Astron. Astrophys. 187, 889–892 (1987)

1987A&A...187..889J

ASTRONOMY AND ASTROPHYSICS

Radiation formation of a non-volatile comet crust

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Received February 9, accepted June 29, 1987

Summary. Ion irradiation of the outer meters of a cometary surface can produce new molecular species in the solid state. Because of the interfaces with the interplanetary vacuum these species segregate in an irreversible way into a nonvolatile residue and new very volatile species. The latter are ejected directly or lost when the comet enters the inner solar system. Therefore, a comet exposed to background particle radiations in the Oort cloud obtains an outer web of non-volatile material ($\sim 10^2\,\mathrm{g\,cm^{-2}}$) which will lead to the formation of a substantial "crust". When a new comet enters the inner solar system there will be early activity, initial fizzures in the crust and the break-off of unstable pieces of the crust, due to warming of subsurface species. If this comet enters a periodic orbit in the inner solar system the remaining mantle should be continuously hardened due, primarily, to thermal processing. There will also be permanently active regions on such a comet which were initially shaded from the cosmic ray radiation when the comet was in the Oort cloud or which subsequently lost their crust.

Key words: comet crust – radiation modification

1. Introduction

Results from the missions to Uranus and Halley clearly indicate that the solid matter on/in those objects (satellite and ring surfaces, comet nucleus and dust) contains radiation processed ices or organic materials (e.g. Smith et al., 1986; Krimigis et al., 1986; Kissel et al., 1986a, b). These findings have drawn attention to the results obtained from laboratory experiments studying the production of organic residues from carbon-containing gases or frozen targets irradiated by electrical discharges (e.g. Sagan and Khare, 1979; Sagan et al., 1984), by UV light (e.g. Allamandola et al., 1980; Greenberg, 1982) and by energetic ions (e.g. Cheng and Lanzerotti, 1978; Foti et al. 1984; Lanzerotti et al., 1985). Such experiments can help answer a number of important questions about these dark outer solar system materials (i) What are their properties (chemical composition, physical structure)? (ii) When and where have the materials been formed and processed: in the presolar interstellar medium, in the early stages (e.g. T-Tau phase) of the solar evolution, or in "situ" after the formation of the various objects? (iii) are the differences these materials exhibit in different objects due to different formation scenarios or do they only reflect different evolutive stages of the same process?

In this paper we describe a particular in situ radiation processing effect, the formation of a cometary "crust" activated by cosmic-ray irradiation in the Oort cloud. The recent observations of the nucleus of P/Halley indicate that it has a very low albedo and that the gas and dust primarily effuse from very localized regions. If the volatile material is assumed to have been distributed fairly uniformly throughout the nucleus when the comet was formed, then these observations would imply that there are large regions in which the nucleus has aquired a thermally stable "crust" with a tensile strength sufficient to contain the internal subliming gas pressures. Alternatively, the nucleus may be very heterogeneous with the non-active regions containing primarily rocky, meteoritic materials (e.g. Mendis, 1985). Here we consider the first possibility, and show that radiation-induced changes in the outer layers can create a thermally stable "crust" prior to entry into the inner solar system.

The organic nature of the crust and the existence in the comet of radiation-processed materials is suggested by the results from dust particle analyzer experiments (PUMA, PIA) on Vega and Giotto (e.g. Kissel et al., 1986a, b). These experiments found that a large fraction of the carbon is in cometary dust particles and a large number of these particles are composed of light elements (CHON). In addition, infrared emission bands observed both from Vega-1 at ~ 3.3 and $\sim 7.5\,\mu$m (Combes et al., 1986) and from the ground at $3.4\,\mu$m (Wickramasinghe and Allen, 1986) have been attributed to the vibrations of C – H and C = O groups in the cometary grains. These results would seem to support the model proposed by Greenberg (1982) in which comets are an aggregate of pre-cometary (interstellar) grains (Table 1). These consist of a silicate core plus an inner organic-refractory mantle formed by photon irradiation of condensed molecules in the interstellar clouds with, possibly, a contribution from cosmic-ray irradiation (Johnson et al., 1983; Strazzulla et al., 1983; Lanzerotti et al., 1987). Finally the grains have an outer "icy" mantel of molecules condensed prior to solar system formation.

This model of the nucleus does not directly account for the inhomogeneous, involatile crust observed. Also it is not clear that the interstellar grains as described can survive the early solar system processing (e.g. Strazzula, 1986), although this is debated (Grim and Greenberg, 1987: Moore and Donn, 1987). However, because the grain forming process (condensation of refractories followed by formation of organics and condensation of volatiles) can also occur in the early solar system we use the model of a pre-

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Table 1. Grain composition[a]

Component	Mass fraction
Silicates	0.23
Carbon	0.06
Organic refractory	0.19
H_2O	0.20
CO	0.03
CO_2	0.04
(H_2CO, HCN, CN, H_2, HCO,...)	0.27

[a] From J.M. Greenberg (1986), two grain types contributing

cometary grain in Table 1 in order to describe the formation of a stable cometary crust. Below we review the relevant laboratory data and then apply these to the mantle formation process (Johnson et al., 1986).

2. Radiation modifications

It is well established that ionizing radiations (UV, X-rays, γ-rays, electrons, fast ions) alter low temperature molecular solids such as condensed gases and organics. The irradiations initially produce radicals (bond breaking) during the electronic relaxation processes. At the low temperatures (10–20 K) in the Oort cloud individual radicals can, in principle, be stored for considerable periods. Radical recombination is then induced in very narrow temperature regions during the warm-up of such materials. This appears as an enhanced volatility in the ices (Moore et al., 1983; Johnson et al., 1983; Greenberg, 1982). Therefore Whipple (1977), Donn (1976), Shullman (1972) and others have proposed that, if the outer layers of a comet were modified by ionizing radiations, a comet newly introduced into the inner solar system could become active at rather larger than expected distances from the sun, consistent with observations of many comets (e.g. Sekanina, 1982). The storage of a high density of radicals requires extremely small diffusion coefficients and/or large recombination barriers as the radical and its parent are generally not displaced many lattice distances. Therefore, the possibility of annealing the broken bonds needs to be examined for Oort cloud temperatures and those temperatures in the interior of an evolved comet when considering transient releases of material in the inner solar system.

On the other hand, if the *local* density of the excitations is high, permanent alterations are directly produced in the material without warming. This occurs along the "track" of a fast ion, in the "spurs" associated with secondary electrons produced by energetic electrons, ions or photons, or when the irradiation dose is high. These alterations have been shown to contain, in addition to radicals, both very volatile and involatile components if the materials contain carbon or sulfur. For example, irradiation of organics results in the formation of carbon residues *and* the production of H_2, O_2, CO, etc. (Venkatesan, 1984; Brown et al., 1987). Recent experiments have roughly quantified the radiation precipitation of residues. Moore et al. (1983) have shown that an interstellar ice mixture (H_2O, NH_3, CH_4) forms a residue (of the order of 1 %) after an average dose of only 10 eV/molecule. In pure materials, such as CO and SO_2, a small fraction (of the order of a few percent) of the material is converted into a residue (Chrisey et al., 1985; Haring et al., 1984; Moore, 1984) after somewhat higher doses, whereas in H_2S, CS_2 (Boring et al., 1985) and CH_4 (Foti et al., 1984; Lanzerotti et al., 1985) most of the material is converted into a residue (after ~200 eV/mol). This is especially the case for very energetic protons. Lanzerotti et al. (1987) have also studied the sample thickness dependence and ionization density effect on residue formation in condensed CD_4.

Besides condensed gases, all organics are readily carbonized while releasing volatiles and producing black residues (Venkatesan, 1984; Strazzulla et al., 1984; Calcagno et al., 1985). Such processes occur efficiently due, in part, to the enhanced diffusion initiated by the incident ions. This produces a segregation in the material, after long exposure, with the involatile species accreting into a porous condensed material and the volatile species brought to the vacuum interface or stored in the large defects and pores in the solid. Such materials can also contain unreacted radicals, depending on the thermal history. Therefore, ion irradiation causes progressive evolution in the target as the time of exposure to the ions (the fluence) increases. This affects both the chemical composition and the optical properties of the bombarded layers, as seen in Table 2 for a frozen methane target bombarded by MeV protons. The original target evolves from clear to dark black as the H to C ratio decreases with increasing fluence. In pure water ice, although the material becomes porous upon irradiation (Johnson et al., 1985), residue formation does not proceed. Therefore, at very low temperatures, the irradiated H_2O remains a stable mix of radicals and small molecules.

The organics produced by ion irradiation exhibit, in their IR spectra, bands due to C–H and C=C groups (Strazzulla et al., 1984), with band depths which evolve with ion fluence (Calcagno et al., 1985). In particular, they exhibit a complex feature around 3.4 μm (CH_2 and CH_3 stretching vibrations) similar to the one observed on many astronomical objects including Halley (Combes et al., 1986; Wickramasinghe and Allen, 1986). In fact, the 3.4 μm feature is also produced in such materials by other ionizing radiations, such as UV (Greenberg, 1986). Such spectra also indicate that the new organics produced by ion bombardment "forget" the chemical nature of their original parents. They respond primarily to the average H/C ratio exhibiting similar spectral properties roughly independent of the original target and bombarding ion and energy (Calcagno et al., 1985). Because the above results for ions are obtained whatever the original form of the carbon, they can be applied to many astrophysical situations, including comets, in which there is considerable H_2O.

3. Comet surface alteration

A number of authors (Draganic et al., 1984; Moore et al., 1983; Johnson et al., 1983; Pirronello et al., 1982; Whipple, 1977) have discussed the implications of galactic cosmic ray irradiation in the Oort cloud. This irradiation acts on a fluffy porous object which may be composed of grains that are already highly processed (see Table 1). The cosmic ray ions lose their energy in these grains by direct ionization and by inducing nuclear reactions.

Due to the absence of solar modulation effects, cosmic ray ions in the Oort cloud should have significantly higher intensities at energies below a few GeV/nucleon than those presently measurable within the heliospheric boundary at 50–100 AU from the Sun (Fisk, 1974). Protons at energies less than 300 MeV would deposit energy by direct ionization in cometary surface depths less than 100 grams/cm^2. At higher energies the secondary products of nuclear interactions in cometary ices (i.e., H_2O) would deposit

Table 2. Summary of the evolution of frozen methane under bombardment by MeV protons at 10 K

H^+/cm^2	Dose (eV/mol)	C/H [a]	Resulting material [b]	Color
0	0	1/4	Frozen methane (~10 K)	Clear
$2\ 10^{16}$	100	1/3(1/1)	Org. residue 50% (~300 K)	Yellow
$5\ 10^{16}$	250	1/2(1/0.7)	Org. residue 75% (~300 K)	Brown
$1\ 10^{17}$	500	1/1.5(1/0.5)	Carbonaceous 90% (~300 K)	Black

[a] Brackets are the resulting C/H ratios after heating to (~300 K)
[b] Percents are approximate fractions of original carbon in residue after warming

Table 3. Cosmic ray ion doses [a]

Depth (m)		Dose ($4.5\ 10^9$ yr)	
$1\ g\,cm^{-3}$	$0.2\ g\,cm^{-3}$	Mrad	(eV/molecule) [b]
0.1	0.5	$3\ 10^5$	600
1	5	$1\ 10^5$	200
5	25	$1\ 10^4$	~ 20
10	50	$3\ 10^3$	~ 2

[a] Data from Ryan and Draganic (1986); data in Strazzulla (1986) exclude the important nuclear interations
[b] Based on methane equivalent

much of the initial proton energy at depths of order 100 g/cm^2 (Cooper, 1983). On the other hand the large fluxes of protons measured at energies below 30 MeV within the solar system (McDonald et al., 1974) would penetrate to depths of order of one gram/cm^2. Locally accelerated ions at 100 keV energies in the cometary magnetosphere would affect only a micron-thick outer layer. Comparison of predicted differential fluxes for protons and electrons in interstellar space (Fisk, 1974) indicates that the electron fluxes may be significantly larger at energies below 100 MeV. In this case the electrons might also make a significant, perhaps even dominant contribution to irradiation of the outer 100 g cm^{-2} layers of cometary nuclei. According to Ryan and Draganic (1986) at a depth of one meter in a non-porous icy object (therefore many meters in a porous aggregation of grains) every molecule would have received an average of ~200 eV of energy in $4.5\ 10^9$ yr. This dose increases rapidly with decreasing depth (Table 3) although the total dose in the outer layers depends on the energy spectrum assumed for the low energy ionizing particles. Draganic et al. (1984) also estimate the dose of radiation due to radioactive decay which occurs throughout the comet. These are much smaller (~3 eV/molecule), altering only a few percent of the material. Therefore, the principle alternation occurs in the surface layers.

In carbon and sulfur containing materials significant residue formation can occur at the cosmic ray doses in Table 3. Using the composition in Table 1 and the results in Table 2, at a depth ~100 g cm^{-2} the overlayers on the grains are depleted in volatiles (e.g. Johnson et al., 1983) and the organic molecules and the organic mantles are highly carbonized. The residues obtained on warming have been shown to be black porous, locally compacted, filamentary materials that are stable at room temperature (Moore et al., 1983; Calcagno et al., 1985). At the low temperature of the Oort cloud, the external and internal surfaces of the porous residues, made from the irradiated organics and ices, would be coated with volatile molecular species. Most H_2 presumably would diffuse out of the porous surface at these temperatures (Brown et al., 1987), with some trapped in defects and bubbles. These materials would also contain some radicals. The levels of ion irradiation in Table 3 also enhance adhesion between the new non-volatile residues, the modified organics, and the silicate grain cores (Strazzulla et al., 1985; Johnson et al., 1985; Johnson and Lanzerotti, 1986). Therefore, cosmic rays produce highly processed organic material (about ~40% of the original by mass) and bind together grain cores (~27% by mass) at depths of the order of 100 g cm^{-2}, so that, after a long residence period in the outer solar system the comet has acuired a "crust" with a web-like construction of refractory materials. Because the original comet is not a smooth sphere, but rather a locally irregular aggregation of a weekly compacted material we imagine this "crust" is not uniform. That is, there are numerous large cracks, crevices, and shadowed surfaces with relatively pristine material not irradiated by the cosmic rays.

On warming this object residual radicals will react and the very volatile gases in the porous "crust" will be lost leaving a dark residue depleted in volatiles which covers a more volatile underlying material. The final state is much like that described by Fanale and Savail (1984) in which a thin layer is produced by thermally enhanced adhesion and volatile depletion. In the present model a much thicker volatile-depleted mantle is formed by the radiation alteration processes described above. In the active "surface" regions, which were not fully exposed to the cosmic ray flux, thermally produced crusts will temporarily form after each release of material.

Subsequent warming of the dark "crust" will continue the depeltion of volatiles. Heat will only slowly be conducted into the underlying regions partially depleting the volatiles below the porous "crust". The net effect would be the formation of a relatively thick outer mantle ($\gtrsim$100 g cm^{-2}) so that gas ejection would come preferentially from regions lacking such a mantle. However, with a sufficiently rapid thermal increase on close approach, the radiation produced mantle may be broken, releasing volatiles and giving a cometary burst which would also contain large amounts of dark refractory debris and possibly, reactive material depending on the thermal history of the interior. In those regions in which the mantel survives, the continuous thermal compaction and additional ionizing radiations will act to harden the "crust". For the grains ejected from active regions, subsequent radiation modification occurs due to the locally-produced cometary plasma and, eventually, solar particles (Strazzulla, 1985; Johnson and Lanzerotti, 1986).

4. Conclusion

That some radiation processing of a cometary material has occurred is suggested by the depletion of H and the significant percent of carbon and sulfur in a refractory form. Further, this refractory material is often fragile and underdense, consistent with the expectations for a radiation processed organic material. This processing may have been produced in the grains prior to accretion due to UV photon and cosmic ray bombardment, a shock in the interstellar medium, or in the early period of the formation of the solar system.

The radiation-induced alteration of the outer meters of a comet in the Oort cloud, however, is certain to occur. This results in the formation of more volatile molecular species and the precipitation of new refractory materials when carbon or sulfur are present as organics or condensed molecules. This can account for the enhanced activity of new comets, the formation of a dark, thermally stable "crust", and the existence of locally active regions (see also Sekanina, these proceedings). Clearly there may be other scenarios for producing the observed mantle as the aggregate of grains is initially porous and , possibly, dark (Greenberg, 1986). The principle question that needs to be answered is the degree of completion of the mantle forming process described here and the ability of this mantle to survive the heating produced on entering the inner solar system. However, this problem pertains to *all models* that begin with a mixture of ices and refractory materials. In the present model, the cosmic ray irradiation process significantly enhances the ability to form a thick mantle of refractory material.

Acknowledgements. We acknowledge helpful comments from Z. Sekanina, and J.M. Greenberg. REJ acknowledges the support of the NSF Astronomy Division under grant AST-85-11391

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