from the leading hemisphere for  $\sim 50$  years and has just recently started or resumed. In either case, the unusually high temperature for the 1986 event may imply that there is another class of volcanic activity not directly related to earlier high-temperature events.

A major issue concerning volcanism on Io is the relative roles of sulfur and silicate melts in magmatic processes on the satellite. Shortly after the Voyager flyby, most workers focused on the role of sulfur compounds, principally S and SO<sub>2</sub>, in producing the spectacular eruptive plumes, which were interpreted as S and SO<sub>2</sub> geysers (16). However, the amount of S in the upper crust of Io and the composition of the material in volcanic calderas and in flow structures surrounding volcanic centers remain unresolved questions. On the basis of the scale of both positive and vertical relief on the satellite, Clow and Carr (17) argued that silicates and silicate volcanism must play a major role in forming the topographic features of Io's surface; the high albedo and spectral reflectance of the surface indicate that at least a surficial layer of S-rich material and perhaps S lavas occur in some areas (18).

The temperatures inferred for the volcanic areas observed by Voyager and for earlier telescopic observations have all been below ~700 K. Temperatures near 700 K are compatable with molten sulfur, and lower temperatures could be produced by a cooler crust covering portions of the melt. A model of silicate volcanism on Io, again with a range of temperatures attributed to different degrees of cooling, has also been developed to match the infrared observations (19), and the previously reported temperatures cannot be used alone to distinguish between these two possibilities. The model temperature for the event reported in this paper, 900 K, is higher than that reported for previous events (20). Because the boiling temperature of S in a vacuum is 715 K, such a high temperature virtually rules out pure molten S as the major constituent of the magma in this eruption. A source temperature of 715 K and a size chosen to match the 8.7-µm data cannot account for the 4.8-µm data; similarly, if the size is adjusted to match the 4.8-µm data, the 8.7-µm data are not matched (Table 2).

If molten S is ruled out as the source of the 1986 event, what are the remaining possibilities? Some other S compounds with boiling points higher than 900 K, such as Na polysulfides (11), have been suggested as surface materials on Io or as constituents of lava lakes; eruptions of these materials could satisfy the data. However, given the other evidence for silicate volcanism in at least some places on Io and the virtual certainty that tidal heating produces molten silicates

in the upper regions of Io's interior, we conclude that the high temperature of the event of 7 August 1986 is strong evidence for active silicate volcanism on the surface of Io. Molten S remains a likely candidate for other types of observed activity (as has been previously suggested), and the presence of  $SO_2$  gas around plumes and on the surface (3, 21) and the escape of S and O into the magnetosphere of Jupiter indicate that S plays a major role in some of Io's volcanic activity. Silicate volcanism and S volcanism, whether primary or produced by remobilization during silicate eruptions, probably both occur at various times and places on Io.

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the 4.8-µm variation with rotation is similar to the visible light curve [D. Morrison and N. Morrison, in Planetary Satellites, J. A. Burns, Ed. (Univ. of Arizona Press, Tucson, 1977), pp. 363-378]; and for solar phase angle, assuming that the phase coefficient was 0.022 magnitudes per degree.
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# Effect of the Orbital Debris Environment on the High-Energy Van Allen Proton Belt

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Orbital debris in the near-Earth environment has reached a number density sufficient for a significant collisional interaction with some of the long-lived high-energy protons in the radiation belt. As a result of a continuing buildup of a shell of man-made debris, the lifetimes of high-energy protons whose trajectories remain below 1500 kilometers will decrease to the point where in the next decades we can expect a noticeable reduction in their fluxes.

NTRODUCTION OF MAN-MADE OBJECTS such as Earth-orbiting spacecraft, spent rocket casings, and other kinds of debris into the near-Earth environment has not only raised concern about the safety of astronauts but has also created the potential for permanently altering the near-Earth trapped radiation environment. I have used the National Aeronautics and Space Administration-Department of Defense (NASA/ DOD) Civil Needs Database for orbital debris (1) together with moderate assumptions about future international space traffic to calculate lifetimes of high-energy protons (arbitrarily defined as protons with energy greater than 55 MeV) in the Van Allen radiation belt, subject to the assumption that in time the protons will collide with the particulate orbiting material and be absorbed by it. My results suggest that for low L values (L = 1.2 to 1.6) and high  $B_{\text{mirror}}$ 

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Fig. 1. Orbital debris environment (1) for the year 1986 and its projection for 2010. Each curve represents the total cross section of all sizes of debris particles per unit altitude.



points  $(h_{\min} = 200 \text{ to } 500 \text{ km})$  the projected characteristic lifetimes are currently counted in decades but will decrease to years by the year 2010, which is comparable to lifetimes resulting from atmospheric absorption. Here L represents the McIlwain parameter (2), which characterizes the proton magnetic drift shell and which can roughly be identified with the maximum distance of the particular magnetic field line from the center of Earth, measured in Earth radii;  $B_{\text{mirror}}$  is the strength of the magnetic field at which a particular proton is reflected during its bounce motion and which in the South Atlantic Anomaly occurs at a characteristic altitude,  $h_{\min}$ . Such a decrease in proton lifetimes implies a corresponding decrease in the energetic particle fluxes in those regions and, as a side effect, may decrease the radiation hazard as well as make higher altitude orbits available to manned flight. As a result, long-term monitoring of high-energy proton fluxes is essential to check this hypothesis.

High-energy proton fluxes in the Van Allen radiation belt are governed by a series of dynamic processes, among which are radial diffusion from higher L values, cosmic-ray albedo neutron decay (CRAND), atmospheric absorption, and slow collapse of Earth's magnetic dipole fields (3). For low L values and high particle energies only CRAND, atmospheric absorption, and the decay of Earth's magnetic dipole are generally deemed to be important. Atmospheric absorption varies with the solar cycle and intensifies as the atmosphere responds to an increase in solar heating and expands to higher altitudes during solar maxima. Reasonably good agreement has been achieved between theoretical predictions and experimental measurements of proton fluxes (4, 5). On this basis, it is possible to predict the lifetimes of trapped high-energy protons. Although different investigators have made somewhat different assumptions about the dynamic processes affecting the trapped proton fluxes, it is safe to say that for equatorially mirroring protons with energies in the hundreds of millions of electron volts that are trapped at L = 1.3 to 1.7, the lifetimes are in the hundreds of years. At L less than 1.3 or at low pitch angles (or both), the lifetimes are in the tens of years.

In recent years concern has been raised about a steady buildup of orbital debris in the near-Earth space environment (6). Such an increase poses a significant problem to the long-term integrity of large space structures and to the presence of humans in low Earth orbit. Because energetic protons in the inner part of the radiation belt travel enormous distances during their lifetimes (a 145-MeV proton travels at one-half the velocity of light) and the aggregate of the debris represents a relatively large geometric cross section, I undertook to determine whether there is a reasonable chance that protons at low radial distances would interact with the debris in a finite period of time.

The current (1986) and projected future (2010) debris differential cross section can be calculated as a function of altitude (Fig. 1). These data represent the NASA/DOD Civil Needs Database, which is calculated from radar measurements available in the monthly Satellite Situation Reports published by NASA Goddard Space Flight Center (1). The projection is based on assumptions about future international traffic: the U.S.S.R. is expected to continue the present level of activity, whereas the U.S. level of activity is expected to increase slightly. Most of the debris is concentrated in a shell between about 200 and 1500 km. In 1986 the total cross-sectional area of the debris environment between the surface of Earth and 2500 km was about  $1.5 \times 10^4$  m<sup>2</sup> or about three football fields. By 2010 it is expected to increase by about a factor of 8.

The present study presupposes that, given enough time, every energetic proton that executes the usual three adiabatic motions of (i) gyration about a magnetic field line, (ii) bounce along it, and (iii) a drift perpendicular to it has a finite probability of colliding with a piece of orbital debris. The collision probability is proportional to the geometric area of the piece. I also assumed that upon collision each proton is absorbed, either by being stopped outright or through sufficient energy degradation to remove it from consideration as a hazard to manned flight. To establish for what energies this holds true, it is necessary to determine the average thickness of the debris pieces.

From a direct knowledge of the origin of a number of orbital debris pieces, Badhwar (7) has determined a relation between their mass M (in kilograms) and their radar cross section  $A_{\rm rcs}$  (in square meters)

$$M = 36 A_{\rm rcs}^{1426} \tag{1}$$

If I now assume a flat plate geometry for the orbital debris, then for a given density n I can write the thickness t as

$$t = (36/n) A_{\rm rcs}^{0426}$$
 (2)

The largest area contribution is from pieces with a radar cross section of about 5  $m^2$ . Assuming a density of 2700 kg/m<sup>3</sup>, I obtain a typical thickness of 0.026 m, which corresponds to a stopping range in aluminum for 82-MeV protons, whereas protons with energies greater than 140 MeV lose less than half of their energy in that thickness. Above that value the proton range is sufficiently high that a single penetration through a piece of debris only reduces the energy somewhat without significantly affecting the lifetime.

The probability P that a proton suffers a



**Fig. 2.** Characteristic lifetimes of protons for the drift shells L = 1.2, 1.3, 1.4, 1.5, and 1.6 as a function of  $B_{\min}/B_{\min ror}$  for the years 1986 (**A**) and 2010 (**B**).

**Fig. 3.** Characteristic lifetimes due to orbital debris of 30-, 55-, and 120-MeV protons in the South Atlantic Anomaly for the years 1986 and 2010. Also shown are lifetimes of 55-MeV protons due to atmospheric absorption for solar maximum and minimum (9).



collision in an increment of distance ds, after traveling a distance s, is given by

$$dP = -P(s)\sigma(s)N(s)ds \qquad (3)$$

t (years)

Both the average cross section of the debris particles  $\sigma$  and the number density of those particles *N* are a function of *s* along the proton trajectory. Because the energy is conserved before the collision, the proton velocity  $\nu$  is a constant and I can write

$$\ln P(t) = -\nu \int_0^t \sigma(t) N(t) dt$$
 (4)

If I carry out the integral for one drift period  $t_d$  along the proton trajectory, I can define the characteristic life of a trapped proton as

$$\mathbf{r} = \frac{t_{\rm d}}{\nu \int_{0}^{t_{\rm d}} \sigma(t) N(t) dt}$$
(5)

To determine how much time a proton spends at any particular altitude, I used the guiding center approximation in conjunction with the International Geomagnetic Reference Field for 1985 (IGRF 1985) (8). The guiding center approximation substitutes the motion of the guiding center (the center of gyration about the field line) of the proton for the actual trajectory. In many cases this simplifies the calculations without impairing their accuracy. The debris data were obtained from the NASA/DOD Civil Needs Database (16). The integration was carried out along the geomagnetic field lines between appropriate mirror points. The field lines were separated by 10° intervals in longitude to approximate the effect of the westward drift of the proton around Earth. For this study I selected protons at L values of 1.2 to 1.7 and a variety of pitch angles. I expect that orbital debris will have a strong effect on those particles.

Two families of curves can be generated for 1986 and 2010 representing 55-MeV proton characteristic lifetimes due to absorption by debris for different values of *L* plotted as a function of  $B_{min}/B_{mirror}$  (Fig. 2, A and B). The lowest points on each graph correspond to a minimum altitude for the mirror point of about 100 km, which puts them well into the region of strong atmospheric absorption. The lifetimes of protons in 2010 will be shorter by about a factor of 10 than those in 1986. This, of course, is a direct outcome of a roughly tenfold increase in the projected cross section of the orbiting debris. The shortest lifetimes are found for protons at the lowest L values and the lowest equatorial pitch angles, and, indeed, protons of virtually all pitch angles at L = 1.2 remain trapped within the heart of the debris belt. The equatorial pitch angle of a particle is the angle (or the supplement of the angle if it is greater than 90°) made by its velocity vector with the direction of the magnetic field at its minimum along the field line. The significance of lifetimes due to orbital debris can be assessed only in comparison with lifetimes due to other processes such as atmospheric absorption, cross L diffusion, and the collapse of Earth's dipole. Atmospheric absorption is due mainly to ionization losses, with nuclear interactions contributing a negligible amount. In other words, if the proton lifetimes due to the presence of orbital debris are comparable to or shorter than the lifetimes due to other processes, orbital debris will have an impact on the flux of trapped protons.

As part of a theoretical study of solar cycle modulation of protons that mirror at low altitudes off the geomagnetic equator, Dragt (9) provided a useful procedure for lifetime calculations. Using his method to calculate lifetimes, I find that for the period around the year 2010 during solar minimum, at altitudes between 500 and 1500 km, the lifetimes of protons due to the debris are either comparable to or shorter than the lifetimes due to atmospheric absorption (Fig. 3). This means that in the not-toodistant future during solar minimum the low-altitude proton fluxes will be lower than expected from atmospheric absorption alone.

Farley and Walt (5) have developed a

theory of the equilibrium of equatorial highenergy proton fluxes that is based on a combination of albedo neutron decay, atmospheric absorption, and radial diffusion, and that was found to be in good agreement with data from Orbital Vehicles 3 and 4.

Schulz and Paulikas (10) and Heckman and Lindstrom (11) have shown that the present rate of decay of the geomagnetic dipole field leads to a time scale for the change of proton energy that is of the order of a thousand years. A comparison of time scales can be carried out for change of proton energy from the decay of Earth's dipole field, from radial diffusion in the equatorial plane at constant µ, from collisions with the atmosphere for three values of  $\mu$ , and from interactions with orbital debris for the same three values of  $\mu$  [Fig. 4 (10)]. Here µ, the first adiabatic invariant, is defined as the perpendicular energy of the particle divided by the local magnetic field. In the case of the interaction of protons with orbital debris, in accord with my assumptions the characteristic time for the energy change can be identified with proton lifetime due to orbital debris absorption.

In 1986 the characteristic lifetimes of protons at or below L = 1.3 were comparable to or less than those due to atmospheric absorption, which up till then was the domi-



**Fig. 4.** Characteristic lifetimes (10) of high-energy protons in the equatorial plane as a function of L for two values of the diffusion coefficient D (dashed lines), due to the decay of Earth's magnetic dipole field (horizontal line at  $\tau = 1000$ ); due to atmospheric absorption for  $\mu = 0.4$ , 1.0, and 2.6 GeV/G (dotted lines); and due to interactions with orbital debris for the same values of  $\mu$  in the year 1986 and 2010 (six solid, steeply rising lines).

nant factor determining flux levels at those L values. By 2010 orbital debris absorption as a loss mechanism will be responsible for the shortest lifetimes below L = 1.4 and thus will be the most important factor determining the ambient fluxes of high-energy protons in the Van Allen belt.

The low-altitude regions of the magnetosphere are subject to solar cycle variations. Thus a test of the proposed hypothesis with appropriate radiation detector-bearing

spacecraft will require the sampling of equatorial regions above about 700 km or at 1.2 < L < 1.7.

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## A Synchrotron X-ray Study of a Solid-Solid Phase Transition in a Two-Dimensional Crystal

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A measurement and interpretation on a molecular level of a phase transition in an ordered Langmuir monolayer is reported. The diagram of surface pressure  $(\pi)$  versus molecular area of a monolayer of chiral (S)-[CF<sub>3</sub>-(CF<sub>2</sub>)<sub>9</sub>-(CH<sub>2</sub>)<sub>2</sub>-OCO-CH<sub>2</sub>- $CH(NH_3^+)CO_2^-$  over water shows a change in slope at about  $\pi_s = 25$  millinewtons per meter. Grazing-incidence x-ray diffraction and specular reflectivity measurements indicate a solid-solid phase transition at  $\pi_s$ . The diffraction pattern at low pressures reveals two diffraction peaks of equal intensities, with lattice spacings d of 5.11 and 5.00 angstroms; these coalesce for  $\pi \geq \pi_s$ . Structural models that fit the diffraction data show that at  $\pi > \pi_s$  the molecules pack in a two-dimensional crystal with the molecules aligned vertically. At  $\pi < \pi_s$  there is a molecular tilt of 16° ± 7°. Independent x-ray reflectivity data yield a tilt of  $26^{\circ} \pm 7^{\circ}$ . Concomitant with the tilt, the diffraction data indicate a transition from a hexagonal to a distorted-hexagonal lattice. The hexagonal arrangement is favored because the -(CF<sub>2</sub>)<sub>9</sub>CF<sub>3</sub> moiety adopts a helical conformation. Compression to 70 millinewtons per meter yields a unit cell with increased crystallinity and a coherence length exceeding 1000 angstroms.

large variety of Langmuir monolayers at the air-water interface show sharp discontinuities in their surface pressure-molecular area  $(\pi - A)$  diagrams that are indicative of phase transitions (1). However, structural studies at the molecular level have until now been hampered by experimental difficulties. Grazing-incidence x-ray diffraction and specular reflectivity measurements (2-10) have recently become important tools for the structural investigation of Langmuir monolayers. We have performed such measurements on monolayers of compound 1

$$\begin{array}{c} CF_{3}\!\!-\!\!(CF_{2})_{9}\!\!-\!\!(CH_{2})_{2}\!\!-\!\!OCO\!\!-\!CH_{2}\!\!-\!\\ CH(NH_{3}{}^{+})CO_{2}{}^{-} \end{array}$$

at the air-water interface, using the liquid surface diffractometer at the synchrotron xray beamline D4, Hasylab, Deutches Elektronen-Synchrotron (DESY), Hamburg.

This compound was chosen for study for the following reasons. The  $\pi$ -A diagram of 1 (Fig. 1) shows a change in slope at a surface pressure of 20 to 30 mN/m which we designate as  $\pi_s$ , corresponding to A = 30 to 35 Å<sup>2</sup>. Compound 1 is one of a series of  $\alpha$ -amino acid surfactants that were designed for the study of oriented crystallization of the  $\alpha$ -form of glycine at the monolayer-water interface (11). The induced crystallization of  $\alpha$ -glycine at the interface under the monolayer in various states of compression indicated a mismatch between the packing arrangement of the glycyl head groups of 1 and that of  $\alpha$ -glycine. Thus we studied the monolayer by x-ray methods to elucidate, at a molecular level, its structure on both sides of the phase transition. In terms of x-ray scattering, 1 has several advantages for structural determination. The fluorocarbon chain has a much higher x-ray scattering power than the corresponding hydrocarbon chain and is more rigid. Further, the glycyl head groups should, by virtue of intermolecular hydrogen bonding, "fix" the molecular

packing in the monolayer, preventing rotational disorder.

Monolayers of 1 were spread from solutions in chloroform:trifluoroacetic acid (96:4) onto a water surface in a temperature-controlled Langmuir trough placed on the diffractometer and maintained at 20°C. Details of the experimental conditions are given elsewhere (3, 9). At high  $\pi$  one peak appeared (Fig. 2); as pressure was decreased, the peak shifted position, widening and becoming less intense, until at about 25 to 30 mN/m it split into two peaks. The phase transition is clearly indicated by the dspacings, which along with the integrated intensities and the peak half-widths [inversely related to the coherence length L by the Scherrer formula (12)] are displayed as a function of surface pressure in Fig. 3. The increase in half-width at lower  $\pi$  is accompanied by a 60% decrease in integrated intensity. Rotation of the sample around an axis normal to the water surface showed that the monolayer is a two-dimensional powder. No other diffraction peaks were detected in



Fig. 1. Diagram of surface pressure versus surface area  $(\pi$ -A) of compound 1 at 20°C. Solubility problems lead to unreliability in the concentration of solutions of 1, and therefore of the measurement of molecular area in the isotherm. Thus no values are given. The limiting area per molecule (A) was assigned from the x-ray diffraction data (28.5  $Å^2$  per molecule).

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