten times that of the aliphatic components. On the other hand, the relative abundance of $-\text{CH}_2-$ and $-\text{CH}_3$ groups, an index of the length of aliphatic chains, is comparable to that of aliphatics in the interstellar medium.

The significance of the organic solids on Iapetus is that their source appears to be the interior of the distant Saturn satellite Phoebe, a captured Kuiper Belt object. Phoebe, in turn, inherited the organic inventory from the solar nebula in which it accreted, probably at a heliocentric distance somewhat greater than 20 AU. The degree to which the condensable organics in the solar nebula reflect the original composition of the Solar System's nascent molecular cloud and what degree of processing occurred in the nebula are unknown (Pendleton and Cruikshank 2014). However, some primitive meteorites and interplanetary dust particles carry a D/H isotopic signature very similar to that of interstellar organic molecules (Pizzarello et al. 2006), and some meteorites contain unaltered interstellar grains (Davis 2011). As noted above, other isotopes in meteorites date their component materials to presolar times. These characteristics show that at least some original molecular cloud components were cycled through the solar nebula and survived during the condensation of planetary bodies without being completely chemically altered.

The material from which Phoebe accreted should be some combination of interstellar ices and mineral grains, plus solid organic matter and some fraction of the same material processed in the solar nebula. It is in this sense that the comparison to relict carbonaceous molecules in comets may be relevant, since Phoebe can, by virtue of its bulk composition and its capture from a distant region in the Solar System, be considered a member of the comet clan, albeit a very large one. The dominant form of carbon in interstellar dust includes hydrogenated amorphous carbon (Pendleton and Allamandola 2002), as well as polycyclic aromatic hydrocarbons (PAHs), which are relatively refractive. In solar nebula models by Kress et al. (2010), PAHs are destroyed inward of $\sim 2\text{ AU}$, while less stable aliphatic hydrocarbons are destroyed at somewhat greater solar distance. Thus, the presence of both aromatic and aliphatic hydrocarbons in the dust emanating from Phoebe is consistent with their formation and preservation at substantially greater radial distances. Interstellar ices carry inclusions of small dust particles consisting of hydrocarbons and more refractory kerogen-like macromolecular organic solids. The kerogens originate in interstellar

space by UV irradiation of ices on grains of carbon and silicates, and the resulting coated grains were incorporated into the solar nebula. Beyond the zone of terrestrial planet formation, some of the kerogens, together with silicates, became the refractory component of Kuiper Belt objects, carbonaceous meteorites, and other icy bodies, some of which are now satellites of the outer planets. Astronomical kerogen is similar to some synthetic tholins; the distinction between the two classes of organic solids is not great. Prolonged exposure of tholins to the space environment (both UV and charged particle radiation) causes them to darken and eventually become black as they are dehydrogenated and evolve chemically toward spectroscopically featureless graphite (Pendleton et al. 2011). A similar strategy of consideration can be applied for another satellite – Hyperion.

Early results of the *in situ* analysis of 67P/CG comet by the Rosetta mission indicate that the visible surface consists largely of a mixture of opaque minerals and complex macromolecular organic material containing carbon-hydrogen and/or oxygen-hydrogen chemical groups (Cappacconi et al. 2015). Direct chemical analysis on the comet's surface by the Philae lander has detected a number of volatile organic molecules with various combinations of carbon, hydrogen, oxygen, and nitrogen, up to molar mass 62 (Goesmann et al. 2015). These include some of the same chemical groups found in the laboratory synthesis of organic residues by Materese et al. (2015) noted above. The low albedo and reddish color of the surface of this and other comets, together with the direct analysis of 67P supports the contention that comet surfaces are generally dark and red or black in color as a consequence of the presence of organic solids, and that they are likely to be related compositionally to some of the distant asteroids that may be extinct comets (e.g. Hartman et al. 1987).

There appears to be a wide variety of macromolecular organic materials in the Solar System depending on the initial composition of the component molecules and the degree of energetic processing and subsequent chemical evolution. Perhaps more significant are the similarities among them in terms of basic chemical groups they contain. Their colors are varied, but arise from the same fundamental molecular mechanism, and they are retained on planetary surfaces when the more volatile ices are removed. In the specific case of Phoebe and Iapetus in the Saturn satellite system, we will gain further insight when observations are capable of determining the inventory of organic materials that exist in distant Kuiper Belt objects, and thus clarify the possible link to the organics inherited from the Solar System's nascent molecular cloud.

5 Discussion

Frozen hydrocarbons are components of ices of comets. It can be expected that various layers of nuclei of comets are rich with complex aromatics and aliphatics. Frozen cometary hydrocarbons consist of unified structures including solid solutions, polycrystalline mixtures, and substitutional matrices. It has been noted (e.g. Oró et al. 2006), there may be a connection of the complex organic chemistry of comets that includes prebiotic components to the origin of life. Solar ultraviolet radiation, flux of electrons and protons, and the structure of cometary organics would appear to stimulate luminescence phenomena in organic-rich cometary ice that may be detectable. We have suggested that a Shpol'skii matrix in the form of polycrystalline mixtures (PAHs in n-alkanes) might be a significant component of the complex organic substance comprising a major fraction of a comet's mass.

Hydrocarbon sources irregularly distributed in the inner layers of nuclei of comets that have not been processed by solar radiation are cometary relicts. In time of cometary outbursts certain portions of such relict matter is injected into cometary coma where it is subsequently photoexcited. The de-excitation of previously excited molecules (relict molecules) then gives rise to bright luminescence emission. Optical spectra of the cometary bursts could be rich in unknown emission lines or featureless bands especially in the blue range. Photoluminescence spectra of polycyclic aromatic hydrocarbons at temperatures $T > 100$ K have a featureless character in the form of extended blue emission (3990-4910 Å).

Our results have demonstrated potential presence of prebiotics and self-organized substance in ices of comets. The results of our comparative analysis and evidence of similarities of the luminescence properties of porphyrins and their structural analogs might become a qualitative tool for identification of prebiotics and heterocycles during *in situ* experiments (comets, icy satellites, and TNOs). At the same time, similarities in optical properties of complex organics and prebiotics require substantial additional laboratory investigations.

Understanding of process of self-organized substance formation in the space environment has high significance. Formation of self-organized substance in the small bodies of the Solar System might be limited by the following pre-conditions: 1) presence of small icy nuclei cloud in the peripheral part of the Solar System; 2) bombardment of small icy nuclei by the solar and galactic cosmic rays; 3) absorption and accumulation of cosmic ray energy by atomic and molecular systems of relict substance of icy

nuclei; 4) long time preservation of accumulated energy by relict substance of icy nuclei; 5) expenditure of accumulated energy for formation of various type of chemical bonds in molecular systems of relict substance of icy nuclei; 6) abundance of organic compounds in icy nuclei.

Icy cometary nuclei and TNO's substance may absorb and accumulate also the solar electromagnetic radiation on the various heliocentric distances. Expenditure of absorbed energy for providing of the concert type of chemical bond may be a variable process depending on heliocentric distances of icy nuclei. We cannot exclude that formation of self-organized substance of cometary nuclei might be efficient on the large heliocentric distances. The role of radioactive isotopes of cometary ices may be significant in context of formation of self-organized substance.

6 Conclusion

We have considered in this paper, probable presence of frozen hydrocarbon matter in ices of the Solar System, including comets, planetary satellites and TNOs. We have described particularly important physical and chemical peculiarities of such frozen complex organic substance. We have discussed also properties of frozen hydrocarbon particles (FHP) in coma of comets. The probable UV-induced luminescence of prebiotic molecules (enzymes, pigments and proteins) in FHPs may produce optical emission lines coincident in wavelength with a number of unidentified emission lines in comet spectra. This leads to the speculative preliminary conclusion that prebiotics, pigments, and heterocycles, including luciferin and molecules similar to chlorophyll and porphyrins might be included in the inventory of cometary organic relict matter, especially in context of potential exo-cometary research. Of course, the hypothesis we have outlined here requires confirmation, both from additional observations of comets and from additional laboratory work. The potential of detection of prebiotic molecules through their luminescence signatures in comet spectra indicates that a new observational strategy should be implemented, both for Solar System comets and for exo-comets. In the latter case, potential luminescence emissions might be converted to resonance absorptions (at the same wavelengths) that may be detectable in young planetary systems having dense icy clouds in which exo-comets and exo-TNO are forming. Spectra of such systems with high resolution and high signal precision may reveal absorption bands diagnostic of the presence of prebiotic molecules.

Further, we summarize recent studies of the organic spectral signature of three satellites of Saturn observed with the Cassini spacecraft in orbit around the planet. The unique characteristics of this trio of satellites are that they show the spectral signatures of both aromatic and aliphatic hydrocarbons, and the material displaying these signatures originated in the interior of the satellite Phoebe. Phoebe originated far from the Sun in the Kuiper Belt region and was later captured by Saturn. Its origin in the same region as the comets are thought to have condensed strongly suggests strong compositional similarities, including the inventory of included organics. Thus, material ejected from Phoebe's interior by impact and subsequently landing on the surfaces of Iapetus and Hyperion may reasonably be expected to carry the same compositional characteristics as the material in comets, as well as the implications of great age and genetic connections to the solar nebula.

Both the concept of the ejection of frozen hydrocarbon particles from comets and the dispersal of primitive organics by impact into a body like Phoebe speak to the widespread distribution of a rich inventory of relict molecular material of prebiotic interest.

Acknowledgment: Authors express their gratitude to anonymous reviewer for the valuable discussion.

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