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"Sputtering" of Ice by MeV Light Ions

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We have measured the rate of erosion of thin films of water ice at low temperatures by bombardment with MeV hydrogen, helium, carbon, and oxygen ions. The effective "sputtering coefficients" are orders of magnitude higher than those anticipated from conventional sputtering theories. For example, for helium at 1.5 MeV, ~ 10 H_2O molecules are removed for each incident ion. We believe that the erosion process is closely associated with atomic ejection following ionization in the region near the surface.

Sputtering of metallic or covalent bonded solids is now a rather well understood phenomenon[1] with material being ejected from the surface as a result of the nuclear collision cascades set up in the solid. The situation is very different for ionic solids, such as alkali halides,[2,3] where the amount of sputtered material does not appear to depend on the nuclear stopping processes. There is a paucity of experimental information on the sputtering of condensed gases[4]—a subject of considerable astronomical importance. Radiation damage and channeling in ice crystals have previously been studied,[5] but without observation of the erosion phenomena reported in this paper. Erosion effects have apparently been observed in studies of the energy loss of MeV light ions through thin frozen films of Ar, N_2, and O_2,[6] but have not been quantitatively determined. In this paper we present the first measurements on the sputtering or erosion coefficients of water ice by energetic particles.

We have used Rutherford backscattering and thin-film techniques in our experiments. A vitreous carbon surface is cooled with a Cryotip[7] helium transfer tube to controlled temperatures between 15 and 110°K. Ice is grown on this surface by admitting H_2O vapor as a broad stream from a tube which the cold surface faces. The inset to Fig. 1 shows the geometry of the experiment. A typical growth rate is ~ 600 Å/min. Films have been prepared between 250 Å and 1.5 μm in thickness in this way. Under these conditions of deposition the ice film should be amorphous[8] and our visual observations are consistent with this expectation. The films are also stable. Even at 110°K the sublimation rate of ice is less than a monolayer a day. The erosion of the films has generally been carried out with the eroding beam electrostatically swept over a 4-mm-diam aperature to produce a uniform eroded region. For backscattering analysis, the beam is collimated to 1 mm diam, and can be located to ex-

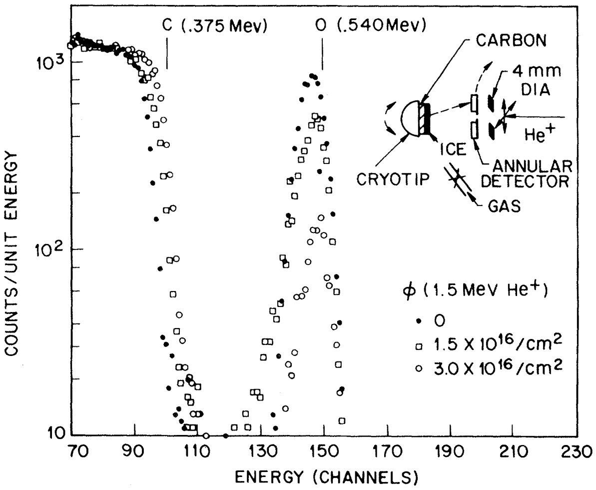

FIG. 1. Spectra of backscattered 1.5-MeV He ions from an ice film on carbon at three different stages in the erosion of the film by 1.5-MeV He ions. Erosion is carried out with a beam scanned to fill a 4-mm-diam aperture. Backscattering spectra are taken with a 1-mm detector aperture. Note that the backscatter peak from oxygen decreases with erosion and the backscattered edge for C moves to higher energy. The C and O marks indicate the energies of backscattering from C and O is they were at the surface. The energy scale is in channels of a multichannel analyzer.

amine different regions of the crater. The crater bottom is uniform and no pileup effects around the edge have been observed.

Energy spectra of backscattered MeV helium ions reveal the film thickness in two ways as shown in Fig. 1. The oxygen of the film is directly observed. The presence of the water film is also evident in the shift of the high-energy edge of the spectrum of ions backscattered from the carbon substrate, since such ions lose energy on passing through the film on entry and exit. Figure 1 shows spectra for a freshly grown film on carbon and from the same film after two different doses of 1.5-MeV He^+ ions have eroded the film.

Figure 2 shows the ice film "thickness" as a function of dose for the film of Fig. 1. The thickness has been expressed as the number of oxygen atoms per square centimeter (deduced from the oxygen peak) and as the number of water molecules per square centimeter (deduced from the C edge shift). This later calculation contains the assumption that the film is composed of H_2O. The good agreement between the two measures supports this assumption. The nearly linear decrease of film thickness with dose allows extraction of a "sputtering" or erosion coefficient defined as the number of ejected H_2O molecules per incident ion.

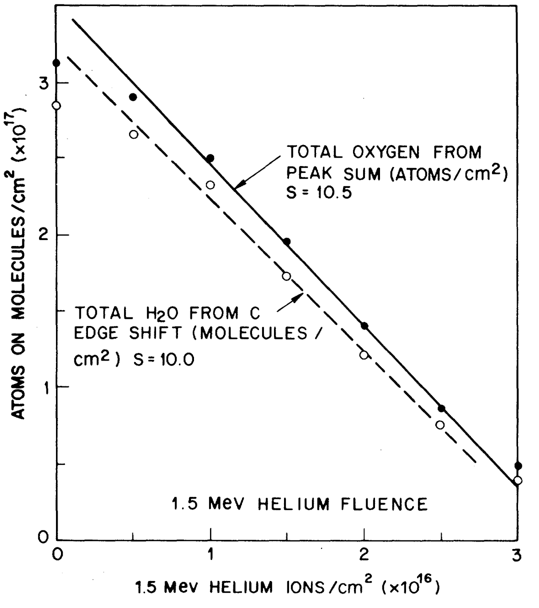

FIG. 2. The thickness of the H_2O film of Fig. 1 as a function of the fluence of 1.5-MeV He ions. The number of oxygen atoms in the film is determined from the area of the oxygen peak. The number of water molecules in the film is determined from the shift of the C edge in the backscatter spectrum. The absolute magnitude of the two quantities depends only on the stopping powers of He ions in water and carbon. Values from Northcliffe and Schilling (Ref. 9) have been used. The erosion coefficients, S, deduced from the slopes of the two data sets are very similar.

Eroding currents have generally been 0.5 to 5 nA/mm^2 for which the erosion coefficent is found to be independent of current. Most of the beam power is deposited directly in the substrate because the range of the eroding ions is much larger than typical film thicknesses. At significantly higher currents the erosion coefficient increases sharply, indicating the onset of film heating and sublimation. No differences in erosion coefficients have been found for different initial film thickness from 250 Å to 1.5 μm, indicating that the erosion process is occurring near the film-vacuum interface and is not governed by the film-substrate boundary.

Table I summarizes the erosion coefficients we have measured. An upper limit is indicated for 5-keV electrons. The erosion values for helium at 1.5 MeV are found to be insensitive to substrate temperature over a wide range (unlike the published results for alkali halides).[3] A modest energy dependence has been measured for hydrogen between 0.5 and 1.5 MeV. The measurement accuracy is approximately ± 5% but the reproducibility of the erosion coefficients is about ± 20%. The source of this variability is not known.

We believe that H_2O is being lost stoichiometrically from the film. We do not know the nature of the erosion products, however. It is quite possible that water molecules are coming off in clusters. Clusters are found in sputtering of metals, though they usually do not constitute a major fraction of the sputtering yield.[10]

Table I includes a column "calculated sputtering coefficient." These values are deduced using conventional Sigmund sputtering theory for metals[1]:

$$S(E) = [0.04\alpha S_n(E)/U_0]\ \text{Å}^{-2},$$

where α is a quantity ~ 1, S_n is the nuclear stopping power, and U_0 is the surface binding energy, in this case chosen to be equal to the sublimation energy of water molecules, ~ 0.3 eV. The nuclear stopping power of the sputtering ions is used in this calculation, since such stopping processes set atoms of a solid directly into motion. The calculated yields are far below our measured values.

TABLE I. Measured and calculated erosion or sputtering coefficients, S, and electronic and nuclear stopping powers for the projectiles of the experiment.

Ion	Energy (MeV)	T (°K)	S (molecules/ion)	Stopping power (10^{-15} eV cm^2/molecule) Electronic[a]	Nuclear[b]	Calculated sputtering coeff. (molecules/ion)
^1H	1.5	30	0.2 ± 0.04	6.8	0.0026	0.0035
	0.5	30	0.4 ± 0.08	17.1	0.007	0.0092
^4He	1.5	15	10 ± 2	71	0.036	0.048
	1.5	30	10 ± 2			
	1.5	100	10 ± 2			
^{12}C	1.5	30	520 ± 100	189	1.08	1.4
^{16}C	1.5	30	640 ± 130	201	2.6	3.5
e	0.005	30	< 0.2	0.4	...	...

[a] From Northcliffe and Schilling, Ref. 9.

[b] Scaled from stopping power in carbon as given by Gibbons, Johnson, and Mylroie (Ref. 11).

Figure 3 is a plot of the erosion coefficients of Table I for 1.5-MeV ions and the calculated Sigmund sputtering values which are several hundred times too small. Also plotted are the electronic stopping powers of the four ions in ice. In molecular solids electronic energy loss processes leading to the excitation of electrons and the breaking of covalent or hydrogen bonds may be very effective at promoting dissociation and fragmentation of the solid. The mass dependence of the electronic stopping power is not steep enough to account linearly for the experimental results. Nonlinear electronic processes must be involved. The nonlinearities are on a particle-by-particle basis, since the results do not depend on beam current.

We believe that the erosion mechanism is akin to the mechanism involved in track registration phenomena[12,13] in which heavily ionizing particles produce a highly ionized core region from which the atoms or molecules are ejected. The effectiveness of the process increases rapidly with the ionization track density. The insensitivity of our erosion coefficients to film thickness indicates that the erosion mechanism is not due to the escape of excited species over the entire track length (the ions penetrate through to the substrate in all cases). It seems likely that a roughly conical region, centered axially on the particle track and with dimensions 10–100 Å, is contributing to the erosion, the size of the region being controlled by the ionizing track density. In track registration, cylindrical regions with radii of this order are found to be of controlling importance.

During progressive erosion of the ice films, we have sometimes observed a substantial change in the film thickness uniformity. Not only does the film grow thinner than average in some re-

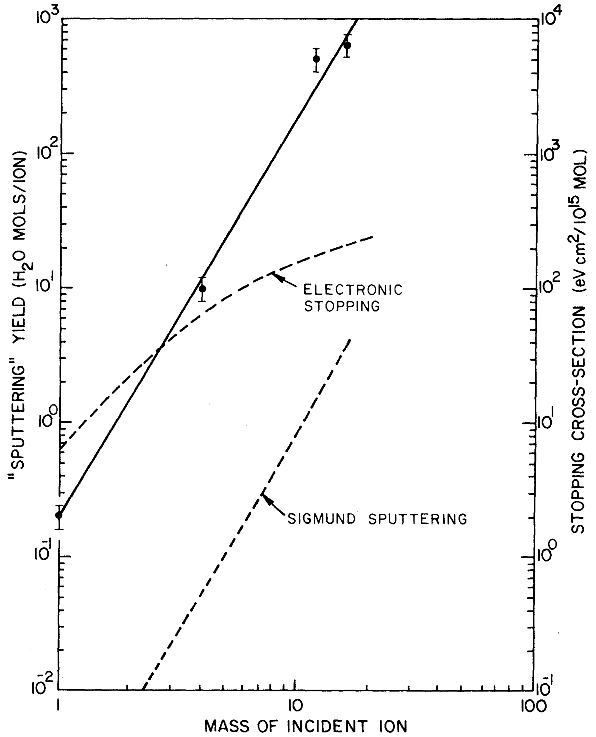

FIG. 3. The "sputtering yield" of ice bombarded by 1.5-MeV ^1H, ^4He, ^{12}C, and ^{16}O ions is shown as a function of mass. The solid and dashed lines are the nuclear and electronic stopping power of 1.5-MeV ions in ice.

gions but it grows thicker than even its original thickness in others. This effect is evident in the low-energy shape of the O peak in Fig. 1. After the $1.5\times 10^{16}/\mathrm{cm}^2$ helium ion fluence, although the peak area has decreased, there are contributions to the peak at lower energies than in the as-grown film. These contributions come from thick regions in the film. Visual inspection of the films shows they change from being invisibly transparent to highly reflecting as though snowflakes were forming in the region of bombardment. We believe we are observing the transformation of amorphous to polycrystalline ice at temperatures well below the ~140°K normal transformation temperature. The details of the changes in film thickness are not reproducible, perhaps because of differences in nucleation at the substrate surface or because of embryonic crystallites in the amorphous films.[8]

In summary, we have observed very large erosion coefficients for ice from thin films subjected to MeV ion bombardment. Even for the lightest ions the coefficients are far larger than that expected from a sputtering process. It appears that electronic processes must be involved in a nonlinear way, analogous to the formation of etchable tracks in molecular materials. Large erosion coefficients for molecular frosts may have important consequences in the balance of planetary atmospheres, in determining the size distribution of ice particles in interplanetary space, and in the dynamics of comets in the outer solar system. Various aspects of these astronomical implications will be presented elsewhere.[14] Such large erosion coefficients may also be important in desorption of frosts formed on the cryopanels of neutral beam injectors for fusion systems and subjected to bombardment by stray components of the injecting beams.

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Molecular Order versus Conformation Changes in the Liquid-Crystal Phases

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Deuteron magnetic resonance splittings and their temperature dependence from deuterated liquid-crystal compounds are analyzed in terms of molecular conformation and orientational order. Three order parameters are found to be necessary to explain the smectic-C (S_C) spectra whereas only two are required for the nematic (N), S_A and S_B phases. The data are consistent with the concept that the preferred conformation of the molecule remains unchanged at the N-S_C, N-S_A, and S_A-S_B phase transitions as well as throughout the temperature range of these phases.

During the past several years there has appeared in the literature a substantial amount of deuteron magnetic resonance data from several of the thermotropic liquid-crystal phases.[1-5] These data were obtained from a variety of different compounds in which one or both of the end-