3. N. V. Sidgwick, *The Chemical Elements and Their Compounds* (Oxford Univ. Press, London, 1950), vol. 2, pp. 990–91.
3a. J. H. Simons, *Flourine Chemistry* (Academic Press, New York, 1950), vol. 1, pp. 90–92, 96.
4. F. Dudley, G. Gard, G. Cady, *Inorg. Chem.* **2**, 228 (1963).
5. S. M. Williamson and C. W. Koch, *Science* **139**, 1046 (1963).
6. H. H. Claasen, H. Selig, J. G. Malm, *J. Am. Chem. Soc.* **84**, 3593 (1962).
7. Work supported by the Office of Naval Research, project Nonr-3085(01).

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Surface Features of Metallic Spherules

Abstract: *Metallic spherules of variable character have been recovered from Antarctic snow. Three types were recognized from their surface features: type I, smooth, polished spherules, apparently produced by surface melting of the particles upon entry into the earth's atmosphere; type II, spherules with a corrugated surface caused by differential hardness of internal, intersecting lamellae, but modified by superimposed pits; and type III, spherules with random, circular depressions or pits apparently resulting from impact with submicroscopic particles. Spherules of types II and III were too small to have suffered abrasion by impacts in the earth's atmosphere, and it is postulated that their surfaces may have been produced by erosion in space. Preservation of these surface details would have been possible if entry into the atmosphere took place at low velocities and low-angle trajectories.*

Murray (*1*) was the first to recognize surface details on metallic spherules of extraterrestrial origin. He noted that some spherules possessed a large surface depression or "cupule," while others had a "crystalline" surface or "granular" appearance. Later, Buddhue (*2*) reported the discovery of similar metallic spherules with "a number of shallow, dimplelike depressions," but noted that otherwise their surfaces were smooth and shiny. To investigate the surface features of such particles further, we examined, under optical and electron microscopes, samples recovered from Antarctic snow.

The metallic spherules studied were selected as representative of those which occur in the snow of the southern Antarctic Peninsula region (Ellsworth Land) (*3*). Electron probe analyses of apparently identical material indicated the following elemental composition: Fe, 65 to 70 percent; Mn, 1 to 2 percent; Ti, trace; Si, trace. These results correspond to the composition of the mineral magnetite, which was found to be the primary mineralogical component by mineragraphic and x-ray tests. The spherules were microscopic in dimensions, the average size being only about 40 μ in diameter. Their surface features are at least two orders of magnitude smaller. Three types of spherules were recognized from surface features: type I, smooth, polished spherules with no apparent surface detail; type II, spherules of lower luster and a corrugated surface, comprised of two regular sets of lamellae; these lamellae intersect at approximately right angles and show pronounced relief, creating surface "ridges" and "furrows"; type III, spherules of variable luster, with randomly oriented, approximately circular depressions or "pits." In the samples examined, spherules which displayed surface features (types II and III) were on the order of three times more abundant than those which did not (type I).

Figure 1 shows an optical micrograph of a type-II spherule under high magnification. Unfortunately, it was only possible to bring a small portion of the spherule into focus. Nonetheless, the figure shows the regular pattern of intersecting lamellae characteristic of this spherule type. The relief between adjacent lamellae is clearly demonstrated by the shadow patterns.

Details of the surface microtopography of type-II and -III spherules were studied under the electron microscope by the carbon replication technique (*4*). The spherules were carefully transferred to a clean, thin, glass cover slip by a fine, sable-hair brush wetted with ethanol. They were then preshadowed *in vacuo* with platinum in two directions mutually perpendicular to one another at an angle of incidence of about 45°, and then carbon was evaporated over the specimen. The glass slide and spherules were dissolved from the replica by floating them over several changes of HF and HCl. The resulting carbon replica film was washed in distilled water and lifted onto a 200-mesh grid; electron micrographs were made of representative fields, with a Siemens Elmiskop I instrument.

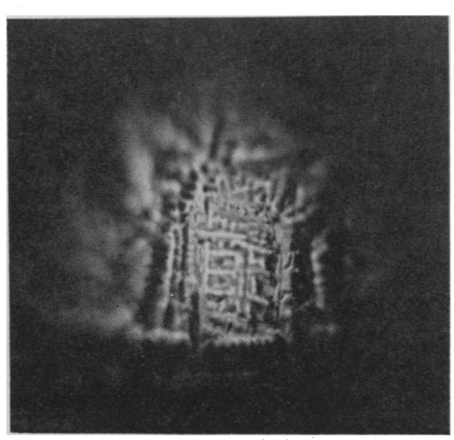

Fig. 1. Optical micrograph of type II metallic spherule from Station 496, Antarctic Peninsula Traverse. [about × 3000]

Fig. 2. Electron micrograph of type-II metallic spherule from Station 464, Antarctic Peninsula Traverse.

Figure 2 shows part of the surface structure of a type-II spherule at a magnification equivalent to visual examination of a portion of a sphere several meters in diameter. As in Fig. 1, two sets of lamellae which intersect approximately at right angles can be observed. Each lamella is about 0.5 μ in width. In addition, Fig. 2 reveals the presence of shallow, circular depressions or pits superimposed on the lamellar pattern. Polished surfaces of individual spherules revealed that mineralogical components of the spherules occurred as lamellae which oriented in at least two directions. It would appear that the regular array of surface features on type-II spherules is a manifestation of their internal lamellae; differential hardness of the lamellae comprising the spherules probably produced the surface relief.

Figure 3 shows part of a type-III spherule. Roughly circular pits with steep, ridge-margined walls and level floors are randomly scattered over its surface. Some pits appear to overlap,

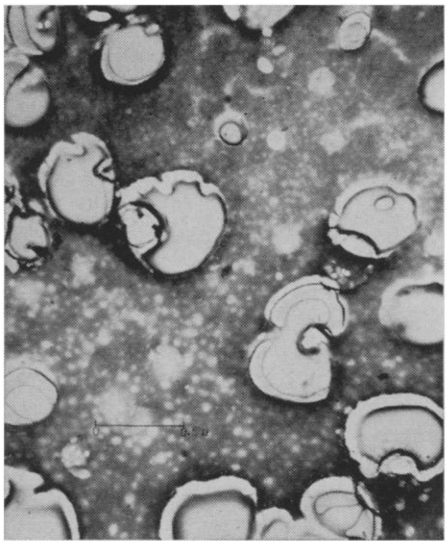

Fig. 3. Electron micrograph of type-III metallic spherule from Station 224, Antarctic Peninsula Traverse.

but most are separated from their neighbors by at least a thin wall. Most of the pits are about 0.5 μ in diameter, although a few shallower pits about 0.1 μ across are present. The larger pits often show an intricate internal structure. In many cases, a complex, deeper area is located near one side of the pits. In view of the random occurrence and diverse character of the surface pits, it would be difficult to maintain that they were produced by internal features of the spherules. Perhaps the pits represent impacts of submicroscopic particles upon the microscopic spherules while in space.

If it is assumed that the type-III spherules may have resulted from impact of smaller particles with the spherules, it is possible to estimate the diameter of impacting particles by the equation of Charters and Summers (*5*), using the measured dimensions of the pits and spherule density (*6*):

$$d_c = 2(2.28)\left(\frac{\rho_p}{\rho_t}\right)^{2/3}\left(\frac{V}{V_s}\right)^{2/3} \quad d$$

The diameter of impacting particles which could produce such pits was found to be about 0.04 μ. It is interesting that Hemenway *et al.* (*7*) found extremely small (about 0.01 μ in diameter), high-density particles, or "nanometeorites," to exist in large quantities at high altitudes over Antarctica. Particles of the proper size are thus present, but it remains to be proved that impact of these particles upon the surfaces of the larger spherules while in space could have produced the pits observed.

We consider it unlikely that terrestrial corrosion could have produced the surface features. These spherules were recovered from snows of recent age (less than 25 years old), which were kept frozen until processed in our laboratory. Corrosion would have been impeded by the short time that temperature-reduced chemical reactions could have proceeded. Furthermore, no reagent stronger than ethanol was applied to the spherules prior to examination under the optical microscope. Techniques employed in spherule manipulation or mounting could hardly be responsible for the surface features, because the instruments used were many times larger than the entire spherules. Abrasion of one spherule against another during processing could not have produced the surface textures. Because of their small size, a cushion of air would prevent contact and abrasion between spherules (*8*).

The smooth surfaces of type-I spherules were apparently produced by surface melting upon entry into the earth's atmosphere. Under Krinov's definitions (*9*), these would be considered *micrometeorites*. If, on the other hand, the surface details of type-II and type-III spherules were produced by erosion in space and were preserved during passage through the earth's atmosphere, these particles would be considered *cosmic dust;* their form being unchanged from what it was in space. However, type-II and type-III spherules are about an order of magnitude larger than particles normally considered cosmic dust. For these particles to have been preserved during entry, they must have traveled at low velocities and low-angle trajectories (*10*). It is possible that this requirement could have been satisfied, as low velocities of dust particles in the earth's dust cloud were demonstrated by Dole (*11*), and low-angle trajectories for atmospheric entry were described by O'Keefe (*12*).

If the surface details of type-II and type-III spherules were produced by space erosion, it would appear that surfaces in space may be considerably attacked over extended periods of time (*13*).

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References and Notes

1. J. Murray and A. F. Renard, *Proc. Roy. Soc. Edinburgh* **12**, 474 (1883).
2. J. D. Buddhue, *Meteoric Dust* (Univ. of New Mexico publications in meteoritics, No. 2, 1950).
3. J. C. Behrendt, *Science* **137**, 601 (1962).
4. D. E. Bradley, *Brit. J. Appl. Phys.* **5**, 96 (1954).
5. E. H. Davison and P. C. Winslow, Jr., "Space debris hazard evaluation," *Natl. Aeron. Space Admin. Tech. Note D-1105* (1961).
6. Symbols: d_c = crater diameter (0.5 μ); ρ_p = particle density (estimated at 5 g/cm^{-3}); ρ_t = target density (5 g/cm^{-3}); V = particle velocity (estimated at 20 km/sec^{-1}); V_s = velocity of sound in target material (5000 m/sec^{-1}); d = diameter of impacting particle.
7. C. L. Hemenway, E. F. Fullam, L. Phillips, *Nature* **190**, 867 (1961).
8. R. A. Bagnold, *Physics of Wind-Blown Sand and Desert Dunes* (Methuen, London, 1941).
9. See R. A. Schmidt, *A Survey of Data on Microscopic Extraterrestrial Particles* (Univ. of Wisconsin Geophysical and Polar Research Center Research Rept. 63-2, Jan. 1963).
10. D. W. Parkin and W. Hunter, *Advan. Astron. Astrophys.* **1**, 106 (1962).
11. S. H. Dole, *The Gravitational Concentration of Particulate Matter in the Space Near the Earth* (RAND Corp. Memo. RM-2879-PR, 1962).
12. J. A. O'Keefe, *Science* **133**, 562 (1961).
13. Supported by grants from the National Science Foundation and the research committee of the University of Wisconsin Graduate School from the Wisconsin Alumni Research Foundation. We thank Prof. P. J. Kaesberg of the department of biochemistry at the University of Wisconsin for permission to use the electron microscope and the associated laboratory facility. This is Geophysical and Polar Research Center contribution No. 115.

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Late Twilight Glow of the Ash Stratum from the Eruption of Agung Volcano

Abstract. *Observation of the height of the dust layer responsible for the onset of brilliant sunsets in the 30°N zone since September 1963 gives evidence that the ash has diffused from the eruption of the volcano Agung on Bali. A height of 22 km is derived for the top of the primary stratum.*

Since early September 1963 the appearance of strong coloration of the clear sunset and sunrise sky has given evidence that the ash from the eruption of the volcano Agung on Bali (8°25′ S) has diffused into the northern hemisphere. We have had the opportunity to observe the growth of the brilliant gold sunsets from our surveillance of the twilight sky for noctilucent clouds, a task aided by the very clear atmosphere of the Southwestern states. The presence of the glow stratum became quite conspicuous late in September, particularly because of its asymmetry with respect to the position of the sun. On 29 and 30 September the glow was centered 10° to 20° south of the solar