

ION IRRADIATION OF ASPHALTITE: OPTICAL EFFECTS AND IMPLICATIONS FOR TRANS-NEPTUNIAN OBJECTS AND CENTAURS

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Abstract. Trans-Neptunian Objects (TNOs) and Centaurs show remarkable colour variations in the visual and near-infrared spectral regions. Surface alteration processes such as space weathering (e.g., bombardment with ions) and impact resurfacing may play an important role in the colour diversity of such bodies. Ion irradiation of hydrocarbon ices and their mixtures with water ice transforms neutral (grey) surface colours of ices to red and further to grey. Along with the ices, TNOs and Centaurs probably contain complex carbonaceous compounds, in particular, complex hydrocarbons. Unlike ices, such refractory organic materials have originally low visual albedos and red colours in the visible and near-infrared ranges. Here we present the first results of ion irradiation experiments on asphaltite. Asphaltite is a natural complex hydrocarbon material. The reflectance spectra of asphaltite in the 0.4–0.8 μm range have been recorded before irradiation and after each irradiation step. We demonstrate that irradiation of this red dark material with 30 keV H^+ and 15 keV N^+ ions gradually transforms its colour from red to grey as a result of carbonization. A moderate increase in the visual albedo has been observed. These results may imply that the surfaces of primitive red objects optically dominated by complex refractory organics may show a similar space weathering trend. Our laboratory results were compared with published colours of TNOs and Centaurs. A broad variety of spectral colours observed for TNOs and Centaurs may be reproduced by various spectra of irradiated organics corresponding to different ion fluences. However, such objects probably also contain ices and silicate components which show different space weathering trends. This fact, together with a lack of information about albedos, may explain difficulties to reveal correlations between surface colours within TNO and Centaur populations and their other properties, such as absolute magnitudes and orbital parameters.



1. Introduction

Dark primitive small bodies of the solar system – low albedo asteroids, cometary nuclei, TNOs, Centaurs, dark planetary satellites – are known to show a variety of surface colours (Cruikshank, 1987; Hartmann, 1999). While geometric albedos remain relatively low, their visible and near-infrared spectral slopes may range from neutral (grey) to positive (red). One possible reason for the reddish colours of dark distant objects may be a formation of certain organic products on their surfaces due to space weathering of the ice components (Thompson et al., 1987; Andronico et al., 1987). Alternatively, red colors of the reddest and least-evolved dark objects may result from the presence of intrinsic complex refractory hydrocarbon components (Moroz et al., 1998). Aromatic and aliphatic hydrocarbons are found in carbonaceous meteorites, IDPs, and cometary dust, they are widespread in interstellar medium (Hayatsu and Anders, 1981; Kissel and Krueger, 1987; Pendleton and Chiar, 1997). It is reasonable to suggest that such organics may be significant components of many dark distant objects of the solar system including TNOs and Centaurs. In order to provide red colors in combination with low albedos, such materials should be structurally disordered, having relatively high H/C ratio and relatively low carbon aromaticity (a fraction of aromatic C with respect to aliphatic C) (Moroz et al., 1998). Thermal evolution of such organics results in carbonization accompanied by a loss of H, structural ordering, increasing aromaticity, growth of large polycyclic aromatic clusters, and decreasing spectral slope without a significant change in the visual albedo (Moroz et al., 1998).

A general decrease in the spectral slope within a population of distant dark objects with decreasing solar distance is well-documented. Such a colour trend may be due to a dominance of relatively “primitive” red organic components on the surfaces of the most distant and least-evolved bodies (comets, TNOs, D-type asteroids) and the increasing contribution of more thermally evolved (carbonized) surface organic components for the objects orbiting closer to the Sun (P-, and, finally, C-type asteroids).

However, some dark objects which could have hardly been formed at significantly different heliocentric distances still show remarkable colour variations (Luu and Jewitt, 1996; Di Martino et al., 1997; Dahlgren et al., 1997; Barucci et al., 2001; Doressoundiram et al., 2002). This probably indicates that surface alteration processes such as space weathering (e.g., ion bombardment, UV-irradiation) and impact resurfacing play an essential role in the colour diversity of dark small bodies. In particular, materials forming small bodies in the outer Solar System are subjected to irradiation by energetic ions during their evolution from (pre)solar grains through planetesimals to the entire object (Strazzulla and Johnson, 1991). Most experiments simulating ion irradiation have been performed on ices and ice mixtures (see reviews by Johnson, 1998; Strazzulla, 1998; Moore et al., 2001; Strazzulla et al., 2001). Ion irradiation of hydrocarbon ices and their mixtures with water ice leads to a formation of a refractory residue stable at room temperature.

The residue has a complex structure and after prolonged irradiation evolves to a hydrogenated amorphous carbon with a neutral colour. Moroz et al. (1998) suggested that ion irradiation of red complex hydrocarbon materials would induce a comparable alteration trend (carbonization) but ion irradiation experiments have not been performed on such materials.

Here we present the results of the first ion irradiation experiments on natural complex hydrocarbon material (asphaltite) accompanied by spectral reflectance measurements after each irradiation step. Nikolaeva et al. (1991) proposed solid oil bitumens (including asphaltite) as suitable reference materials for comparisons with refractory extraterrestrial organic matter. Their properties and their possible relevance as analogue materials are discussed in detail by Moroz et al. (1998). The H/C atomic ratio of asphaltite is higher and carbon aromaticity is lower than those of organic matter from known carbonaceous meteorites. It is possible that asphaltite is spectrally and structurally comparable to a less evolved organic matter of TNOs and comets.

2. Asphaltite Properties

The asphaltite (gilsonite) sample from Izhem, Timano-Pechora Basin, Russia, was provided by Moscow State University (Russia). The sample has been extensively studied by Moroz et al. (1998). The asphaltite sample used in this study is labeled as “#3” in the paper by Moroz et al. (1998). It is composed of 81.6 wt.% C, 9.5 wt.% H, 6.4 wt.% S, 1.3 wt.% O, and 1.1 wt.% N when normalized to 100 wt.%. Atomic ratios H/C and O/C are 1.4 and 0.012, respectively (Moroz et al. 1998). Carbon aromaticity f_a derived from C^{13} NMR is 0.335 and density is about 1 g/cm^3 . Compared to most other solid oil bitumens, asphaltite is rich in H and has a relatively disordered chemical structure. Polycyclic aromatic structural units are small. Therefore, it is bright and transparent in the infrared spectral range due to a large optical gap (McMichael et al., 1954). It is very dark in the visible range due to a broad complex electronic absorption typical of polycyclic aromatic hydrocarbons (Brown, 1955; McMichael et al., 1954). Its long-wavelength wing causes a steep positive (red) spectral slope in the visible and near infrared region. The slope is very sensitive to a particle size of asphaltite (Moroz et al. 1998).

In addition, in the infrared region asphaltite shows a number of vibrational absorption bands mostly due to aliphatic and aromatic functional groups (Moroz et al., 1998). The most intense absorption features are fundamental bands due to stretching and bending of CH_2 and CH_3 groups (near $3.4 \mu\text{m}$ and $7 \mu\text{m}$) and due to out-of-plane bending of aromatic C–H ($11\text{--}13 \mu\text{m}$). A weak complex combination absorption feature, mostly due to CH_2 and CH_3 groups, is present in the near-infrared region ($2.3\text{--}2.5 \mu\text{m}$).

3. Sample Preparation and Experimental Procedures

Sample preparation, ion irradiation experiments and spectral reflectance measurements have been performed in the Laboratory for Experimental Astrophysics at Catania Astrophysical Observatory (Italy). The asphaltite sample labeled as “dust” was prepared by rubbing a solid asphaltite sample on a SiC sandpaper. The mean particle size of the asphaltite “dust” on the SiC substrate is about 5 μm .

The experimental apparatus includes an ion implanter (Danfysik 1080-30), a vacuum chamber, a tungsten lamp, and a FTIR spectrometer (Bruker Equinox 55). The asphaltite samples were irradiated in a vacuum chamber with 30 keV H^+ and 15 keV N^+ ions. The incidence angle of an ion beam is 45° . Reflectance spectra in the 0.3–0.8 μm range have been acquired both *ex situ* using a Perkin–Elmer Lambda-19 spectrophotometer (after a removal of the sample from the chamber) and *in situ* (in the chamber) relative to a BaSO_4 standard. The spectra were recorded before irradiation and after each irradiation step. Bitumens (Moroz et al. 2004) and some other red organic solids such as Titan tholins (Roush and Dalton 2004) show negligible spectral changes at cryogenic temperatures. Therefore, we performed our experiments at room temperature.

4. Results of Ion Irradiation Experiments

Shown in Figure 1 are spectra of asphaltite “dust” sample before and after irradiation with 30 keV H^+ and 15 keV N^+ ions. The spectra in extended visible range were acquired “*in situ*”. An irradiation of the dust sample by 30 keV protons does not produce significant spectral effects. We proceeded to irradiate these slightly altered “dust” samples by heavier nitrogen ions (15 keV N^+). Irradiation of the sample by heavier ions causes an increase in brightness in the visible range, darkening in the near-infrared region, and hence a decrease in spectral slope (flattening). In addition, originally concave spectral curve of asphaltite becomes straight after the irradiation. Similar effects are observed after irradiation of the samples with 60 keV Ar^{++} ions (Moroz et al., 2004). Since incident ion beam irradiates the surface of the “dust” sample at a fixed angle (45°), an essential part of the surface remains unirradiated. These unirradiated asphaltite areas contribute to the resulting spectrum. We expect that in nature, where ions bombard the surfaces of airless bodies at various angles, the optical effects of ion irradiation at similar doses are more pronounced than in our experiments.

The spectra acquired *in situ* and *ex situ* show no significant differences. In the near-infrared spectral region (0.7–2.5 μm) the irradiation results in a decrease in reflectance of the sample, and hence a reduction of an overall near-infrared spectral slope (Moroz et al., 2004).

The ion irradiation produced an increase in brightness in the visible range (Figure 1). Moreover, the brightening is well detectable both with the naked eye and

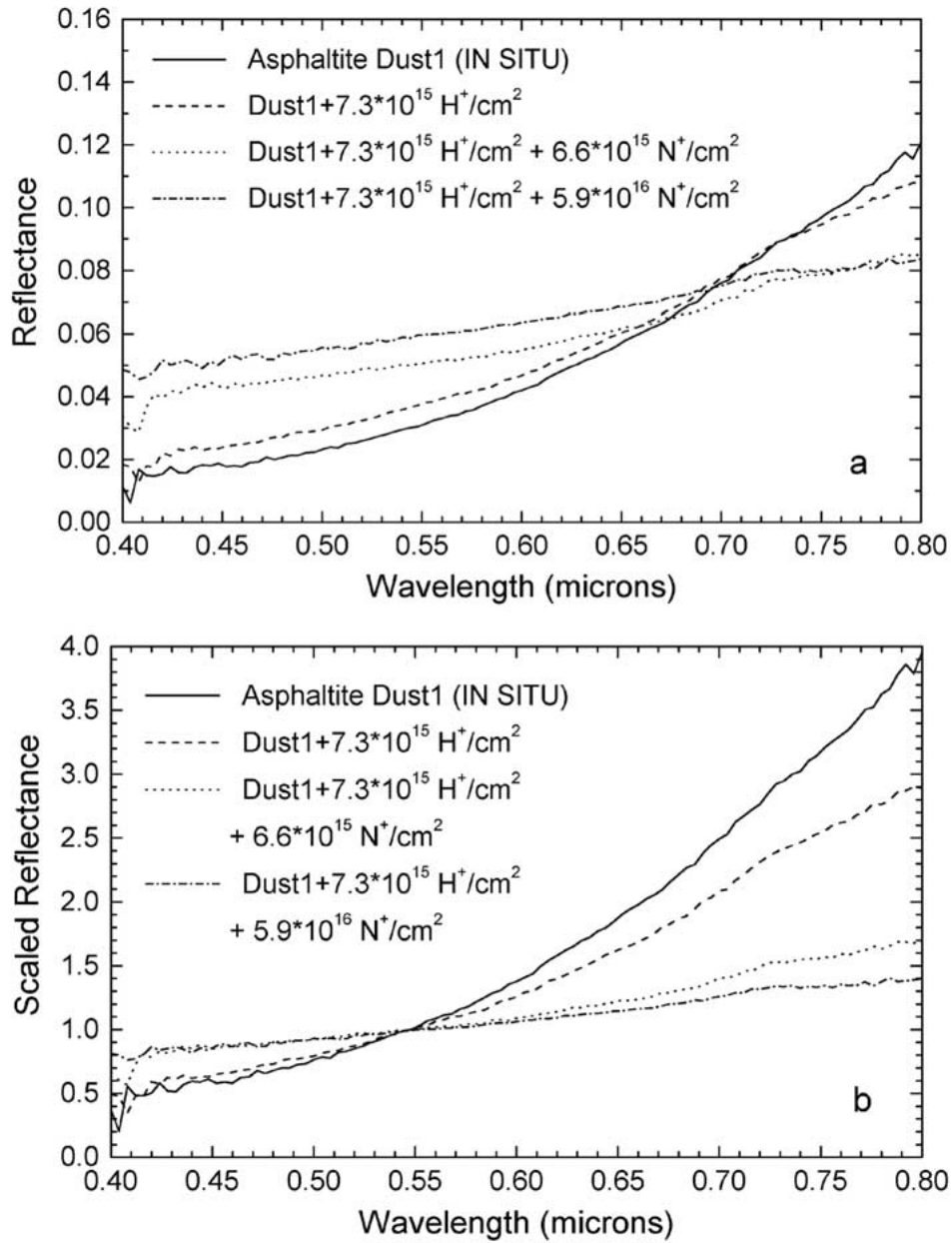


Figure 1. Reflectance spectra of asphaltite “dust” sample before and after irradiation with 30 keV H⁺ and 15 keV N⁺ ions. (a) Absolute reflectance spectra. Note increase in brightness as a result of irradiation. (b) Spectra normalized to 1 at 0.55 μ m. The spectral slope decreases with increasing ion fluence.

under the microscope. Although ion implantation may affect a micro-roughness of the surface, a microscopic examination of the irradiated samples does not favour micro-roughness changes as a reason for the brightening. More likely, the reflectance rise in the visible range and the drop of reflectance in the near-infrared are due to modification of the chemical structure of organic material under ion fluence. Such a structural transformation should lead to a significant change of optical properties of the irradiated asphaltite. The irradiated asphaltite shows a loss of hydrogen-containing functional groups, i.e. gradual carbonization. Optical constants of asphaltite in the visible range have not been measured yet, but its low reflectance and the spectral behavior as a function of particle size (Moroz et al., 1998) indicate that the imaginary part of refractive index (k) in the visible region is high. Apparently, carbonization induced by ion irradiation causes a further gradual growth of absorption coefficient so that optical density of irradiated layer progressively grows with increasing exposure to ion fluence. Optical density in the visual range becomes high enough for surface scattering to dominate the scattering behaviour. As a result, brightness in the visible range progressively increases. In the near-infrared region absorption coefficient of asphaltite is much lower and spectral behavior is controlled mostly by volume scattering. Therefore, an increase in absorption coefficient induced by carbonization should lead to the darkening in this spectral region.

Even after the highest fluences of 15 keV N^+ used in this study asphaltite spectra do not become completely neutral (“grey”). The irradiated layer is rather optically thin so that the unirradiated underlying material may contribute to the spectral properties of the sample, in particular, in the long-wavelength part of the spectrum. Furthermore, due to a shadowing effect it was impossible to irradiate the whole surface of the samples. It is possible that ion irradiation of the surfaces of the primitive solar system bodies causes complete “neutralization” of the positive spectral slope.

The 30 keV protons turned out to be much less effective in changing the optical properties of asphaltite than the 15 keV N^+ ions. Due to their high initial velocities (2.4×10^8 cm/s) the 30 keV protons penetrate much deeper (up to ~ 5000 Å) into the target than the slower (4.5×10^7 cm/s) 15 keV N^+ ions. Most of the latter are stopped at depths less than 700 Å. We calculated the damage produced in asphaltite by the two sorts of ions using the TRIM (Transport of Ions in Matter) code (Ziegler et al., 1996). The calculations have shown that the thickness of asphaltite layer where most damage by 30 keV protons is concentrated is higher (about 2000 Å) than in the case of 15 keV N^+ ions (about 600 Å). However, the 30 keV protons produce atomic displacements in the target mostly at depths between 2000 and 4000 Å. Most damage in the asphaltite (3% of C-atoms displaced) occurs at depths of ~ 3000 Å, while the upper layer of irradiated asphaltite contains less than 1% of displaced C-atoms. Small amount of displacements of C-atoms by protons is due to a low proton mass. At the end of their path where damaging elastic collisions occur, very few 30 keV protons retain sufficient energy to reach the displacement

threshold energies of target atoms. At such a low level of damage at least an upper zone of the implanted layer may contribute to the reflectance spectrum in a way similar to unirradiated asphaltite.

Due to their lower initial velocity and the mass close to that of C-atoms, the 15 keV N⁺ ions are damaging almost from the beginning of their path. They produce displacements of C-atoms via elastic (nuclear) collisions with the target ions at depths from 0 to about 600 Å. As a result, heavier 15 keV N⁺ ions induce much more atomic displacements in asphaltite (70 C-atoms per incident ion) than 30 keV H⁺ ions (6.6 C-atoms per incident ion). At fluence of 15 keV N⁺ ions of 6.6×10^{15} cm⁻², about 100% of C-atoms are displaced in the maximum of the damage profile (at depths of 200–300 Å). At fluence of 5.9×10^{16} cm⁻², all C-atoms in the 600 Å-thick damaged layer are displaced more than once. Thus, the significantly higher number of atomic displacements and the location of the damaged layer close to the surface appear to be responsible for the higher effectivity of 15 keV N⁺ ions vs. 30 keV protons in modifying the asphaltite optical properties in our experiments.

5. Implications for TNOs and Centaurs

A flux of nitrogen ions in solar wind at the heliocentric distance of 40 AU is about $4 \text{ cm}^{-2} \text{ s}^{-1}$. Then it would take $\sim 0.8 \times 10^8$ years for a surface of a TNO at 40 AU to be exposed to a fluence of N⁺ ions corresponding to the highest N⁺ fluences used in our experiments (about 10^{16} cm^{-2}). However, a concentration of N⁺ ions in solar wind is low (about 6×10^{-5}). Therefore, the time of $\sim 0.8 \times 10^8$ years represents the upper limit. We attempted to estimate the lower time limit taking all solar wind ions into account. To obtain such an estimate, we used the criteria of an equal energy deposition and an equal damage of the target. The time needed at 40 AU to deposit energy equal to that deposited by N⁺ ions in our experiments is 1.4×10^5 years. However, 1 keV protons dominating the solar wind would induce much less atomic displacements and hence less damage than the heavier N⁺ ions used in our study. To take this into account, one should evaluate the time scale needed for all major solar wind components at 40 AU to produce a radiation damage equal to that produced in our experiments. To characterize a radiation damage, we used a number of displaced carbon atoms as a criteria. Using the TRIM code we calculated a contribution to a number of displaced C-atoms per incident ion from all major solar wind ions according to their energy and concentration in the solar wind. The time necessary for solar wind at 40 AU to produce a radiation damage (represented as a number of C-displacements) equal to that produced in our experiments is 2.7×10^5 years. The time scales are obtained assuming that the surface is continuously covered with an asphaltite-like material. Most energy deposition and surface damage induced by solar wind is due to protons despite their low effectivity. Note that the solar wind affects only very thin asphaltite surface

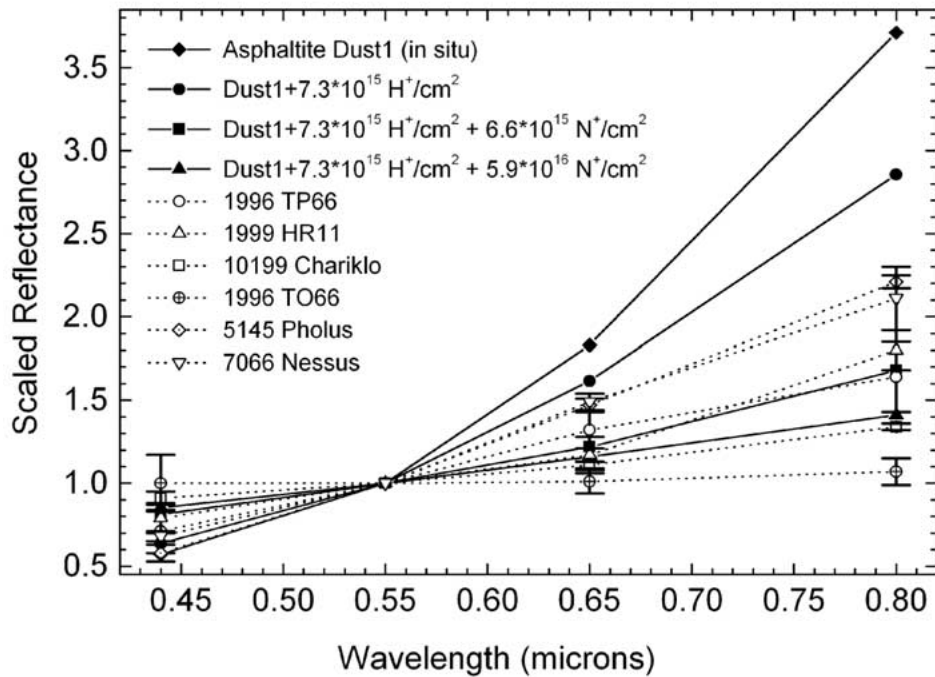


Figure 2. Laboratory spectra scaled to 1 at $0.55 \mu\text{m}$ and recalculated to BVRI system. The BVRI colours of selected TNOs and Centaurs are plotted as well for comparison. (Data from Luu and Jewitt, 1998; Tegler and Romanishin, 1998; Davies et al., 1998, 2000; Barucci et al., 1999, 2001; Hainaut et al., 2000; Doressoundiram et al., 2001).

layer of $\sim 1200 \text{ \AA}$. In order to produce a damage at higher depths, more energetic ions of solar flares and galactic cosmic rays are required.

Our results demonstrate that ion irradiation of naturally red hydrocarbon material gradually neutralizes its spectral slope in the visible and near-infrared spectral regions. If dark red organic materials optically dominate the surfaces of a population of collisionally evolved primitive objects, then it is reasonable to expect a negative correlation between the spectral slope and the size of the object. Redder objects representing “fresh” collisional fragments would have smaller sizes than more neutral objects whose surfaces have been exposed to an ion flux for longer times. Indeed, observational data consistent with this scenario exist for Hilda and Trojan dark asteroids (Jewitt and Luu, 1990; Dahlgren et al., 1997).

Shown in Figure 2 is a comparison between BVRI colours of several Centaurs and TNOs and our laboratory data for asphaltite dust irradiated by 30 keV protons and 15 keV N^+ . If the surfaces of these objects are optically dominated by red hydrocarbons, then the objects with more neutral colours should have “older” surfaces. However, situation seems to be more complicated for TNOs and Centaurs, since these objects probably contain hydrocarbon ices as well. The ices show a different alteration trend. Bright but spectrally neutral ices become dark and red as

a result of ion irradiation, while a long-term exposure to ion flux darkens them further and neutralizes their spectral slope. TNOs and Centaurs probably contain both ices and complex refractory organics as well as silicates. The latter are known to redden as a result of space weathering. The actual spectral alteration trend induced by space weathering would depend on that component which optically dominates the surface. The result may depend not only on the volume percentages of the components in the mixture but on their textural relationship as well. Both contents and textures of mixed phases may vary from object to object within a population of TNOs and Centaurs. Therefore, the actual alteration trend may be difficult to predict. Moreover, information about colours alone without known albedos may be insufficient for a reliable interpretation of the observational data sets. A neutral colour of the observed surface may be interpreted as a “fresh” ice (high albedo) or, alternatively, as a severely “space weathered” carbonized surface (low albedo).

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