slightly tempting to refer to them as "small" grains. The major contribution of the work of Bless and Savage (*1*) is that it shows (Fig. 7) that the amount of the far-ultraviolet extinction is variable from star to star. Looking at the figure, we can easily imagine that greater or lesser amounts of a second wavelength-dependent extinction component are combined with a Mie-type falloff in extinction (marked *T* in the figure) of the larger dust grains. The conclusion that the particles are small is not necessary, however, as a larger size and a lower index of refraction will produce an identical result (*10*). Without meaning to be comprehensive, we shall mention several possibilities. Small iron particles can reproduce most of the observed reddening curve (*13*) and are efficient absorbers rather than scatterers, although it is not immediately clear that they would scatter relatively less at 1500 Å than they (or graphite) would at 2000 Å. The usual objection to iron is that more of it would be required than we expect to exist in any form in interstellar space, if the interstellar material originates in stars. Differential light pressure between large and small dust particles could conceivably produce the separation needed to explain the variability in extinction from star to star, and observations of θ Orionis in the far ultraviolet support this hypothesis (*1*). These measurements show much less than the expected extinction and indicate a large deficiency in the "second component" in this region of high radiation pressure.

Stecher and Donn (*14*) have suggested that the "small particle" extinction might be caused by the dielectric mode of graphite, but this seems difficult to reconcile with the observed variability from star to star. Hydrogen mantles on graphite particles were very tentatively suggested by Bless and Savage (*1*), following the presentation of the idea by Hoyle, Wickramasinghe, and Reddish (*15*). The (presumed) low index of refraction of solid hydrogen accounts for the appearance of the added extinction in the far ultraviolet, and the result of our experiment is easily explained in terms of the strong forward-scattering phase function that would be expected because the photons would go off into Monoceros instead of being scattered at right angles toward the earth. Finally, perhaps the ease of evaporation of a hydrogen mantle could explain the variation of the far-ultraviolet extinction from star to star and its deficiency in such high-flux regions as θ Orionis. Greenberg and others (*16*) have emphasized the great difficulty of cooling grains to the point where a hydrogen mantle can form. A recent discussion of the problem (*17*) suggests that perhaps mantles on SiO_2 are a better possibility; we have not investigated the consistency of this suggestion with our experimental result. Also, Solomon and Wickramasinghe (*18*) have studied the formation of solid H_2 coatings on grains in dense interstellar clouds, and have shown that the process is quite feasible at densities of the order of 10^4 molecules per cubic centimeter. Hence, prior to the formation of the early-type stars, the grains in the Orion dust clouds could easily have acquired H_2 coatings.

Finally, we must consider the possibility (suggested by the variability shown in Fig. 7) that the dust in Barnard's Loop simply does not contain any of the "small grain" (or "H_2 coating") component. One possibility exists for partially testing this. The hot star HD 113167 falls in the same general direction as part of the Loop, and is visible (very faintly) in our photographs (Fig. 3). Because this star probably lies beyond the Loop, its far-ultraviolet intensity should indicate to what extent "small grain" extinction is taking place in this direction in the sky. Although the stars HR 2031 and 2058 are also in the right direction, and were clearly detected, they cannot with certainty be said to lie beyond the Loop dust.

To summarize, we have shown that the far-ultraviolet spectral intensity of the Loop is much less than its near-ultraviolet intensity. If the near-ultraviolet radiation is starlight scattered by dust, the newly discovered dust component that extinguishes far-ultraviolet radiation is either more strongly absorbing or has a much more strongly forward-directed scattering function than the dust component that scatters the near-ultraviolet radiation. These conclusions provide a new constraint on the nature of the newly discovered dust component.

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Carbon Dioxide Clathrate in the Martian Ice Cap

Abstract. *Measurements of the dissociation pressure of carbon dioxide hydrate show that this hydrate ($CO_2 \cdot 6H_2O$) is stable relative to solid CO_2 and water ice at temperatures above about 121°K. Since this hydrate forms from finely divided ice and gaseous CO_2 in several hours at 150°K, it is likely to be present in the martian ice cap. The ice cap can consist of water ice, water ice + CO_2 hydrate, or CO_2 hydrate + solid CO_2, but not water ice + solid CO_2.*

On the basis of the infrared radiometer experiment of Mariner 7, Neugebauer *et al.* (*1*) have reported that the temperature of the ice cap of Mars is 153°K. On the basis of the radio occultation measurements from Mariner

Table 1. Dissociation pressures of carbon dioxide hydrate.

Temperature (°K)	Pressure (mm-Hg)
192.54	164.1
186.75	108.7
182.15	77.0
176.86	50.8
171.54	31.51
167.07	21.06
162.37	13.24
151.52	4.01

6 and 7 (*2*), the partial pressure of CO_2 on Mars is given as 6.5 mb. In order for solid CO_2 (dry ice) to form, as proposed by Leighton and Murray (*3*), the required conditions would be a pressure of 13.1 mb at a temperature of 153°K or a temperature of 148°K at a pressure of 6.5 mb.

A temperature of 153°K and a pressure of 6.5 mb are consistent with the formation of the carbon dioxide clathrate hydrate. Refinements of the infrared radiometer data give a temperature for the ice cap of 148°K (*4*), a value consistent with the presence of solid CO_2 (*5*). The revised data are also consistent with the presence of the CO_2 clathrate hydrate. The possibility that CO_2 hydrate is present on Mars has been discussed (*6*), but the temperatures and pressures then accepted (180°K and 90 mb) are insufficient to stabilize CO_2 hydrate.

The CO_2 hydrate was first prepared by Wroblewski (*7*) and studied by several workers (*6, 8, 9*). It is a structure I hydrate with a cubic unit cell of 12 Å (*10*), containing 46 molecules of water and eight cages into which the CO_2 can fit. This is the same structure as that of the clathrate hydrate of air (Craigite) which occurs in the Antarctic ice cap below about 1200 m (*11*). The ideal formula is $CO_2 \cdot 5.75H_2O$, but the actual formula is closer to $CO_2 \cdot 6.0H_2O$ (*9*) because the cages are not completely filled with gas molecules (*12*). The hydrate has the same appearance as ice.

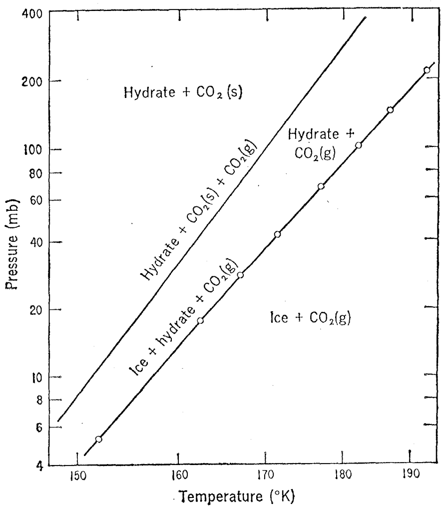

Fig. 1. Phase diagram of carbon dioxide hydrate. Experimental dissociation pressure measurements, ○; vapor pressure of solid CO_2, ——.

We have measured (*13*) the dissociation pressures of CO_2 hydrate between 152° and 193°K. The data are given in Table 1 and can be expressed by the equation

$$\log P(\mathrm{mb}) = 10.5591 - 1338.4/T - 6.585 \times 10^{-3}T \quad (1)$$

where T is the absolute temperature. The temperature at which the dissociation pressure of CO_2 hydrate is 6.5 mb is 153.18°K.

The dissociation pressures of CO_2 hydrate and the vapor pressures of CO_2 are shown in Fig. 1. The CO_2 vapor pressures (*14*) can be expressed by the equation

$$\log P(\mathrm{mb}) = 11.3450 - 1470.2/T - 4.1024 \times 10^{-3}T \quad (2)$$

Equations 1 and 2 intersect at 121.22°K. Below this temperature, CO_2 hydrate is not stable because the dissociation pressure of this hydrate is greater than the vapor pressure of solid CO_2. This temperature is very approximate because of the extrapolation involved and the small angle at which the two lines intersect. This temperature can be called the "lower critical decomposition temperature," in analogy to the upper critical decomposition temperature of 10.20°C and 44.50 atm (*9*), above which CO_2 hydrate is not stable relative to liquid CO_2 and H_2O. Carbon dioxide hydrate is the only hydrate known to have a lower critical decomposition temperature. For other hydrates the slope of the line for hydrate + ice + gas is steeper than that of the line for solid + gas; thus the hydrate is stable to 0°K.

The heats of the reactions

$$CO_2 \cdot 6H_2O = CO_2(g) + 6H_2O(s)$$

($\Delta H_{121°K} = 5680$ cal per mole of CO_2) and

$$CO_2(s) = CO_2(g)$$

($\Delta H_{121°K} = 6450$ cal per mole of CO_2) can be calculated from Eqs. 1 and 2. These values correspond to 37.3 cal per gram of hydrate and 146.6 cal per gram of CO_2, respectively. The heat of the reaction

$$CO_2 \cdot 6H_2O = 6H_2O(s) + CO_2(s)$$

is −770 cal per mole of CO_2 or −5.1 cal per gram of hydrate at 121°K. Therefore, if the temperature drops below 121°K, the hydrate will heat up on decomposition, with the result that the remaining hydrate will be stabilized.

In general, it can be said that above about 121°K, ice is not stable in the presence of solid CO_2. Figure 1 shows the stable phases in the CO_2—H_2O system at low temperatures. At a temperature of 153.2°K and CO_2 pressures below 6.5 mb, ice and CO_2 (gas) are present. At 6.5 mb, ice + hydrate + CO_2 (gas) are in equilibrium. At pressures between 6.5 and 13.1 mb, only hydrate + CO_2 (gas) are in equilibrium. At 13.1 mb, hydrate + CO_2 (solid) + CO_2 (gas) are in equilibrium. At pressures above 13.1 mb, only hydrate and CO_2 (solid) are present.

In order that these thermodynamic equilibria be applicable to Mars, the rate of formation of hydrate must be sufficiently rapid. The rate of formation of hydrate is critically dependent on the state of subdivision of the ice. In our experimental system the formation and decomposition of hydrate followed first-order kinetics. The rate constants (*15*) were 0.22, 0.71, 1.4, and 2.2 hour^{-1} at 152°, 162°, 167°, and 172°K, respectively. This corresponds to a heat of activation of 5.9 kcal, which is comparable to the 5.1 kcal observed for the transformation of cubic ice to hexagonal ice in this temperature range (*16*). The state of subdivision of the water ice on Mars is unknown, but it is likely to be very finely divided because of the very small amount of water in the atmosphere. In our experience ice produced by the condensation of water from the air forms hydrate more rapidly than finely ground ice.

The formation of carbon dioxide hydrate in the martian atmosphere is a possibility because the adiabatic temperature gradient is large enough to permit the formation of solid CO_2 at high altitudes. The hydrate would therefore be stable at altitudes lower than those where solid CO_2 could form as long as the temperature is above about 121°K. However, the amount of water vapor in the atmosphere is so small that the occurrence of hydrate could not be extensive in the martian atmosphere.

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14. This is a least-squares fit of the values between 123° and 173°K given by C. H. Meyers and M. S. Van Dusen [*J. Res. Nat. Bur. Stand.* **10**, 381 (1933)] and which are reproduced in *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, ed. 44, Cleveland, Ohio, 1963), p. 2428.
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$$\ln [(P_0 - P_\infty)/(P - P_\infty)] = kt$$
where P_0, P_∞, and P are the initial pressure, the equilibrium pressure, and the pressure as a function of time, respectively, k is the first-order rate constant, and t is time in hours.
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Apollo 12 Lunar Samples: Trace Element Analysis of a Core and the Uniformity of the Regolith

Abstract. *Four core and soil samples from Apollo 12 are enriched in a number of trace elements of meteoritic origin to virtually the same degree as Apollo 11 soil. An average meteoritic influx rate of about 4×10^{-9} gram per square centimeter per year thus seems to be valid for the entire moon. A sample from a light gray, coarse-grained layer in the core resembles lunar basalts in composition, but is enriched by factors of 10^4 to 10^5 in bismuth and cadmium.*

In our study of Apollo 11 lunar samples (*1*) we found that lunar soil was enriched in about a dozen siderophile or volatile elements that are abundant in meteorites (Ir, Au, Bi, Tl, and others), while lunar rocks were depleted in these same elements. From these data we concluded that lunar soil contained about 1.9 percent meteoritic material of a composition similar to carbonaceous chondrites and that the moon had formed in the earth's neighborhood (*1, 2*).

Our conclusions hinged on the tenuous assumption that the Apollo 11 samples were typical of the moon as a whole. We now find that the Apollo 12 samples largely confirm our earlier results, though with some important modifications.

Seven Apollo 12 samples (~0.1 g each) were available for the present study: two crystalline rocks (12002 and 12051, the latter measured in duplicate); four samples from core tube 12028, representing depths of 13 to 38 cm below the surface; and a contingency fines sample (12070) collected some 10 m northwest of the landing site. The core tube sample was taken 240 m due south of the landing site, near the southern rim of Halo crater.

The samples were analyzed by neutron activation, with the use of procedures described previously (*1, 3*). A few substitutions were made relative to our Apollo 11 work: Cu and Co were dropped, while Se and Te were added. The data are shown in Table 1. Sample type is indicated in the brassiere-cup notation used by the Lunar Sample Preliminary Examination Team [LSPET (*4*)]: A and B for fine- and coarse-grained rocks, C for breccias, and D for soil.

Before turning to a discussion of the data, we shall note the difficulties encountered for five elements. Several of the In and Ag values were again spuriously high, owing to the widespread use of In-Ag gaskets on Apollo sample containers. The Cd and Te activities contained appreciable contributions from uranium fission, requiring corrections of up to 25 percent. The Pd results determined via ^{111}Ag by the reaction $^{110}\mathrm{Pd}(n,\gamma)\ ^{111}\mathrm{Pd}(\beta^-, \nu)\ ^{111}\mathrm{Ag}$ were most severely affected. The fission contribution was estimated at about 90 percent for rocks and 60 percent for soil. We are, therefore, not reporting individual Pd values for Apollo 12 samples, only upper limits of $\leqq 0.5$ part per billion (ppb) for rocks and $\leqq 20$ ppb for soil. Because of this interference, our Pd results for Apollo 11 rocks and BCR-1 basalt (*1*) must also be revised downward to $\leqq 0.5$ ppb, and those for soil and breccias, to $\leqq 5$ ppb.

The most striking result is the spectacular enrichment of Cd and Bi in the 13- to 14-cm layer of core 12028. This sample is described as consisting of "a coarse layer of angular rock fragments, minerals, and glass; comprised mostly of olivine grains and olivine-rich gabbro," with a median grain size of approximately 4.9 mm (*4*). The LSPET report notes that this material is fairly abundant at the Apollo 12 landing site and may be of distant origin: "Along many parts of the traverse made during the second period of EVA [extra-vehicular activity], the astronauts found fine-grained material of relatively high albedo. This material is at the surface in some places. It is possible that this discontinuous deposit of light gray material may be the feature that is observed telescopically as a ray of Copernicus."

Compositionally, this sample certainly differs from typical soil in its lower content of elements characteristic of a meteoritic component (Ir, Au, Zn, Br, and Te) or enriched in soil for other reasons (Tl, Rb, and Cs). But its content of Cd and Bi far exceeds that of all lunar samples and all meteorites studied to date.

Its Ag content also is unusually high and apparently not due to contamination from In-Ag gaskets. Contamination from this source consistently gives In ≫ Ag, but in sample 12028,66 In (42 ppb) is less abundant than Ag (301 ppb).

The remaining core samples are of quite uniform composition in regard to both "meteoritic" and "indigenous" elements. The only slight irregularities are the low Tl and Te contents in samples 12028,90 and 12028,121, respectively. This is surprising, in view of the distinct differences in color and grain size [see figure 9 in (*4*); location of our samples is given in footnotes to Table 1].

If we disregard sample 12028,66 and compute averages for the AB rocks and bona fide D samples, we obtain values close to those from Apollo 11. The D averages (lines 5 and 6 from the bottom of Table 1) are especially similar,