

rected toward one element, it is possible that pyroclastic layers could be more definitely characterized chemically by measuring suitable trace-element ratios. Such measurements might prevent confusion of the effects of enrichment by alteration with inherent elemental abundances; this confusion affects the use of TiO_2 as an identifying parameter.

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References and Notes

1. D. R. Crandell, D. R. Mullineaux, R. D. Miller, M. Rubin, *U.S. Geol. Survey Profess. Paper 450-D* (1962), p. 64.
 2. H. A. Powers and R. E. Wilcox, *Science* **144**, 1334 (1964).
 3. R. Fryxell, *ibid.* **147**, 1288 (1965).
 4. S. S. Goldich, *J. Geol.* **46**, 17 (1938).
 5. S. Aomine and K. Wada, *Amer. Mineralogist* **47**, 1024 (1962).
 6. N. M. Short, *J. Geol.* **69**, 534 (1961).
 7. A. K. Baird, *Norelco Reporter* **8**, No. 6, 108 (1961).
 8. Localities for all samples can be furnished on request.
 9. Color notation for dry powders follows Munsell Soil Color Charts (1954).
 10. D. R. Mullineaux, *Geol. Soc. Amer. Special Paper 76* (1964), p. 285.
 11. ———, personal communication.
 12. C. A. Hopson, A. C. Waters, V. R. Bender, M. Rubin, *J. Geol.* **70**, 635 (1962).
 13. TiO_2 content is an effective discriminant for a somewhat different and much broader problem involving volcanic rocks—the discrimination of oceanic-island and circumoceanic Cenozoic volcanics [F. Chayes and D. Métais, *Carnegie Inst. Washington Year Book 63* (1964), p. 179].
 14. Roald Fryxell, D. R. Mullineaux, Virginia Steen, John Westgate, and R. E. Wilcox made available to us many samples without which this study could not have been undertaken. We are particularly indebted to Roald Fryxell for helpful comments on many occasions, and thank William Kohler, D. R. Mullineaux, Virginia Steen, and R. E. Wilcox for reviewing the manuscript.
 15. B. N. Moore, *U.S. Geol. Survey Bull.* **875** (1937), p. 159.
 16. Analyst: G. K. Czamanske.
- * Present address: U.S. Geological Survey, Washington, D.C.

27 September 1965

Radiation Sintering of Lunar Dust

Abstract. Protons in the solar wind displace atoms in the grains of lunar dust. These atoms may, through diffusion, sinter the dust layer into a partly coherent but still highly porous structure.

It has been variously suggested (1) that nearly all the moon's surface is covered by a layer of fine dust. Optical evidence seems to indicate that this layer is exceedingly porous and that the micron-size particles cast shadows whenever the angle of the incident light

is not normal. The exceedingly low thermal inertia of the surface can also be explained by means of this model, although the conclusions are less direct. These factors, which are related to the basic question of the mechanical strength and rigidity of the surface, are critical for the landing of a moon probe.

Several authors have suggested that corpuscular radiation from the sun, which consists primarily of protons, may produce coloration (2) of lunar dust and even sputtering, which could explain the polarization behavior (3) and perhaps could increase cohesion between dust particles (4). Increase of cohesion seems unlikely because very high doses, corresponding to about 10^5 years of unperturbed exposure to solar protons, would be necessary to obtain it. I wish to draw attention to the possibility that the protons may lead to gradual sintering of the particles of lunar dust into a relatively rigid but open—that is, not dense—structure, without sputtering. By sintering I mean gradual transition from a local mechanical contact to a rigid local bond between two grains without formation of a solid mass. Recent experiments done at the Brookhaven National Laboratory show that $80\text{-}\mu$ diamond dust sinters near 50°C when exposed to a fast (about 1 Mev) neutron flux of about 10^{20} neutrons per square centimeter (5). Similarly, $40\text{-}\mu$ Al_2O_3 dust is sintered at approximately the same temperature after irradiation of 6×10^{18} neutrons per square centimeter (6). Unfortunately the lowest total neutron flux at which these phenomena occur is not known.

Essentially all solid-state reactions take place because of the availability and motion of crystal lattice defects such as vacancies or interstitial atoms. Dienes and Damask (7) and others (8) have shown that neutron or proton irradiation can accelerate these reactions by a factor of 10^6 or more because it increases the concentration of vacancies and interstitial atoms above that normally present. It is essential, however, that there be enough thermal agitation to provide for the motion of these defects. It is well known that interstitial atoms in ionic solids (9) and metals (10) can move at temperatures as low as 10°K . Inasmuch as the temperature of the lunar surface varies between about 150° and 350°K one can safely assume that at

least the interstitial atoms have enough mobility, especially when the sun is high in the lunar sky. The rather immobile vacancies may lead to formation of color centers or to luminescence.

In making quantitative estimates it is important to note that neutrons displace atoms in all kinds of solids only by direct elastic collisions. On the other hand, charged particles such as protons can loose energy and produce displacements not only by elastic collisions but also by double-ionization (11) processes in insulating crystals. The exact composition of the lunar surface is not known, but one suspects the presence of various hard oxides such as quartz and magnesium oxide (2, 3, 12). Inasmuch as Al_2O_3 resembles these rocks more than diamond does, the data from Brookhaven on Al_2O_3 are of primary significance. The Debye temperature, melting point, and type of bonding suggest that the mobility of defects in these oxides is comparable. One expects also that the rate-controlling process is the motion of the interstitial oxygen. The results obtained at Brookhaven on sintering of Al_2O_3 indicate that the number of displaced atoms in each grain is about 20 times greater than the number of atoms on its surface. A large fraction of the atoms will reach the surface because of the outward strain gradient. One can thus expect that, under these conditions, local sintering will occur when the number of displaced atoms reaching the surface is perhaps 10 times as great as the number of atoms on the surface.

The average proton flux impinging upon the lunar surface can be divided into: (i) solar wind (13), or expanding solar corona, of a mean energy of about 4 kev and a flux of 10^8 particles per square centimeter per second; (ii) the newly discovered, high-energy, continual flux (14) of high-energy protons which varies from perhaps 1 to 10 particles $\text{cm}^{-2} \text{sec}^{-1}$ at 2 Mev to $1/10$ particle $\text{cm}^{-2} \text{sec}^{-1}$ at 10 Mev; and (iii) protons associated with solar flares (15) which can reach 10^3 particles $\text{cm}^{-2} \text{sec}^{-1}$ at 1 Mev and a rapidly decreasing flux at higher energies. While theoretical and experimental information about the production of defects and the range of high-energy protons is fairly good, the situation with 4-kev protons is rather uncertain. From various con-

siderations one can estimate that the solar wind or plasma protons are scattered and absorbed within a few tenths of a micron of the surface of the solid and that each proton produces about seven displaced atoms. Thus in a few months each fresh particle of dust should be sintered to its neighbors at the points of contact. This is much less than the time required for sintering through sputtering. Nevertheless, this efficient sintering process is limited to the outermost layer of the dust. It is also continually inhibited by the impact of micrometeorites and by breaking up by larger meteorites (16). Deeper layers of the dust are sensitive only to the more energetic protons. Thus 2-Mev protons will be stopped within less than 0.1 mm of the surface of the dust layer and 10-Mev protons will not reach beyond 1 mm. The flux of protons of higher energy, even if one includes the solar flares, is relatively low, and the defects the protons produce are spread over a much thicker layer. Thus, while a sintering process under these circumstances is possible on the scale of thousands or millions of years, its efficiency is critically dependent upon the meteorite bombardment. It appears thus that radiation sintering of lunar dust may play an important role in determining the mechanical properties of the outermost lunar surface. In a quantitative comparison of all the various phenomena which affect the cohesion and formation of surface dust, the recently discussed chemical degradation (17) should also be taken into account. Evidently much careful experimental and theoretical work is needed before the whole problem of the structure of the lunar dust layer is understood.

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References and Notes

1. See, for instance A. Dollfus, in *Physics and Astronomy of the Moon*, Z. Kopal, Ed. (Academic Press, New York, 1962) or Z. Kopal, *The Moon* (Chapman and Hall, London, 1963).
2. T. Gold, Intern. Astron. Union (Comm. 16)—NASA Conf. on the Surface of the Moon, Goddard Space Flight Center, April 1965.
3. B. W. Hapke, *ibid.*
4. G. K. Wehner, in *The Lunar Surface Layer*, J. W. Salisbury and P. E. Glaser, Eds. (Academic Press, New York, 1964), p. 532.
5. D. Keating, private communication.
6. P. Levy, private communication.
7. G. J. Dienes and A. C. Damask, *J. Appl. Phys.* **29**, 1713 (1958).
8. A. Spilners and R. Smoluchowski, Symp. on Reactivity of Solids, Amsterdam, 1960.
9. N. Itoh, B. S. H. Royce, R. Smoluchowski, *Phys. Rev.* **137**, A1010 (1965).
10. See, for example, A. C. Damask and G. J.

- Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1964).
11. See J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1962).
12. F. E. Wright, F. H. Wright, H. Wright, in *The Moon, Meteorites and Comets*, B. M. Middlehurst and G. P. Kuiper, Eds. (Univ. of Chicago Press, Chicago, 1963).
13. M. Neugebauer and C. W. Snyder, *Science* **138**, 1095 (1962).
14. D. A. Bryant, T. L. Cline, U. D. Desai, F. B. McDonald, *Goddard Space Flight Center Rept. X-611-65-107* (1965).
15. Amer. Astron. Soc.—NASA Symp. on the Physics of Solar Flares, Goddard Space Flight Center, Oct. 1963.
16. W. R. Corliss, *Space Probes and Planetary Exploration* (Van Nostrand, New York, 1965).
17. J. J. Naughton, I. L. Barres, D. A. Hammond, *Science* **149**, 630, 1965.
18. I am indebted to several participants of the 1965 conference at Goddard (2, 3) and to A. C. Damask and G. J. Dienes for discussion.

28 September 1965

Intercrystalline Links in Bulk Polyethylene

Abstract. *Strength-promoting intercrystalline links in polyethylene, crystallized from the melt, have been observed under the electron microscope. The links measure up to many thousands of angstroms in length (depending upon the molecular weight of the polymer) and are of the order of 100 Å in diameter. Their formation appears to be initiated by molecular chains which contact, and begin to crystallize upon, the surfaces of two or more different crystals, often some distance apart. Deposition continues until these molecular bridges are pulled taut. More molecules are laid down upon the bridges to build up the larger links, which are themselves crystalline and may well be extended-chain single crystals.*

When crystallized from the melt, synthetic high polymers such as polyethylene develop spherulitic structures which consist, in the main, of chain-folded lamellar crystals (1). It is evident from the ductility and strength of these materials, however, that neighboring lamellae are probably bound by ties stronger than those provided by Van der Waals attraction between planes of molecular folds, even in the case of lamellae whose surfaces are in intimate contact. Consequently, it has generally been thought that molecular folding is not as regular in polymers crystallized from the melt as it appears to be in single crystals grown from dilute solution. Some molecules (tie molecules) participate in the growth of two or more adjacent lamellae, thereby providing relatively short molecular

links which reinforce the structure (2). We now report what we believe to be the first direct observation of intercrystalline links in a melt-crystallized high polymer. These links are much more substantial (and thus much stronger) than has been anticipated. The links have been revealed by co-crystallizing fractionated samples of linear polyethylene with $n\text{-C}_{32}\text{H}_{66}$, this hydrocarbon diluent being removed later by dissolution in xylene at room temperature to expose the skeletal structure of the high polymer.

The photograph on the cover of this issue is an electron micrograph of the boundary between spherulites grown at 95°C in fractionated polyethylene (weight = average molecular weight, $\bar{M}_w$, = 726,000) blended with 50 percent of $n\text{-C}_{32}\text{H}_{66}$. The fibrillar links, which bridge radial arms of the spherulites and also the boundary between these spherulites, measure up to 15,000 Å in length and are between 30 and 300 Å in diameter. They are a genuine growth feature and not an artifact resulting from deformation of the sample. Electron-diffraction analysis of selected areas indicates that chain molecules lie parallel to the long axes of the links, and we have reason to believe that each link may be an extended-chain single crystal.

No intercrystalline links were found in polyethylene of molecular weight 4500 and only a few relatively short links were observed in polymer of molecular weight 27,500. In fractions of higher and higher molecular weight, however, links were found in increasing profusion, and their maximum length ($l_{\max}$) obeyed the relation $l_{\max} \sim 20 (\bar{M}_w)^{1/2}$ Å. Since the average maximum dimensions of a coiled chain (the average distance between the segments furthest removed from one another) should vary as $(\bar{M}_w)^{1/2}$, this relation suggests the following interpretation of our observations.

At the appreciable supercoolings generally employed in crystallizing high polymers from the melt, chain molecules may occasionally come into contact with, and begin to crystallize upon, the surfaces of different, and often widely separated, crystals. These molecules continue to crystallize until they are pulled taut. In some manner not as yet clear (possibly with assistance from entanglements) further molecules condense upon the nuclei provided by the bridges established initially in this way.