

N₂O production. If the stimulatory effect of soil disturbance on soil-water transport of N₂O is as large at other disturbed sites as it is at HBEF, then the total N₂O emission rate (soil-air diffusion plus soil-water degassing) from disturbed soils may be higher than previously reported (21).

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Placers of Cosmic Dust in the Blue Ice Lakes of Greenland

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A concentration process occurring in the melt zone of the Greenland ice cap has produced the richest known deposit of cosmic dust on the surface of the earth. Extraterrestrial particles collected from this region are well preserved and are collectable in large quantities. The collected particles are generally identical to cosmic spheres found on the ocean floor, but a pure glass type was discovered that has not been seen in deep-sea samples. Iron-rich spheres are conspicuously rare in the collected material.

TYPICAL METEORITIC DUST IN THE 0.1- TO 1-mm size range melt during entry into the atmosphere to form "cosmic spheres." The spheres, and the rare particles that enter without melting, are an important resource of extraterrestrial material that is probably a relatively unbiased sampling of the millimeter meteoroids that traverse the inner solar system. Particles of this size produce visual meteors in the night sky and account for the bulk of the 10⁴ tons of extraterrestrial material annually accreted by the earth. The major collection site for cosmic spheres has been deep-sea sediments where spheres are found in moderate concentration because of the exceedingly low accumulation rate of terrestrial particulates. However, even in the deep-sea clays with the highest known concentrations of cosmic dust the spheres larger than 0.5 mm are only 10 parts per billion of the total sediment

mass, and it has not been possible to collect adequate numbers of large spheres and unmelted particles (1). Particles larger than 500 μm are required for certain analysis techniques, such as the measurement of trace elements and isotopic analysis of O, Ti, and the cosmogenic (cosmic ray product) isotopes ²⁶Al, ¹⁰Be, and ⁵³Mn (2).

In addition to deep-sea sediments, it has long been recognized that clean polar ice deposits could be good collection sites for small meteoritic particles (3). Although some spheres have been found in ice, it was not expected that significant numbers of

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particles could be recovered because the spheres should be highly diluted in the ice. We report the discovery of a highly effective concentration mechanism occurring in the melt zone of the Greenland ice cap that has produced the highest known concentration of cosmic spheres on the earth. The spheres are concentrated by the melting of glacial ice and subsequent formation of placer deposits in "aufeis" lakes that seasonally form directly on the ice surface. The concentration process involves the following sequence: the particles fall onto the surface of the ultra-clean interior of Greenland, they are buried and become incorporated into ice, the glacial ice flow carries the particles outward toward the coastal region, during the summer ice melts in the ablation zone, and the liberated particles are carried by running water to placer deposits that form in shallow basins. The existence of this process was postulated on the basis of examination of aerial photographs, and its reality was tested by an expedition to Greenland in the summer of 1984.

The selection of a collection site and the initial idea for the concentration process was based on aerial photographs of the ablation zone that were taken in 1958 by Bauer (4). The photographs show valley and hill structures on the ice field delineating collection basins with diameters on the order of 10 km. They also reveal the existence of a patchy accumulation of dark sediments on the bottoms of "blue" lakes formed at the center of the collection basins. The lakes are seasonal, but their locations should be somewhat invariant with time as the basins reflect the permanent topography of the basement rock over which the ice cap is flowing.

In July 1984, a five-man expedition with 700 kg of equipment camped for 1 week in the ablation zone of the Greenland ice sheet, near Søndre Strømfjord (5). The camp site (67°09'N, 49°38'W) was situated about 20 km from the ice sheet margin at an elevation of 930 m. From radioecho sounding (6) and ice sheet profile theory (7) the thickness of the ice at the collection site is estimated at 600 to 800 m. Preliminary ice flow model calculations suggest that the surface ice around this location is 1500 to 2000 years old, and that the ice was originally deposited in the snow accumulation zone 100 to 150 km further inland, at an elevation of about 1750 m (8). This is supported by stable isotope analysis of ice samples collected at the camp site (9). From the inland site of deposition, the accumulated annual snow layers, originally 0.3 to 0.4 m thick (in terms of ice equivalent thickness) moved downward into the ice sheet and outward toward the margin. When the equilibrium line (the line where the annual loss of ice by melting



Fig. 1. Collection of dark sediment from a blue ice lake. Particles are vacuumed off the lake bottom and pumped to a 100- μ m sieve on the lake shore.

exactly balances the annual mass input by snow deposition) is reached, the ice layers begin to move up relative to the surface and then resurface downslope from the equilibrium line. The further inland the ice was originally deposited, the closer to the ice margin the ice will reappear, and the older the surface ice will be (10).

At the camp site, the annual melt rate amounts to about 1 m per year (11), exposing about seven of the original annual layers.

Meltwater streams at the surface are removed from the surface by water running into the ice sheet through crevasses or running off the ice sheet margin. Lakes form in local hollows at the surface, and the dust is concentrated by sedimentation processes. At present it is not possible to assess the degree of dust removal from the ice surface by meltwater, since up to now the surface meltwater system in the marginal zone of the ice sheet has not been studied in sufficient detail.

The major recovery effort was conducted on a 600-m-long lake that had a strong central current of about 3 m sec^{-1} . Patches of dark sediment that covered the lake bottom were vacuumed from the bottom with hand-held plastic tubing connected to a water pump. Sediment was recovered from a 60- m^2 area where the bottom deposit was less than 5 mm thick. The water depth in this area was about 1 m and the current was on the order of 0.3 m sec^{-1} . The lake bottom ice was very rough, composed of a myriad of small holes with depths of less than 1 cm. The jet of sediment-laden water delivered by the water pump was either directed to a 100- μ m stainless steel sieve (Fig. 1) or the surface of a magnetic particle collector. About 10 kg of sediments at least 100 μ m in size and 50 g of magnetic separates were recovered (12).

Preliminary laboratory observation of the samples showed that the bulk of the sedi-

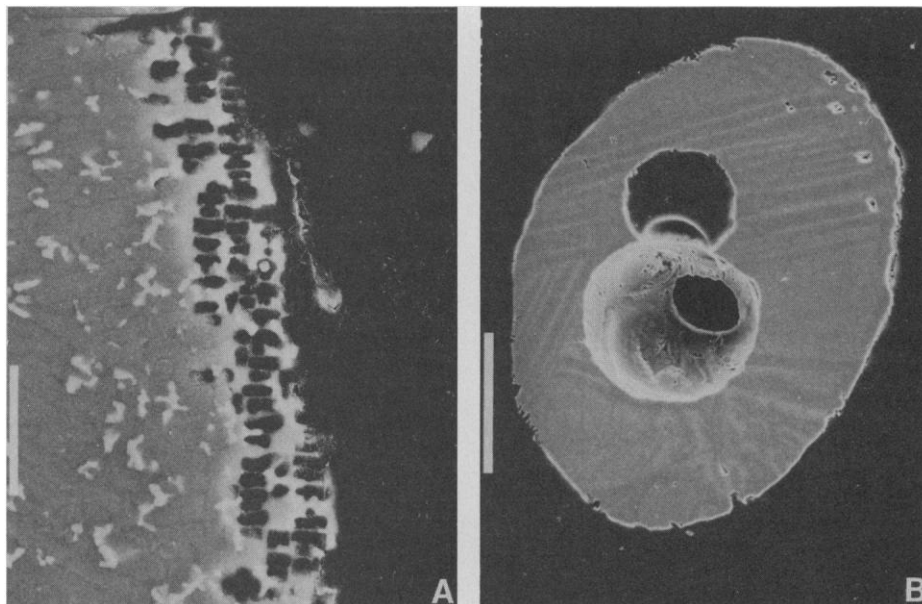


Fig. 2. (A) SEM image of the edge of sectioned Greenland spherule. The dark areas are epoxy and the phases in descending order of brightness are magnetite, olivine, and glass. At the edge of the sphere olivine has been etched out leaving only glass and magnetite, a weathering pattern not seen in cosmic deep-sea spheres. Scale bar, 10 μ m. (B) Polished section of a glass-rich sphere whose composition lies in the silicon-rich, iron-poor area of Fig. 3. The large vesicles in the center of the particle are relatively common in the silicon-rich spheres but rare in spheres of normal chondritic composition. Scale bar, 100 μ m.

ment is composed of "cocoon" of microscopic fibers in which mineral grains are entrapped. These cocoon structures are composed of a very pure variety of blue-green algae (13). Several techniques for disaggregating the cocoons were used (14). One purely mechanical method that was quite effective was to place the sediment into a large stainless steel sieve and brush it with a hard nylon brush under running water. Examination of liberated grains by scanning electron microscopy (SEM) showed an abundance of 100- μ m or larger spheres with chondritic elemental composition similar to extraterrestrial stony spheres found in deep-sea sediments. The concentration of these spheres is about one particle per gram for sizes larger than 100 μ m. This concentration is 100 to 1000 times that found in deep Pacific Ocean sediments.

More than 100 spheres larger than 100 μ m were potted in epoxy and sectioned for detailed SEM and electron microprobe studies in Seattle. Several unmelted extraterrestrial particles were identified and were also sectioned. In general the Greenland particles are similar in elemental composition, mineralogy, and texture to spheres and rare unmelted particles previously identified in deep-sea sediments and shown to be extraterrestrial because of their content of cosmogenic ^{26}Al , ^{10}Be , and ^{53}Mn (2). As is the case with the deep-sea particles, the most common spheres have chondritic (solar) relative abundances for Mg, Al, Si, Ca, Ti, Mn, and Fe (Table 1). The most common consist of olivine lamellae with minor magnetite grains and residual glass filling the micrometer or submicrometer channels between olivine grains. This texture is similar to that of barred olivine chondrules. A few percent of the spheres have porphyritic textures and roughly 5% of the particles contain relict (unmelted) grains of forsterite or enstatite.

In most respects the Greenland samples are identical to their counterparts found in deep-sea sediments, but there are several conspicuous differences. A notable difference is that the Greenland spheres are much less weathered. Typical stony deep-sea spheres have lost a significant fraction of their glass by dissolution and in extreme cases all the glass has been removed and the olivine grains have been attacked as well. The Greenland spheres show signs of alteration but it is usually minor and confined to the spherule periphery. The nature of the alteration is also different. Glass and olivine etch at more comparable rates and in some cases olivine is actually lost faster than the glass (Fig. 2A). This difference could be due either to the chemical environment or biological processes. The comparatively pristine nature of the Greenland samples must be

Table 1. Electron microprobe analyses of sectioned Greenland spheres.

Compound	Sample (% by weight)								
	G1C4	G1C8	G1C10	G1C13	G1C18	G1C21	G1C23	G1C24	G1A11
MgO	26.15	28.32	24.65	27.90	25.66	23.37	27.49	27.23	28.33
Al ₂ O ₃	2.81	3.20	3.27	2.78	3.07	2.85	3.08	3.21	2.80
SiO ₂	36.87	38.04	37.96	39.29	37.10	35.91	38.06	38.96	42.39
CaO	2.88	2.76	1.95	2.47	2.27	3.65	2.83	1.28	1.51
FeO	30.38	27.14	31.05	26.57	30.81	33.22	27.97	28.71	23.44

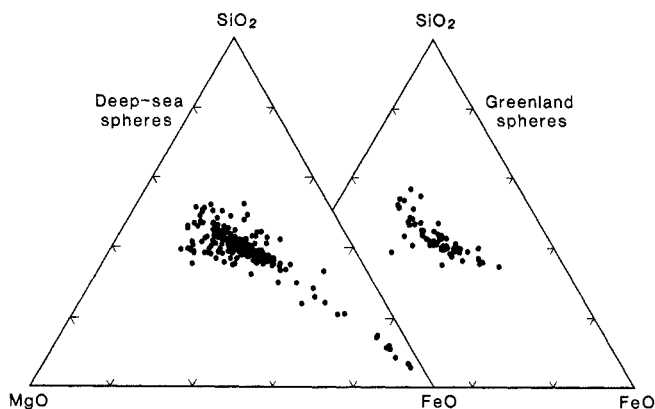


Fig. 3. Broad-beam electron microprobe analyses of the unweathered interiors of 62 Greenland and 279 deep-sea spheres. The Greenland spheres have a relative overabundance of high silicon and low iron particles and deficiency of high iron spheres.

due in part to their short terrestrial lifetimes. The Greenland spheres are only a few thousand years old whereas those on the sea floor are typically more than 10,000 years old. Even spheres resting on the surface of the sea floor are typically this age because of vertical mixing by burrowing organisms. The preservation of the Greenland samples is also enhanced because they are frozen in solid ice for most of their terrestrial lifetimes.

Although the most abundant Greenland spheres are chemically indistinguishable from the most common deep-sea spheres, there are significant differences in the abundances of minor composition groups. Roughly a quarter of the deep-sea spheres are FeNi particles composed of metal, magnetite, and wustite. Only 2% of the Greenland spheres that we collected belong to this group. There are several possible causes of this discrepancy, but perhaps the most likely is that the placer deposits that we sampled may not have retained dense particles. This could also explain why the high iron group of stony spheres (Fig. 3) seen in the deep-sea spheres are not seen in our Greenland samples. If the observed scarcity of iron-rich spheres is actually representative of those that originally fell onto the ice, then the flux of these particles must have been low during the time that the collected sample fell to the earth.

In contrast to the depletion of iron-rich spheres in the Greenland collection, there is an enrichment of the rare high silicon and

low iron spheres (Fig. 3). These particles are close to pyroxene normative composition, and they contain large amounts of glass (Fig. 2B). Two of these spheres are pure glass. We have not found a similar composition glass sphere in the examination of thousands of deep-sea cosmic spheres. The minor element compositions of the high silicon particles are in chondritic proportions, and there is no evidence to suggest that the pure glass spheres are terrestrial. These glass spheres are not found in deep-sea sediments, probably because they do not survive in the ocean floor environment. The Greenland samples thus indicate that chemical weathering probably does cause at least a minor bias in the chemical composition of recovered deep-sea cosmic spheres.

The dark sediments extracted from Greenland blue ice lakes constitute an important mine of large extraterrestrial dust particles. The lake bottoms contain the most highly concentrated and best preserved deposits of cosmic dust known on the surface of the earth. With modest field efforts it seems possible to collect hundreds of grams of millimeter-sized extraterrestrial particles. The bulk of such a collection of millions of particles would consist of material from comets and asteroids although presumably there would also be trace components from the moon, Mars, and possibly other sources. Probably the most important contribution such a collection could provide would be to supply unmelted millimeter particles, some of which would be of cometary origin.

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10. The modeling of the ice flow further indicated that it should be possible to investigate the past variations of this flux of cosmic debris over a time scale of about 10,000 years by sampling the sediments from the margin of the ice field (where the surface ice was formed about 10,000 years ago), up to an area about 80 km away from the margin, where the ablation just barely removes the "last-year" snow layer.
11. During our 10-day stay on the ice we observed a 15 to 20 cm ice retreat using sticks driven into the ice. Assuming a constant melt rate over the mid-June to mid-August melt season, this indicates an annual melt rate of 1 m per year. This rate is consistent with other stick method measurements at similar altitudes and latitudes in Greenland (A. Weidick, *Proc. 8th Int. Conf. Port Ocean Eng. Arct. Cond.*, in press).
12. We only discuss these blue lake samples. However, we also collected about 40 kg of sediments around the lake and our camp site some 50 km from Sønder Strømfjord, in particular on a 10-cm-thick pile of surface sediments that contained about 1 ton of sediment which looked similar to that investigated by D. De Kervain and P. Mercanton in 1912 [*Métt. Groenl.* **59**, 56 (1925)]. We were also provided with samples from the latitude of Jakobshavn by J. M. Gautier and J. M. Loubiere and the U.S. team of R. Scott.
13. These studies were conducted at Montpellier (G. Callot, Laboratoire de Sciences des Sol, Institut National de Recherches Agronomiques, and A. Dubois, Laboratoire de Paléontologie, Université de Montpellier), and at the University of Perpignan (F. Gadel and A. Monaco, Laboratoire de Sédimentologie Marine).
14. This work was done by C. Lafoy, Laboratoire de Séparation de Phases, Bureau de Recherches Géologiques et Minières, Orleans, France.
15. We acknowledge the work of C. Jelano, M. Wheelock, S. Taylor, B. Bates, and B. Doyle on analysis of the samples. We are also grateful to C. Lafoy for work on disaggregation of the cocoons and acknowledge the help of M. deAngelis, D. Donnov, and M. Pourchet (Laboratoire de Glaciologie, Grenoble, France) in preparation of the collection techniques used on the expeditions. The cost of the Blue Lake Expedition was mostly covered by a grant from Institut National d'Astronomie et de Géophysique, France; we also received financial help from Société Française de Production Audiovisuelles. The analytical work was supported by a grant from Programme Interdisciplinaire de Recherches sur l'Environnement du Centre National de la Recherche Scientifique and NASA grant NSG9052.

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Dynamic Atomic-Level Rearrangements in Small Gold Particles

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Small metal particles (<5 nanometers), which are widely used in catalysis, have physical and chemical properties that are markedly different from those of the bulk metal. The differences are related to crystal structure, and it is therefore significant that structural rearrangements in small particles have been observed in real time by using high-resolution electron microscopy. A detailed investigation at the atomic level has been made of the factors affecting the dynamic activity of small gold crystals that are supported on thin films of amorphous carbon, silicon, and germanium. The rate of activity depends mainly on the current density of the incident electron beam and the degree of contact of the particle with the substrate, but this rate decreases rapidly as the particle size is increased. The activity of the particles is very similar on either carbon or silicon, but it is generally less marked on germanium because of increased contact between the particle and the substrate. The electron beam effectively heats the particles, and it appears that their dynamic behavior depends on their thermal contact with the substrate.

DEVELOPMENTS IN INSTRUMENTATION for the high-resolution electron microscope (HREM) have facilitated the observation and recording of dynamic events at the atomic level directly within the microscope. Processes recorded include the motion of defects in gold foils (1), the annealing of defects in cadmium telluride (2), and atomic rearrangements on the surfaces of small gold particles and extended gold foils (3-6). Rapid structural rearrangements also occur in gold crystals smaller than about 5 nm (4-7), but to our knowledge, no detailed study of the various factors affecting these activities has been reported. In an attempt to understand these processes, and also because of the possible links and similarities between these electron beam-induced rearrangements and those that occur during thermal annealing treat-

ments of small particles (8), we have carried out further systematic studies on small gold crystals.

The small gold crystals were originally prepared as cluster complexes containing 55 gold atoms (4). Under electron irradiation, the attached ligands were evaporated, leaving the gold clusters randomly distributed on the supporting substrate. Further irradiation led to the development of bigger crystals, as documented previously (4), and our observations were then concentrated on those particles that were protruding over holes in the support film. For comparison purposes, the holey amorphous substrates were made of silicon and germanium as well as the traditional carbon. Samples were also prepared by direct evaporation of gold. Most of the observations were made with an HREM (JEM-4000EX) that was operated

primarily at 400 kV, although some studies were also made at 200 and 350 kV. The microscope was equipped with a TV system (Gatan 622), fiber optically coupled to an yttrium-aluminum-garnet screen, and this was used both for image viewing and for video tape recording. Typical electron optical magnifications were 600,000 or 800,000 times, with electron current densities at the sample usually ~20 to 25 A/cm², although these values ranged from ~10 to ~80 A/cm² for those particular experiments designed to investigate the dependence on beam current density. Some of the videotapes were later processed with a digital video processing unit (Quantex DS-30) to reduce noise and to improve image contrast. Some observations were made with a 100-kV electron microscope (Philips 400ST) that was equipped with a specimen heating holder.

The images shown in Fig. 1 provide a graphic representation of the structural changes that occurred in the small gold crystals. Each image is a photograph of the monitor screen showing two to four averaged frames from a video tape recording, and the total elapsed time of the sequence is only 20 seconds. The images show the particle, supported on a thin film of amorphous silicon, near to a [110] orientation; they were taken at close to the optimum defocus (an amount out of focus at which one can directly interpret the image), so that the atomic columns appear black.

The sequence of images shown in Fig. 2 is

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