PROPERTIES OF ICES AND GRAINS: AN EXPERIMENTAL STUDY

Bertram Donn
Laboratory for Extraterrestrial Physics
Goddard Space Flight Center
Greenbelt, MD 20771

ABSTRACT

Proton irradiation of a variety of ice mixtures were carried out to study the effect of galactic cosmic ray irradiation of comets in the Oort Cloud. Three significant effects were noted (1) production of new molecules; (2) production of a more energetic ice at low temperatures; (3) production of a non-volatile, complex organic residue. These phenomena suggest various effects on new comets approaching the sun including enhanced activity. Experiments on the condensation of silicate grains provide information on the condensation mechanism and properties of grains. Controlled annealing of the amorphous condensates shows how crystallization occurs. Infrared spectra of different stages of crystallization contain features that may identify composition, structure and history of refractory material.

I. INTRODUCTION

Observational and experimental data on interplanetary objects: comets, minor planets, meteorites and interplanetary dust, has been growing rapidly. However, controlled laboratory experiments needed for a sound and complete interpretation of that information are very limited and increasing at a slow rate. Significant progress has been made with regard to optical properties of zodiacal light particles by means of microwave analogue measurements (Giese, 1980; Greenberg and Gustafson, 1980).

In this report I will describe some aspects of the experimental cosmic chemistry program at Goddard designed to provide some of the missing laboratory data. The first part deals with irradiation of ice mixtures and applies to the interpretation of the cometary nucleus. This work formed part of the Ph. D. research of Marla Moore, University of Maryland Astronomy Program, carried out at Goddard. The second part describes experiments on condensation and properties of silicate grains which were primarily carried out by Joseph Nuth and is taken from his

Richard M. West (ed.), Highlights of Astronomy, Vol. 6, 347–354.

Ph. D. thesis for the University of Maryland Chemistry Department. This research was also done at Goddard.

II. IRRADIATION OF ICE MIXTURES

Several attempts have been made to interpret the behavior of comets believed to be "new" in the sense of coming to the sun from the Oort Cloud for the first time. Such efforts are complicated by effects of cosmic ray irradiation during the comets residence in the Oort Cloud for an interval, generally believed to be equal to the age of the solar system, 4.5×10^9 years. Some consequences of cosmic rays were first proposed by Shul'man (1972). The direct application to "new" comets was made by Donn (1976) and Whipple (1977). Donn suggested that irradiation may polymerize the outer layers making them relatively non-volatile and dark, whereas Whipple proposed increased chemical activity and greater volatility as the cometary ices warm up.

The experiments to be described were designed to tell how cosmic ray exposure may affect cometary ices and are described in detail in a paper to be submitted to Icarus. The results are summarized here. Several mixtures of gases, generally H_2O, NH_3 and CH_4, were condensed on an aluminum disc at about 15K. The ice mixture was then irradiated by a beam of 1 MeV protons from a van de Graaff accelerator for 0.6 - 6 hrs at a flux of $\sim 10^{11}$ protons/cm^{2}s. This flux is many orders of magnitude greater than the interstellar flux. However, the probability of two transient hot spots occurring close enough in space and time to interact is too low to significantly affect the experimental results. In these experiments the energy absorbed in the thin film is about 25% of what would be absorbed by a similar film in the Oort Cloud.

Several significant effects were observed. First to be observed was the formation of new molecules and the loss of the original ice constituents. This was shown by the appearance of new bands in the spectrum and the decrease of the initial features. Table I displays these results.

TABLE I

New Molecules Detected by Infrared Bands

$H_2O + NH_3 + CH_4$	$H_2O + N_2 + CO_2$	$H_2O + N_2 + CO$
C_2H_6	CO	CO_2
CO_2	NO	CH_4*
CO	CH_4	
N-N-N Species*		

*Tentative

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press

Below the original composition are the new molecules detected. In addition, a number of unidentified absorption features were produced. Additional molecules were detected after irradiation by warming the ice sample and analyzing the vapor in a gas chromatograph.

The production of CO and the conversion between CO and CO_2 is of particular interest as possibly accounting for the activity of new comets at large heliocentric distances. It is also noteworthy that CH_4 is produced in ices where not originally present. Because of irradiation, the outer region of new comets can be expected to contain highly volatile stable molecules produced from a reasonable initial composition.

The second significant observation for the purpose of this discussion was the behavior of an irradiated ice mixture under controlled warm-up. The sample was warmed slowly from 19K in steps of 1° or less. Between 19K and 30K pressure increases were observed, frequently as sharp spikes in the pressure curve. Film luminescence was also detected, generally correlated with pressure increases. Luminosity spikes occurred simultaneously with the pressure spikes. Between 30K and 40K, more gradual pressure and luminosity enhancements occurred. Thereafter the sample was quite inactive until 85K when broad luminosity peaks again developed, and continued until about 150K. A sudden pressure increase occurred at 160K. This ended all activity except for the gradual vaporization of remaining volatile material.

Further study of irradiated films needs to be done, particularly to obtain the spectra of bursts. The tentative explanation is that the low temperature activity, $T < 40K$, is caused by recombinations or reaction of species produced by irradiation. The light emission above 80K is assigned to thermal luminescence caused by the release and recombination of trapped electrons in the matrix. Conversion from amorphous to crystalline ice near 154K probably accounts for the last burst of activity.

Additional effects were observed during warm-up experiments which need to be investigated. These include methane absorption in the film without change at 77K for 17 hours and its persistence to 165K. Carbon monoxide was much less volatile in irradiated mixtures than in the original deposit. A comprehensive experimental investigation of the vaporization of ice mixtures is needed to properly model gas emission as a comet approaches the sun.

When irradiated ice films were warmed to room temperature and all volatiles evaporated, a yellowish residue remained. An analysis of the residue by gas chromatography showed a complex, unresolved array of very many peaks. Using the gas chromatograph-mass spectrometer combination a small range of GC eluded material was examined. The largest mass to charge ratio determined was 383.

The increased activity at low temperatures of irradiated ices agrees with Whipple's prediction of an active frosting. The non-volatile residue conforms to my conclusion although the residue contained only about one percent of the sample mass. The fraction corresponds to the energy absorbed at a depth of a few meters. At the surface a large proportion of the ices would be polymerized.

III. VAPOR CONDENSATION OF REFRACTORY GRAINS

All refractory material now present in the solar system is generally believed to have started as small grains (see e.g. Wetherill, 1980). Of this material, much, if not all initially was interstellar grains (see e.g. Cameron, 1978; Wood, 1981). Wherever the grains formed, many have undergone a significant degree of metamorphism (McSween, 1979), before they were incorporated into objects in which they can still be somewhat identified. Additional discussions of these subjects appear in Part V of "Protostars and Planets" (1978).

As was the case for interpreting cometary observations, the interpretation of laboratory analyses of meteorites and the development of theories of the formation and evolution of solar system objects of refractory solids also requires laboratory studies of the condensation of solids from vapor. This needs to be followed by the determination of the properties of the condensates and subsequent alteration by various astronomically appropriate mechanisms.

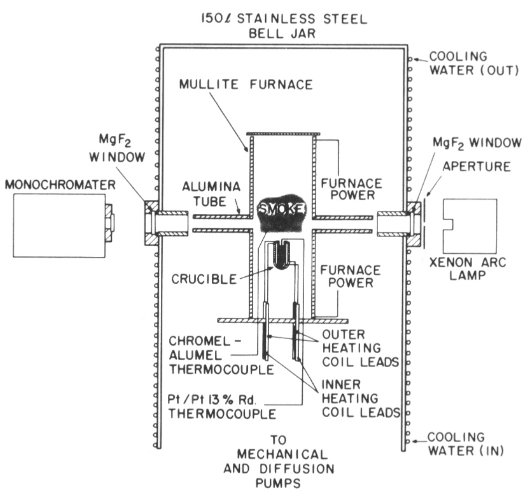

Figure 1. Schematic diagram of the condensation apparatus.

The results described here are the initial phase of a laboratory study of condensation of refractory material from the vapor. Some of

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press

the principal results have been published (Day and Donn, 1978; Donn et al., 1981; Nuth and Donn, 1982a,b). Experimental details are given by Nuth and Donn (1982b).

A brief description of the experiments and results of the program particularly relevant to the present subject are summarized here.

Figure 1 is a schematic of the apparatus. Magnesium silicate smokes were produced by vaporizing silicon oxide powder in the crucible shown and magnesium metal in an adjacent crucible. The ambient gas was 35 torr of hydrogen. Condensed particles were collected from the cover of the furnace, removed and examined. The grains were amorphous magnesium silicates as indicated by the X-ray diffraction pattern and X-ray fluorescent spectra. Electron microscopy examination showed a size distribution around 200 nm. Figure 2 presents the infrared spectra of samples annealed in vacuum at 1000K for 0,1,2,4,8,16.5 and

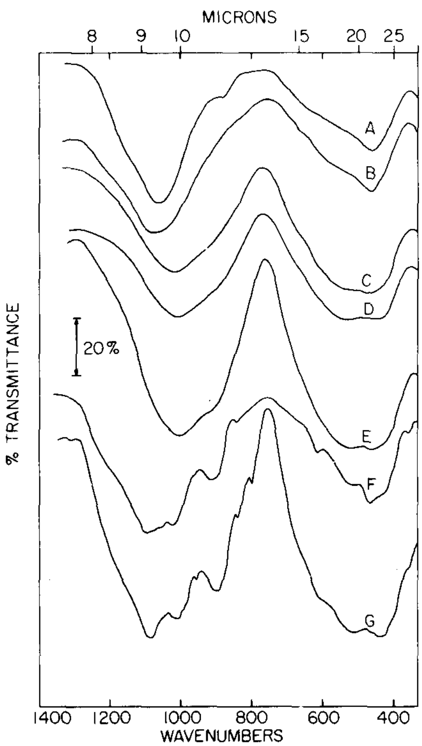

Figure 2. The infrared spectrum of an amorphous Mg-SiO smoke (A) and of smoke samples annealed at 1000K for 1 hr. (B), 2 hrs. (C), 4 hrs. (D), 8 hrs. (E), 16.5 hrs. (F), and 30 hrs. (G).

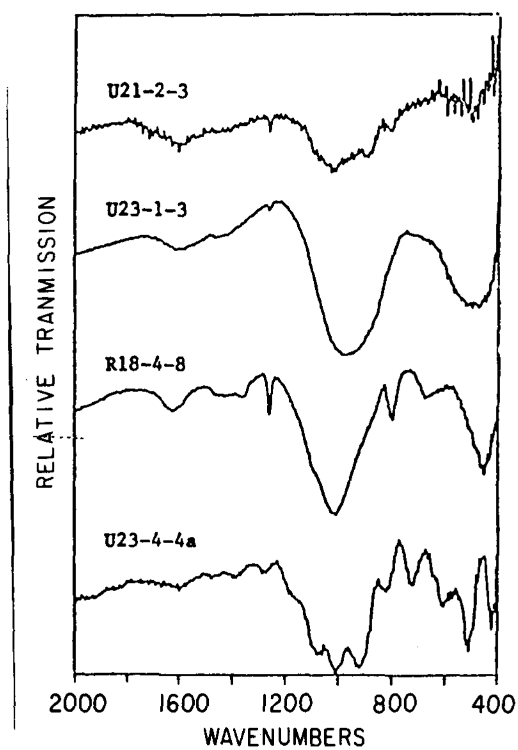

Figure 3. Infrared spectra of four stratospheric "chondritic" micrometeorites.

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press

30 hours. The major features are the initially structureless 10 and 20 μm absorption bands. As annealing proceeds, these shift slightly in position and width and develop secondary peaks. A comparison of the infrared spectrum of partially annealed magnesium silicates with the spectrum of stratospheric interplanetary particles, shown in Figure 3 (Fraundorf et al., 1982), reveals striking and very suggestive similarities. The spectra of circumstellar shells (Nuth and Donn, 1982a) and carbonaceous chondrite matrix material (Knacke and Kratschmer, 1980) also show close general agreement with the laboratory silicates.

Material collected after condensing SiO vapor was a mixture of amorphous Si_2O_3 and SiO_2 grains. The major feature in the infrared spectrum was a strong 10 and 20μm absorption. In addition, each specie has a characteristic weaker absorption. For SiO_2 this is at 12.5μm whereas the Si_2O_3 signature occurs at 11.4μm. At 900K, Si_2O_3 anneals to amorphous SiO_2 in a few hours as shown by the disappearance of the 11.4μm band and the increase at 12.5μm.

The current laboratory results are indicative that such experiments can provide important data for studying refractory interstellar and interplanetary matter.

REFERENCES

Cameron, A.G.W.: 1978, *Protostars and Planets*, ed. T. Gehrels, Univ. Arizona Press, Tucson, USA, pp. 453-487.

Day, K., and Donn, B.: 1978, Astrophys. J. 222, pp. L45-L48.

Donn, B.: 1976, *The Study of Comets*, ed. B. Donn, M. Mumma, W. Jackson, M.A. Mearn and R. Harrington, NASA SP-393, pp. 611-621.

Donn, B., Hecht, J., Khanna, R., Nuth, J., Stranz, D., and Anderson, A.B.: 1981, Surface Sci. 106, pp. 576-581.

Fraundorf, P., McKeegan, K.D., Patel, R.I., Sandford, S.A., Swan, P., and Walker, R.M.: 1982, *Lunar and Planetary Science XIII*, Abstracts, NASA, pp. 229-230.

Giese, R.H.: 1980, *Solid Particles in the Solar System*, eds. I. Halliday and B.A. McIntosh, D. Reidel Publ. Co. (Dordrecht, Holland; Boston, USA; London, England), pp. 1-13.

Greenberg, J.M., and Gustafson, B.A.S.: 1980, Astron. Astrophys. 93, pp. 35-42.

Knacke, R., and Kratschmer, W.: 1980, Astron. Astrophys. 92, pp. 281-288.

McSween, H.Y.: 1979, Rev. Geophys. Space Phys., pp. 1059-1078.

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press

Nuth, J., and Donn, B.: 1982a, Astrophys. J. 257, pp. L103-L105.

Nuth, J., and Donn, B.: 1982b, J. Chem. Phys. 77, pp. 2639-2646.

Protostars and Planets: 1978, ed. T. Gehrels, Univ. Arizona Press, Tucson, USA, pp. 488-624.

Shul'man, L.M.: 1972, *The Motion, Evolution of Orbits and the Origin of Comets*, eds. G.A. Chebotarev, E.I. Kazimirchak-Polonskaya and B.G. Marsden, D. Reidel Publ. Co. (Dordrecht, Holland), pp. 265-270.

Wetherill, G.W.: 1980, Ann. Rev. Astron. Astrophys. 18, pp. 77-113.

Whipple, F.L.: 1977, *Comets-Asteroids-Meteorites*, ed. A.H. Delsemme, Univ. Toledo Press, Toledo, USA, pp. 25-36.

Wood, J.A.: 1981, Earth Planet. Sci. Letters 56, pp. 32-44.

DISCUSSION

DELSEMME: What is the largest depth at which the irradiation of snows could still be significant? Could the anomalous comets producing large amounts of CO^+ be attributed or connected somehow to this surface effect, in which case the cometary population could still be chemically homogeneous in depth?

DONN: Energy deposition drops by a factor of ten at a depth corresponding to about 500 g/cm^2 and decreases much more slowly thereafter (Donn, 1976). It is not likely that CO^+ would so dominate everything else as in comet Morehouse (1908 III). Your suggestion, made to me later, that the rare CO^+ comets are the true "new" comets is an interesting one. It would seem to require that an unexpectedly large number of comets are re-perturbed into new comet orbits.

KELLER: Can you comment on the effects of the transition from amorphous to crystalline ice?

DONN: Such effects have been discussed by Patashnick, by Smoluchowski and by Klinger. They have pointed out that the energy release at about 154K could produce activity and coma formation at much larger heliocentric distance than solar radiation would. We have not investigated this transition in our experiments. The large pressure increase at 160K may be caused by this effect.

GEHRELS: Hoyle and Wickramasinghe in recent issues of Astrophysics and Space Science observe features in the infrared that they match with bacteria. Has anyone looked for such features on comets? Are their matches unique or could they be made with other organic but non-biological substances?

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press

DONN: Cometary infrared observations have only been done with filters at a few wavelengths insufficient to reveal such features. Condensed, discharged material and irradiated ice mixtures (Moore and Donn, Ap. J. 257, pp. L47-L50) yield very similar features. There is a slight (0.03 μm) wavelength difference between H-W and the others. This could be the result of matrix shifts. The E Coli spectra we obtained had somewhat stronger features at 6.56, 8.2 and 9.45 μm that have not been reported in the spectra of interstellar sources. As we wrote in our paper, non-biological material is a much more plausible candidate for features in spectra of astronomical sources than dried microorganisms.

https://doi.org/10.1017/S1539299600005335 Published online by Cambridge University Press