513-91

3X50

N91-71212

FORMATION OF WATER AND METHANE, CATALYZED BY LUNAR DUST

A. L. Cabrera, M. B. Maple, S. K. Asunmaa and G. Arrhenius
University of California, San Diego; La Jolla, California 92037

Implanted solar wind plasma as a resource - The solar corpuscular radiation that over billions of years has been implanted and stored in the lunar surface provides an important link in the record of the evolution of the Moon. The irradiation effects also give useful indications of the surface properties of solid grains in interstellar and circumstellar space. In the present context we will also discuss some related phenomena which may potentially be of technological use. The solar plasma flowing at 10^8 particles/cm^2 sec, penetrate a few hundred Å into the exposed lunar dust and rocks. Erosion and mixing processes expose new material and bury irradiated particles so that a stratified sequence of lunar soil is formed. This sequence, containing the implanted solar wind, extends at least to the two-meter depth that has been sampled. Dust particles of less than one mm in size from highly-irradiated Apollo 15 soils release, on the average, 40 to 70 moles of hydrogen per ton and 5 to 9 of carbon upon heating to 1200°C (1., 2.,). Hydrogen release culminates around 600°C; carbon appears mainly in the form of carbon monoxide with small amounts of methane (0.1 - 8.0 percent of the total carbon) and traces of C_2H_4 and C_2H_6.

In discussion of technological operations on the Moon the suggestion has been made that these gases be extracted from the lunar soil and used as fuels. However, there are several disadvantages to this scheme. The low density of hydrogen and carbon monoxide gases would pose problems in fuel storage and transportation, and since their boiling points are low (H_2, -252.7°C; CO, -191.5°C), storage in liquid state would require strong cooling. Catalytic conversion of hydrogen and carbon monoxide to methane and higher alkanes would be a way to avoid these disadvantages. Perhaps most importantly such a reaction would also provide a source of water from the lunar dust. For production, on the Moon, of water and hydrocarbons from stored solar plasma the reservoir material itself, the lunar dust, may possess the necessary catalytic activity. This case is of unusual interest since the reactants are embedded in the interior of the potential catalyst, which, in turn, seems to have acquired its active state from the implantation process itself.

Lunar dust as a model material for interstellar and circumsolar dust - In a more fundamental scientific application, the lunar dust and its surface properties can be used as a model system for interplanetary and interstellar dust. Although the bulk properties of some meteorite materials are probably even more representative in this respect, compaction and alteration have clearly modified the surface properties of the individual meteorite particles.

FORMATION OF WATER AND METHANE

A. L. Cabrera

It used to be thought that interstellar dust would differ from lunar dust by lacking the effects of corpuscular irradiation. It is now known, as would be expected on the basis of hydromagnetic considerations (see e.g. 3) that dark interstellar clouds (and obviously any circumstellar medium) are magnetized (4.-6.) and characterized by interaction of accelerated charged particles (7., 8.). Consequently, corpuscular irradiation has to be considered a general phenomenon in space, with flux and energy distributions subject to large fluctuations in space and time. Hence one would expect interplanetary as well as interstellar dust to be subjected to corpuscular radiation, and therefore, lunar dust irradiated by the solar wind should be a useful model material.
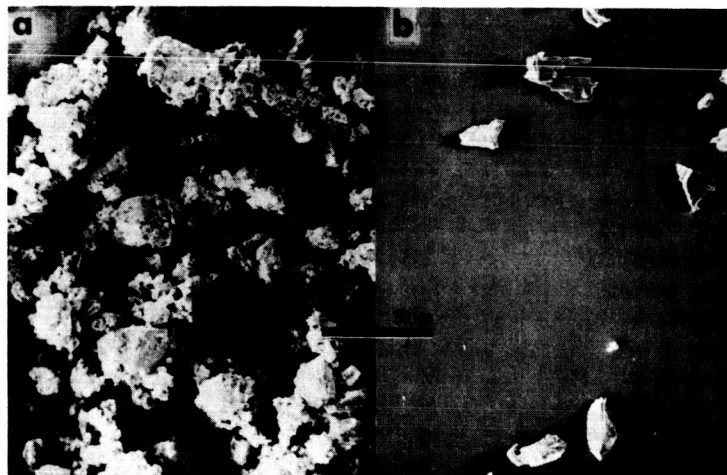

Figure 1. Comparison of the adhesion to mica cleavage surfaces of (a) space irradiated silicate grains and (b) normal silicate grains. The mica surfaces are facing down so that the adhering grains are hanging with the adhesion force exceeding their weight. Both mica sheets were originally completely covered with silicate dust. The lunar dust (a), due to its electret properties, remains extensively adhering while the majority of normal grains (b) have fallen off. The experiment illustrates that the adhesion caused by the persistent internal polarization due to irradiation exceeds the adhesion due to contact forces alone in material which has been in contact with gases for a long time. The lunar dust (a) comes from lunar sample 68501.17, and consists mainly of pyroxene, glass and feldspar. The normal dust consists of pyroxene (augite) from Danville,N.J., ground to a size distribution approximately that of the lunar sample and kept in a closed container for several years. (From 11.)

FORMATION OF WATER AND METHANE

A. L. Cabrera

One of the notable effects of space irradiation on lunar dust is the strong enhancement of interparticle adhesion due to persistent internal polarization (Fig. 1) (9.-12.) induced by charged-particle implantation. This radiation-induced attraction between grains is likely to be an important factor in the growth of particle aggregates in interstellar and circumstellar space.

Among other factors that would affect particle adhesion and cluster growth are unsaturated forces due to the lattice termination at the solid surface. Such forces are particularly effective between clean surfaces such as in vacuum cleaved crystals and on grains freshly condensed from high temperature vapor or plasma (Labeyrie*; 13., 14). Such forces decay as a result of absorption of polar molecules on the clean solid surface; in contrast, (Fig. 1) the polarization adhesion persists at least for times of the order of 10^7 years on the Moon, and in the terrestrial atmosphere for at least the six years that lunar samples have been kept on Earth.

In interstellar and interplanetary space, and also on the Moon, particle attraction, repulsion and acceleration must also be extensively influenced both by the photoelectric effect (15) and by ambipolar diffusion of electrons and ions (16.-19.).

Another surface property of dust in space, potentially modeled by the lunar dust is catalytic activity for molecular reactions, particularly those involving abundant, volatile species, i.e., those which contain He, H, C, O and N. Such reactions on grain surfaces immersed in dilute space plasmas become ineffective without catalytic mediation because at low grain temperature the reaction products do not easily evaporate, and at high grain temperature the reactants are not retained long enough to achieve reaction involving an activation step (20., 21.). Non-activated chemisorption on grain surfaces has consequently been suggested as a major channel for recombination of atomic hydrogen to H_2 molecules (22.) as well as for the synthesis of hydrocarbons (23.).

Catalytic properties of lunar dust - For the technological and scientific reasons outlined above, investigation of the catalytic properties of the lunar dust is of interest. High resolution studies of the extraction of Mn^{+2} from an aqueous solution in contact with lunar dust grains (24.) suggest that manganese deposits were formed and localized in discrete spots with a size of the order of 200-2000Å. These apparent absorption and oxidation centers on the lunar grain surfaces are believed to be lattice defects catalyzing the reactions.

In order to establish quantitatively the catalytic properties of the lunar dust, lunar soil sample no. 10084.30 was evaluated by a microcatalytic technique (25.) using the reaction

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

* reference to early work by J. Labeyrie not at hand

FORMATION OF WATER AND METHANE
A. L. Cabrera

Concentrations of reactants and reaction products were measured using a Hewlett-Packard 5700A gas chromatograph with a thermal conductivity detector. A carrier gas of hydrogen, which served as one of the reactants, was flowed at a rate of 50 cc/min through the reactor over 0.417 gm of the lunar dust and into the gas chromatograph. Pulses of CO of 0.125 cc were injected into the hydrogen carrier stream by means of a Hewlett-Packard gas sampling valve. The production of methane was monitored as the temperature was increased from 52°C to 856°C, with detectable quantities of methane appearing only above 440°C.

The CO methanation data were then converted to plots of $\ln [B \ln (1/1-x)]$ vs $1/T$, where x is the fractional concentration of CH_4. Here, the constant B is equal to F/R T W where F is the flow rate of the reactants, R is the gas constant per mole, and W is the mass of the catalyst. For a first order reaction, the quantity $B \ln(/1-x)$ is equal to the product k K, where k is the first order rate constant of the surface reaction and K is the absorption equilibrium constant (26.). Although we do not know the order of the CO methanation reaction over the lunar soil sample, we have nonetheless identified $B \ln(1/1-x)$ with k K in order to compare its activity for CO methanation with other catalysts for this reaction. The results for CO methanation over the lunar dust sample in the form of a plot of $\ln$ k K vs $1/T$ are shown in Fig. 2 where it can be seen that the data follow a rate law k K=A exp(-E/RT). The pre-exponential factor A is equal to 2.01×10^{-2} moles CH_4/sec gm atm and the apparent activation energy E is equal to 16.5 kcal/mole°K. These results can be compared to unit surface area by noting that lunar soil is characterized by a surface mass ratio of approximately $0.5 m^2$/gm.

The activity of the lunar dust sample for CO methanation is compared to the activities of powdered Ni and Co samples for the same reaction in the $\ln$ k K vs $1/T$ plots of Fig.3. Although the CO methanation data for the Co and Ni catalysts were taken from a previous investigation (27.), they were obtained by means of the same procedure and with the same apparatus which was employed in the present study of the lunar soil sample. The specific surface areas of the Ni and Co samples are 0.7 and $0.3 m^2$/gm, respectively.

Since these values are comparable to the specific areas of the lunar soil samples it can be inferred from the data in Fig. 3 that at least the major component of the lunar soil sample is a much less active methanation catalyst than nickel or cobalt. If, however, the assumption is correct that the catalytic activity is proportional to the radiation damage, then a higher specific activity, not only per unit mass, but also per unit surface area would be expected in the ultrafine fraction of the lunar dust. Becuase grains of small size live a more active life on the lunar surface than larger particles (28.-30.), they receive extreme radiation doses. If the observed activity in the grain fraction (<0.1 cm) resides mainly in the highly radiation damaged particles ($\leqslant 10^{-4}$ cm) which form a mass fraction of the order of 10^{-3} of the sample, then a catalytic activity, similar to an effective industrial catalyst (Fig. 3) would be expected in this submicron grain fraction. This possibility has not yet been explored.

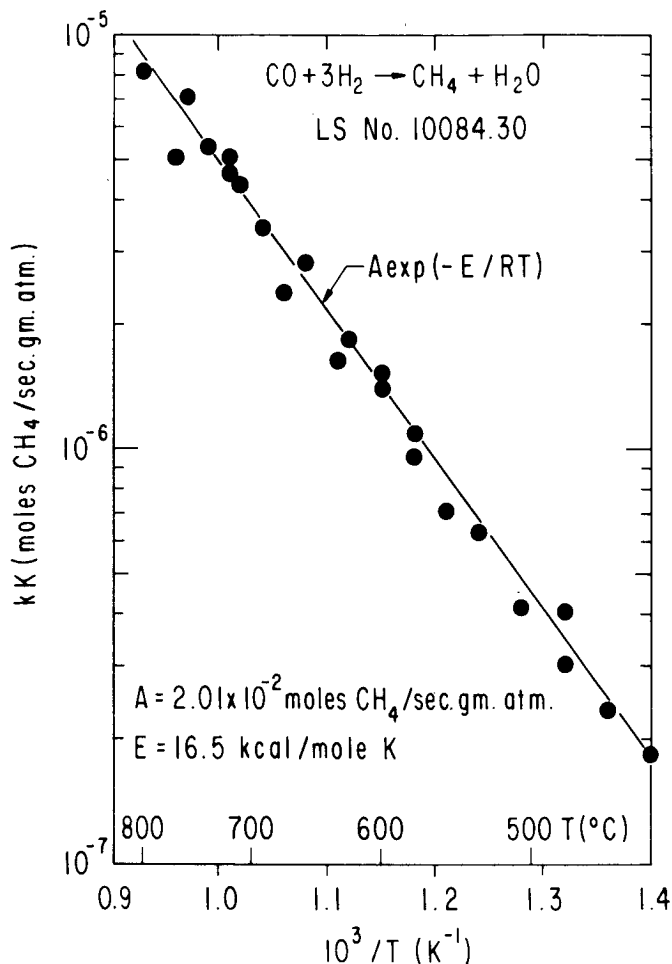# FORMATION OF WATER AND METHANE

A. L. Cabrera

Figure 2.
   Semilogarithmic plot of the reaction rate constant vs. inverse temperature for carbon monoxide methanation over lunar sample no. 10084.30.

Separation and concentration of the source material - If a grain size correlation of the catalytic effect can be verified experimentally, then utilization of the lunar soil for effective catalysis would require separating and concentrating the fine dust. Such a concentration would also be desirable because of the higher yield of gas from implanted solar plasma in small grains; DesMarais et al (2.) found the dust fraction with grain size less than 20 μm to contain about three times as much hydrogen and carbon as the bulk soil sample.

Laboratory scale experiments show that electrostatic separation is a promising technique for this purpose (see Fig. 4). Lunar dust particles can be accelerated in an electric field gradient because of their persistent internal polarization which is caused by the implantation of excess positive charge at depth in the grains, and by any additional surface electric charge.

FORMATION OF WATER AND METHANE

A. L. Cabrera

Figure 3.
Semilograithmic plots of the
reaction rate constant vs. inverse
temperature for carbon monoxide
methanation over lunar sample no.
10084.30, nickel and cobalt. Data
for nickel and cobalt are taken from
a previous study by Luengo et al (27)
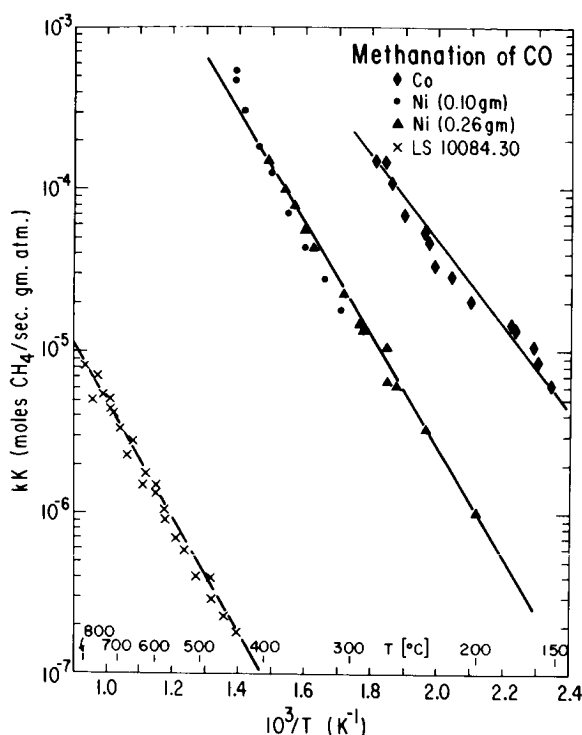
Reaction of implanted atoms - In the catalysis experiment described above, the reacting gases were provided from external sources rather than from the interior of the lunar grains. This procedure permitted the use of the convenient and sensitive pulse technique for precise evaluation of the reaction parameters. If instead the implanted carbon and hydrogen in the grains are used as reactants while the grains are immersed in excess hydrogen, it is possible that under appropriate conditions the equilibrium can be displaced toward the formation of higher alkanes.

Summary - The measurements of the bulk catalytic properties of the lunar dust reported here suggest that information relevant for understanding the chemical role of interstellar and circumstellar dust may be derived from investigation of the ultrafine grain component. This component may also be of technological interest for the production of water and alkanes on the lunar surface.

FORMATION OF WATER AND METHANE

A. L. Cabrera

A

Field Potential

Ground Potential

Volts

Radius of the equipotential surface at the radial distance of the entrance aperture

$V_p = V_a = V_{ab} (\log\frac{r}{a} / \log\frac{b}{a})$

—— 1000v = V_a
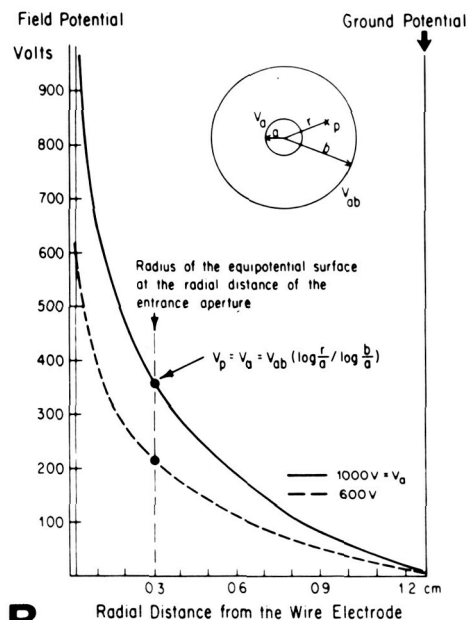
- - - - 600 v

Radial Distance from the Wire Electrode

B

Fig. 4. Electrodynamic separation of charged and polarized components of lunar dust. In the experimental separation device (A) the verticle tube serves as ground electrode and a potential of the order of a kV is applied to a central wire coinciding with the tube axis. The lunar soil sample is intro- duced at the top of the device and at the radial distance a from the central electrode (B). During free fall the grains are deflected in the inhomogenous field (B). Electret grains (and grains with negative charge) are collected on the wire electrode (C) at a verticle position determined by the dipole moment and/or the magnitude of the charge. The central electrode is coated with a thin layer of a tacky resin in order to retain grains at the point of impact.

C

FORMATION OF WATER AND METHANE

A. L. Cabrera

References

1. Flory, D. A., J. Oro, S. A. Wikstrom, D. A. Beaman and A. Lovett, 1973. Organogenic compounds in Apollo 16 lunar samples, in Proceedings of the Fourth Lunar Science Conference (Pergamon, New York) pp. 2229-2240.

2. DesMarais, D. J., J. M. Hayes and W. G. Meinschein, 1974. The distribution in lunar soil of hydrogen released by pyrolysis, in Proceedings of the Fifth Lunar Science Conference (Pergamon, New York) pp. 1181-1822.

3. Alfvén, H. and Fälthammar, C.-G., 1963, Cosmical Electrodynamics, Fundamental Principles, (Clarendon Press, Oxford).

4. Beichman, C. A. and E. J. Chaisson, 1974. Possible evidence for a large magnetic field in the Orion infrared nebula, Astrophys. J. 190: L21-L24.

5. Chaisson, E. J. and C. A. Beichman, 1975. Further evidence for magnetism in the Orion region, Astrophys. J. 199: L39-L42.

6. Clark, F. O. and D. R. Johnson, 1974. Magnetic fields in the Orion molecular cloud from the Zeeman effect in SO, Astrophys. J. 191: L87-L91.

7. Herbst, E. and W. Klemperer, 1973. The formation and depletion of molecules in dense interstellar clouds, Astrophys. J. 185: 505-533.

8. Arrhenius, G., 1976. Chemical aspects of the formation of the solar system, in The Origin of the Solar System, S. F. Dermott, ed. (Wiley, New York) in preparation.

9. Asunmaa, S. K., Liang, S. S. and Arrhenius, G., 1970. Primordial accretion; inferences from the lunar surface. Proc. Apollo 11 Lunar Sci. Conf., Vol. 3, A. A. Levinson, editor (Pergamon Press, New York) pp. 1975-1985.

10. Asunmaa, S. K. and Arrhenius, G., 1972. Interpretation of electrostatic properties of lunar regolith. Proc. 30th Annual Meeting, Electron Microscopy Soc. of America, C. J. Arceneaux, editor, (Claitor's Publ. Div., Baton Rouge) pp. 532-533.

11. Arrhenius, G. and Asunmaa, S. K., 1973. Aggregation of grains in space. The Moon, 8: 368.

12. Arrhenius, G. and S. K. Asunmaa, 1974. Adhesion and clustering of dielectric particles in the space environment 1. Electric dipole character of lunar soil grains, in Lunar Science V (Lunar Science

Institute, Houston) pp. 22-24.

13.   Kamijo, P., U. Nakada, T. Iguchi, M. -K. Fujimoto and M. Takada, 1976. Preparation of fine particles of astrophysical interest by gas evaporation technique. (Submitted to Icarus).

14.   Arnold, J. R. 1976. Condensation and agglomeration of grains, paper presented at IAU Col. 39, Relationships between Comets, Minor Planets and Meteorites, Lyon, France, Aug., 1976.

15.   Feuerbacher, B., R. F. Willis and B. Fitton, 1973. Astrophys. J. 181: 101.

16 .   Arrhenius, G. and Alfvén, H., 1971, Fractionation and condensation in space. Earth Planet. Sci. Letters 10, 253-267.

17.   McCoy, J. E. and D. R. Criswell, 1974. Evidence for a high altitude distribution of lunar dust, in Proceedings of the Fifth Lunar Sciene Conference (Pergamon, New York) pp. 2291-3005.

18.   Gold, T. and Williams, G., 1972. Secondary emission charging and movement of dust on the lunar surface. Sixth ESLAB Symp., Photon and Particle Interactions with Surfaces in Space. Noordwijk, Netherlands, Sept. 26-29, 1972 (abstract).

19.   Mendis, D. A. and N. C. Wickramasinghe, 1976. On the acceleration of interstellar grains, Astrophys. Space Sci. (in press).

20.   Hollenbach, D. and E. E. Salpeter, 1971. Surface recombination of hydrogen molecules, Astrophys. J. 163: 155-164.

21.   Hollenback, D. J., M. W. Werner, and E. E. Salpeter, 1971. Molecular hydrogen in H_I regions, Astrophys. J. 163: 165-180.

22 .   Brecher, A. and Arrhenius, G., 1971, Hydrogen recombination by nonactivated chemisorption on metallic grains, Nature 230, 107-109.

23 .   Anders, E., R. Hayatsu and M. H. Studier, 1974. Interstellar molecules: origin by catalytic reactions on grain surfaces? Astrophys. J. 192: L101-L105.

24.   Asunmaa, S. K., 1976, Kemia-Kemi 2: 469-472.

25.   Kokes, R. J., H. Tobin, Jr. and P. H. Emmett, 1955. J. Am. Chem. Soc. 77: 5860.

26.   Bassett, D. W. and H. W. Habgood, 1960. A gas chromatographic study of the catalytic isomerization of cyclo-propane, J. Phys. Chem. 64: 769.

FORMATION OF WATER AND METHANE
A. L. Cabrera

27. Luengo, C. A., A. L. Cabrera, H. B. Mackay and M. B. Maple, 1976.
     (Submitted to J. Catalysis).

28. Arrhenius, G., Liang, S., Macdougall, D., Wilkening, L. Bhandari, N.,
     Bhat, S., Lal, D., Rajagopalan, G., Tamhane, A. S. and Venkatavaradan,
     V. S., 1971. The exposure history of the Apollo 12 regolith. Proc.
     2nd. Lunar Sci. Conf. (The M.I.T. Press, Cambridge) pp. 2583-2598.

29. Macdougall, J. D., Martinek, B. and Arrhenius, G., 1972. Regolith
     dynamics. In Lunar Science - III, C. Watkins, editor (Lunar Science
     Institute, Houston) pp. 498-500.

30. Arnold, J. R., 1975. Monte Carlo simulation of turnover processes
     in the lunar regolith, in Proceedings of the Sixth Lunar Science
     Conference (Pergamon, New York) pp. 2375-2395.