place primarily in the iron-containing pyroxenes, which are quite sensitive to radiation and temperature (in air) and should be a dynamic system when subjected to the direct solar wind even in vacuum.

Ever since the successful landing of Surveyor 1 it has been observed that gentle disturbance of the lunar soil, except by compression, results in a material which is as much as 30 percent darker than the undisturbed surface (4). We attempted to test several of the proposed explanations for this effect.

1) Ultraviolet bleaching (10). Ultraviolet irradiation of the soil caused albedo increases of approximately 6 percent; this value is of the same order as the disturbance effect observed by Surveyor 5.

2) Packing. The albedo of the soil is affected by the micromorphology of the surface in the sense that the looser the packing, the lower the albedo. The following albedos were obtained, depending on surface preparation: (i) sifted, 0.085; raked with a needle, 0.087; spooned onto a plate, 0.090; jarred by dropping the container from a height of about 5 cm, 0.094; tamped by pressing gently with the flat side of a spatula, 0.10. Since the lunar soil is continually stirred by micrometeorites it is doubtful that the natural condition of the surface is similar to that produced by tamping. Thus packing effects apparently are capable of altering the albedo by up to 10 percent.

3) Particle size (11). The albedos of fractions of fines separated as to particle size by dry sieving were measured with the following results: >149 μ m, 0.089; 74 to 149 μ m, 0.081; 37 to 74 μ m, 0.080; < 37 μ m, 0.079; unseparated, 0.090. Hence albedo differences of about 10 percent might be possible if the upper layer of particles are larger on the average than those below the surface.

4) Lunar varnish (12). Samples of the fines were examined with an optical microscope, a scanning-electron microscope, and an electron microprobe for coatings of dark material which might be scrubbed off by solar wind sputtering, but no definite evidence for such coatings was found. However, under high magnification the surfaces of many grains exhibited peculiar textures, which we were unable to interpret. These may indicate the presence of an amorphous coating on parts of some grains. In order to test the possibility that coatings of carbonaceous material might be present, a thermogravimetric analysis was carried out by heating a soil sample to 1200°C in air and measuring the change in weight (13). The weight of the sample increased continuously and monotonically with temperature because of oxidation, and no decrease, such as might be caused by ignition of a carbonaceous coating, was observed at any temperature.

5) Conclusion. Although several effects can alter the albedo of the lunar soil by up to 10 percent, none of the hypotheses yet advanced to explain the disturbance effect seem capable of completely accounting for all observations, but any or all of the hypotheses discussed here may contribute.

B. W. HAPKE, A. J. COHEN W. A. CASSIDY, E. N. WELLS Department of Earth and Planetary Sciences, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

References and Notes

- Lunar Sample Preliminary Team, Science 165, 1211 (1969). 1. Lunar Examination
- 2. B. Hapke, Planet. Space Sci. 16, 101 (1968).
- R. Wildey, private communication.
 L. Jaffe et al., J. Geophys. Res. 73. 7165 (1968); E. Shoemaker et al., ibid. 74, 6081 1969).
- 5. B. Hapke, in Physics and Astronomy of the Maple, in *Physics and Astronomy of the Moon*, Z. Kopal, Ed. (Academic Press, New York, ed. 2, 1970), vol. 1, p. 72.
 T. McCord, J. Geophys. Res. 74, 3131 (1969); _____, T. Johnson, H. Kiefer, *ibid.*,
- 6. T. (1969); _____, T. Johnson, H. Kielei,, p. 4358; T. McCord and T. Johnson, *ibid.*, p.
- 7. B. Hapke and H. Van Horn, J. Geophys. Res. 68, 4545 (1963).
- 8. Sample preparation by G. Moreland, U.S. National Museum. 9. A. J. Cohen and F. Hassan, Science 167, 176
- (1970). 10. A. J. Cohen and B. Hapke, ibid. 161, 1237
- (1968)A. Felice, J. Geophys. Res. 72, 5721 (1967).
 E. Shoemaker et al., J. Geophys. Res. 73,
- 3989 (1968).

 We thank G. Aubele and the Fisher Scientific Company for performing this analysis.
 We thank B. Greenspan and F. Hassan for assistance. Supported by NASA contract NAS 9-9942

4 January 1970; revised 6 January 1970

Determination of Manganese-53 by Neutron Activation and Other Miscellaneous Studies on Lunar Dust

Abstract. A highly sensitive determination of spallogenic ⁵⁸Mn ($T = 2 \times 10^6$ yr) was accomplished in 0.99 g of lunar soil. The chemical yield of Mn is determined with "carrier-free" ⁵²Mn tracer. During a 23-day reactor irradiation the ⁵³Mn is transformed into ${}^{54}Mn$ (T = 300 days). Appropriate chemical recycling was done by ion exchange and distillation. Interferences of the (n,p) and the (n,2n) nuclear reactions were carefully studied. A ^{53}Mn disintegration rate of 30.3 \pm 5.5 dpm/ kg results. This extremely economic method is proposed for further detailed lunar profile measurements. The Re content, which is of possible cosmochemical interest, was determined to be 11 ppb. Appropriate separation techniques were used. The rather weak and complex thermoluminescence properties made a more basic study advisable. Thermogravimetric analysis, mass spectroscopy, and Moessbauer spectroscopy were applied. The presence of ilmenite, metallic Fe etc., and of an unidentified Fe²⁺-containing compound was deduced. Natural thermoluminescence could not be proved with certainty in our surface sample. However, the complexity of the artificial thermoluminescence demands better defined mineral fractions. The fission track method was used to measure U distribution in glass spherules etc.

Manganese-53, favored by its high production cross section and long halflife of about 2 \times 10⁶ years, is one of the most interesting nuclides in space research. However, detection of the ⁵³Mn nuclide is rather difficult because of its soft x-rays, and only sophisticated "low-level" techniques succeed. This contrasts with 26Al, which can be detected nondestructively by its characteristic y-cascade with fairly high sensitivity. (Even with our 5-g sample of lunar dust, we were able to detect the stronger γ -emitters.)

Working with meteorites, a very sensitive and therefore economic method was found in which we convert ⁵³Mn by neutron capture into γ -emitting ⁵⁴Mn (1-3), as Millard (4) had proposed some years ago.

In 1957 Sheline and Hooper (5) predicted that, in meteorites, the long-lived ⁵³Mn isotope should be produced in relatively high yield. Honda et al. (6) thereafter confirmed this experimentally. Although the half-life of ⁵³Mn is not yet fully established, a half value of (1.9 \pm 0.5) \times 10⁶ years was suggested by Kaye and Cressy (7). They compared the 53Mn activity of an iron meteorite of high terrestrial age with the ⁵³Mn activity of a chondrite with short radiation age. However, the method involves a number of uncertainties, which must be allowed for. Millard showed that the product of the

⁵⁸Mn (n, γ) activation cross section, σ , and the ⁵³Mn half-life, *T*, is (350 ± 100) × 10⁶ barns × years.

From this follows an activation cross section $\sigma = 170$ barns, on the basis of an estimated ⁵³Mn half-life of $T = 2 \times 10^6$ years. The latter value is accepted as the first approximation and has been used in the present study.

The spallation product ⁵³Mn is converted by an (n,γ) -reaction into the ⁵⁴Mn nuclide, and it has been proved that the latter can be identified conveniently by its characteristic 0.84 MeV γ -line. Because stable ⁵⁵Mn is present in the "lunar fines" with an abundance of about 0.2 percent, we preferred to work without any Mn carrier.

"Lunar fines" (0.990 g) were fused with NaOH in a Ni crucible. In order to establish the chemical yield of Mn a practically "carrier-free" ${}^{52}Mn$ (T \simeq 5 days) tracer was used. Dowex 1×8 ion-exchange resin served for purification. For better handling 50 mg of MgO and 5 mg of ZnO (the latter used as internal standard) were added. The chemical yield was 96.0 percent, as determined by means of a short reactor irradiation and nondestructive γ, γ coincidence spectroscopy. Our dust sample (grain size $\leq 100 \mu$) was found to contain 1690 ± 80 ppm normal ⁵⁵Mn. The sample was then reactor irradiated for 23 days, together with 10 mg of MnO₂, 5 mg of ZnO, and 2 Fe-



Fig. 1. Differential thermal and thermogravimetric analysis of lunar dust (sample 10084). Heating rate, 20° C/min; reference, Al₂O₃; sample weight, 5 to 7 mg.

standards in a thermal flux of 8.10^{12} n cm⁻² sec⁻¹ in the FRJ-2 reactor (Dido type) at Juelich. It is important to note that, in the appropriate position, the flux ratio $\phi(\text{fast})/\phi(\text{therm}) \leq 0.001$. Hence, neutron activation results in an activity ratio of

⁵³Mn [dpm] <u>1</u> ⁵⁴Mn [dpm]

At the end of the irradiation the relative flux deviations were controlled by counting the ⁶⁵Zn annihilation radiation in a coincidence circuit. Absolute flux calibrations were done with a standardized ²²Na sample.

The recycling of probe and standards consisted in taking up in 12N HCl, oxidizing with H_2O_2 , adding 47.5 mg Fe (inactive carrier) and treating with a

Table 1. Determination of spallogenic ⁵³Mn in lunar dust.

		Lunar dust fr. V (0.9901 g)	Mn standard	Fe standard
	Weight	1.62 mg Mn	8.03 mg Mn	8.25 mg Fe
Chem. yield	{Pre-irrad. Recycl.	95.9% 89.3%	69.0%	65.2%
Carrier after irrad.		47.5 mg Fe		10 mg Mn
¹ spez ₅₄ [cpm/mg Mn]	$\begin{cases} (n, \gamma) \\ (n, 2n) \\ (n, p) \end{cases}$	7.64 3.14 0.16†	3.14 [*] 0	0 (8.92* per mg Fe)
A _o spez ₅₄ [dpm/mg Mn] at end of irra	$\left. d. \right\} (n, \gamma)$	110.87		
A_{53}	[dpm/kg]	30.3 ± 5.5		

* Neutron flux normalized. † Originating from Fe-traces in isolated lunar Mn.

Table 2. Iron-containing compounds of lunar dust.	
---	--

	Fraction of total iron (%)			
Source	Normal	Magnetic fraction	Nonmagnetic fraction	
Olivinic Fe	19.3	18.8	20.1	
Pyroxenic Fe	34.0	31.7	43.2	
Fe ²⁺ in ilmenite	26.0	18.6	24.9	
Fe ³⁺ in ilmenite	<3.5	<4.6	<3.0	
Unknown compound	10.2	16.8	8.9	
Metallic Fe	>7.0	>9.3	-	

Dowex 1×8 ion exchanger. The eluate was brought to dryness, taken up in 2N HCl and loaded on a cation exchanger (Dowex 50). The eluate was digested with strong H₂SO₄, 1 g of NaIO₄ was added, and finally the manganese distilled at 40° to 50°C under reduced pressure. The distillation was repeated.

Influence of the (n,p) and the (n,2n) interfering reactions is best demonstrated in the Table 1. While the interference of the ⁵⁴Fe (n,p) ⁵⁴Mn process can be suppressed largely by radiochemistry and is only in the range of 2 percent, the other nuclear reaction ⁵⁵Mn (n,2n) is more serious, contributing up to about 40 percent. Clearly the latter interference is dependent mainly on the reactor irradiation conditions, and may be reduced by choosing the highest available ratio of $\phi(\text{therm})/\phi(\text{fast})$.

Whereas the ⁵³Mn content of most of the investigated smaller meteorite is in the range of 300 to 600 dpm/kg, the ⁵³Mn content in lunar dust is found to be only 30.3 ± 5.5 dpm/kg. However, we have to relate this figure to the amount of 13 percent iron present, the main source of spallation nuclides. So, we get a value of ⁵³Mn = 230 dpm/kg Fe of lunar surface material. This still is only about 50 percent of what is found and expected in smaller iron meteorites.

On the other hand, from studies of production rates, one knows that ⁵³Mn is mainly formed by secondary reactions and lower energy primaries and that it shows a pronounced depth effect. An increase of ⁵³Mn up to a 25 cm distance beneath the surface of a spherical iron target is known. Evidently we shall have to account for growth of ⁵³Mn activity if we take samples beneath the moon's surface. Moreover, differing from meteorites, we have to consider a 2π instead of 4π "falling in" of cosmic rays.

Still another point of interest is the relatively long half-life of 53Mn, compared to ³⁶Cl and ²⁶Al. From the high ²⁶Al values (up to 100 dpm/kg) one is inclined to assume that this nuclide is in radioactive equilibrium. If the accretion and mixing rate of lunar dust is found to be high, we should have some doubt that radioactive equilibrium is fully established in the same way for the longer lived ⁵³Mn. Further studies on selected mineral probes-for example, samples of bore-holes, should bring the necessary information about spallation profiles. Since the activation method described is so sensitive, manganese-53 at even greater depths (up



Fig. 2. Thermoluminescence glow curves of lunar dust (sample 10084); (upper curve) 40-mg sample; irradiated for 15 minutes; heating rate, 100°C/min; (lower curve) 47-mg sample; irradiated for 15 minutes; heating rate, 100°C/min.

several meters) should be measurable.

During the last decade the natural β^{-} activity of 187Re was used by us successfully for geological age determinations (8). We showed that the ¹⁸⁷Os abundance varies considerably in the Re-containing minerals and in iron meteorites. It was pointed out, and D.D. Clayton showed this later in a detailed study, that the larger part of the terrestrial (stable) ¹⁸⁷Os should be regarded as having resulted from 187Re decay and that most of that decay occurred before the formation of the solar system. These ideas are based on the now accepted s-process theory.

The β^- energy of ¹⁸⁷Re is extremely weak (~ 2 keV) and a problem arises about the mode of this decay. Quite recently Clayton (9) outlined the possibility that the radioactivity of ¹⁸⁷Re could be dependent on temperature and isotopic measurements of Re from lunar dust ("solar wind") could clarify the interesting problem of 187Re cosmochronology. In view of these cosmological questions, we found it necessary to establish the presence of Re in lunar dust. As the abundance in Fe-meteorites is normally below 1 ppm, only neutron activation with chemistry could succeed. "Fines" (176 mg) were irradiated together with Re standards for 3 days, $\phi = 7 \times 10^{13}$ in the FRJ-2 reactor. Thereafter the mineral was fused by melting with NaOH + Na₂O₂ in the presence of 30 mg of Re-carrier. Several

Fe(OH)₃ precipitations were followed by repeated dry distillation of Re_2O_7 . The decay of ¹⁸⁶Re is observed. The Re content of soil (sample 10084, grains $<100 \mu$) is calculated to be 11.2 \pm 0.4 ppb if one assumes a normal terrestrial isotope abundance.

In the next step it is important to check the isotope ratio ¹⁸⁷Re/¹⁸⁵Re.

The thermodifferential analysis (TDA) and thermogravimetric analysis (TGA) curves (Fig. 1) show distinct temperature regions where gas-loss and recrystallization or annealing occurs. A critical temperature is seen at about 510°C. Oxidation at 800°C leads to a gain in weight of about 2 percent (see the lower TGA curve).

By mass spectroscopy, ratios of ³He/ ${}^{4}\text{He} = 724 \pm 118$, ${}^{20}\text{Ne}/{}^{22}\text{Ne} = 2.34$ \pm 0.04, and ²²Ne/²¹Ne = 22.6 \pm 6 were measured in dust. Only the 20Ne/ ²²Ne ratio is found to be very constant.

Nuclear γ -resonance spectroscopy (with 57 Fe) was done on magnetic and nonmagnetic fractions of lunar fines. No trace of Fe³⁺ was detected. Troilite was practically not observed in the soil but metallic Fe, ilmenite, pyroxene, and olivine were present. The spectra were compared with those of tektites and the existence of an unknown Fe2+-containing compound in the lunar soil is proposed (see Table 2).

For the thermoluminescence study different soil fractions were used. However, after 8 weeks of "storing" time we did not detect any natural THL with certainty. Probably the skin layer of dust is already strongly annealed on the moon. Highest glow intensities occur in the temperature range of 100° to 150°C, if irradiated at 30°C. At $-196^{\circ}C_{\gamma}$ -irradiation the intensity is considerably greater. A 60Co-y-saturation experiment shows that saturation for the soil is reached at a dose of about 10⁶ rads (see Fig. 2).

These preliminary results demand better defined and selected material probes.

> W. HERR, U. HERPERS, B. HESS **B. SKERRA**

Institut für Kernchemie der Universität Köln, Cologne, Germany **R. WOELFLE**

Institut für Radiochemie der Kernforschungsanlage, Jülich, Germany

References and Notes

- U. Herpers, W. Herr, R. Woelfle, "Radioactive Dating and Methods of Low-Level-Counting" (IAEA, Vienna, 1967), p. 199.
 W. Herr, U. Herpers, R. Woelfle, J. Radioanalyt. Chem. 2, 197 (1969).
 U. Herpers, W. Herr, R. Woelfle, "Meteorite Research" (IAEA, Vienna, 1969), p. 387.
 H. T. Millard, Jr., Science 147, 503 (1965).
 R. K. Sheline and J. E. Hooper, Nature 179, 85 (1957).

- 85 (1957).
- G. M. Honda, J. P. Shedlovsky, J. R. Arnold, Geochim. Cosmochim. Acta 22, 133 (1961).
 J. H. Kaye and P. J. Cressy, J. Inorg. Nucl.

- J. H. Kaye and P. J. Cressy, J. Inorg. Nucl. Chem. 27, 1889 (1965).
 W. Herr, R. Woelfle, P. Eberhardt, E. Kopp, "Radioactive Dating and Methods of Low-Level Counting" (IAEA, Vienna, 1967), p. 499.
 D. D. Clayton, Nature 224, 56 (1969).
- 6 January 1970

Specific Heats of Lunar Surface Materials from 90 to 350 Degrees Kelvin

Abstract. The specific heats of lunar samples 10057 and 10084 returned by the Apollo 11 mission have been measured between 90 and 350 degrees Kelvin by use of an adiabatic calorimeter. The samples are representative of type A vesicular basalt-like rocks and of finely divided lunar soil. The specific heat of these materials changes smoothly from about 0.06 calorie per gram per degree at 90 degrees Kelvin to about 0.2 calorie per gram per degree at 350 degrees Kelvin. The thermal parameter $\gamma = (k_{\rho}C)^{-\frac{1}{2}}$ for the lunar surface will accordingly vary by a factor of about 2 between lunar noon and midnight.

The surface temperature of the moon varies from approximately 90° to 385°K between lunar noon and midnight (1, 2).

Cooling of the lunar surface depends on the so-called thermal parameter, $\gamma = (k_{\rho}C)^{-1/2}$, where k is the thermal conductivity, ρ is the density, and C is the specific heat. Most calculations of lunar surface temperature that use earthbased eclipse data (1, 3) have assumed a constant value of γ . However, specific

heats of silicates vary by a factor of 3 or 4 in the temperature range 100° to 400°K. Accordingly, γ should show a nearly twofold variation over the range of lunar surface temperatures.

In order to verify the temperature dependence of γ , we have determined the specific heats at approximately 8°K intervals between 90° and 350°K for the samples 10057 and 10084 from Apollo 11.

The low-temperature adiabatic cal-