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The chemistry of carbon in the lunar regolith

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The current status of knowledge concerning the chemistry of carbon in the lunar regolith is discussed. The respective roles of the solar wind and micrometeorite impact in contributing carbon and providing energy to stimulate chemical reactions and mobilize carbon phases are examined. Most detailed information has been obtained by releasing trapped species and decomposing reactive carbon phases by dissolution of lunar soils in concentrated deuterium labelled acids. The method has substantiated that hydrocarbons deriving from solar wind implanted carbon and hydrogen are present in the silicate. In addition to trapped species, a number of carbon phases chemically bound to the matrix have been recognized. The most important of these are an acid hydrolysable species associated with metallic iron and what appears to be a discrete ionic carbide which liberates acetylene. Although the majority of the solar wind implanted carbon may be released and quantitated by pyrolysis there is little information to identify which elements were bonded to the carbon in the sample, if indeed any bonds were present at all.

1. Introduction

Long before any lunar samples had been returned to Earth it was anticipated (Wänke 1965) that the lunar soil would contain trapped rare gases from the implantation of energetic ions of solar wind origin. This hypothesis, which had been based on studies of so called 'gas rich' meteorites (e.g. Pepin & Signer 1965) was duly substantiated by the large quantities of helium, neon, argon and the other rare gases, which were released in almost the expected isotopic abundances, by heating the lunar fines (L.S.P.E.T. 1969). Rare gas systematics of lunar soils are now, by and large, well understood (Kirsten, this volume) and have proved invaluable in establishing the exposure histories of the various lunar landing sites.

The most abundant elements of the solar system (Cameron 1973), and hence the species most likely to be present in the solar wind, are given in table 1. Many of the elements listed are as abundant as the low atomic number rare gases. Some elements, such as oxygen, silicon, iron and magnesium, would be very difficult to detect when implanted into silicates. Others, particularly hydrogen, carbon and nitrogen, might be expected to be measurable in materials such as the lunar soil, which are highly depleted in volatile elements. Although there had been no published data to suggest the presence of solar wind carbon in meteorites, it was predicted by Draffan *et al.* (1969) that the solar wind might have an important role to play in lunar carbon chemistry. In particular, the accumulation of solar wind hydrogen was expected to influence greatly the nature of carbon species in the lunar regolith. A preliminary look at the Apollo 11 samples revealed that the approach of studying compounds of carbon and other elements released simultaneously with rare gases could provide significant information relevant to an understanding of solar wind bombardment (Abell *et al.* 1970*a*, *b*).

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The purpose of this paper is to examine the current status of knowledge concerning solar wind effects in lunar carbon chemistry. The search for the nitrogen species arising from solar wind bombardment is reviewed by Müller (1975).

Table 1. Abundances of elements in the solar system (Cameron 1973)

(Only elements greater in abundance than 10^5, relative to silicon arbitrarily set at 10^6, are shown.)

element	atomic number	abundance
H	1	3.18×10^{10}
He	2	2.21×10^{9}
C	6	1.18×10^{7}
N	7	3.74×10^{6}
O	8	2.15×10^{7}
Ne	10	3.44×10^{6}
Mg	12	1.06×10^{6}
Si	14	1.00×10^{6}
S	16	5.00×10^{5}
Ar	18	1.17×10^{5}
Fe	26	8.30×10^{5}

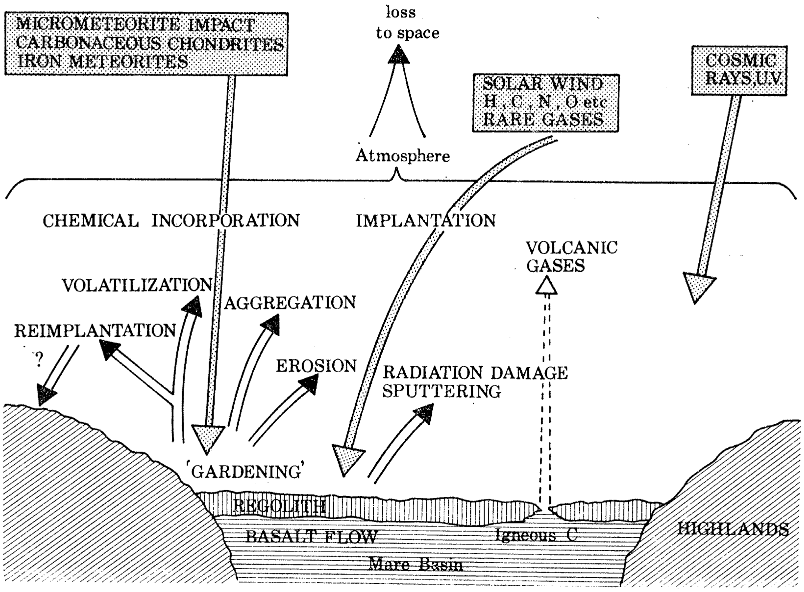

Figure 1. The lunar carbon cycle.

2. The carbon cycle in the lunar environment

A summary of the processes which contribute carbon to the lunar environment and which could provide the energy to induce chemical reactions or relocate the carbon species is given in figure 1.

Primordial carbon, indigenous to the Moon, is highly depleted in lunar igneous and metamorphic rocks (Moore 1974); the contribution from this source to the lunar regolith is believed to be small. Although the amounts of carbon outgassed from basalts into the atmosphere at the time of mare volcanism may have been quite substantial, it is unlikely that much was retained long enough to be incorporated into lunar soils.

The major contributors of carbon to the lunar environment are extralunar in origin. The solar wind will implant C atoms with an energy of about 1 keV/a.m.u. approximately 30 nm into the exposed surfaces of lunar soil grains at a rate of *ca.* 4×10^4 atoms $\mathrm{cm^{-2}\,s^{-1}}$ (calculated from the helium flux given by Buhler *et al.* 1969). Accompanying the carbon will be other reactive elements such as H, N, O and rare gases all having similar energies and fluxes proportional to their relative solar abundance (table 1). In addition to implanting elemental species, the solar wind produces radiation damage layers on the outer surfaces of crystalline grains (Maurette & Price 1974) and physically erodes surfaces at a rate of *ca.* 4.3 pm/year by sputtering (McDonnell & Ashworth, this volume).

Meteorite material contributed to the lunar regolith is most likely to be in the form of micrometeorites, particles having a mass $> 10^{-12}$ g, which impact the soil with a frequency of $4 \pm 3 \times 10^{-5}\ \mathrm{m^{-2}\,s^{-1}}$ (Fechtig *et al.* 1974). Of the meteorites studied terrestrially, carbonaceous chondrites, irons, and the very infrequently encountered ureilites, contain substantial quantities of carbon. Using trace element data, Anders and his co-workers (e.g. Laul, Morgan, Ganapathy & Anders 1971) have estimated that soils could contain 1–2 % by mass of carbonaceous chondrite type 1 material. This class of meteorites can contain carbon up to 5 %, thus the contribution to the lunar surface from this source could be quite extensive. However, since impacts occur at velocities up to tens of kilometres per second, the impacting object is likely to be mostly vaporized and little carbon might be retained. Carbon species already in the soil from other sources, particularly the solar wind, would also be pyrolysed and contributed to the impact cloud. Some gas would be trapped for a finite time in the pore spaces of the microejecta blanket, but the cloud would be rapidly dissipated into the lunar atmosphere and eventually lost to space. The most likely way to incorporate carbon into the soil from gas clouds would involve chemical reactions with iron (Cadogan *et al.* 1972). Because of gas phase mixing, meteorite carbon and solar wind carbon would be indistinguishable (unless isotopically different). However, some material deriving from the meteorite would be among any proportion of volatilized carbon incorporated by a chemical process (Jull *et al.* 1975). Other mechanisms suggested as a means of retaining meteoritic carbon, such as direct condensation on to exposed surfaces (Pillinger *et al.* 1972; Bibring *et al.* 1974*b*), or reimplantation of CO_2 (Hayes 1972) from the lunar atmosphere in a manner analogous to ^{40}Ar (see Signer *et al.*, this volume, for a discussion) may be less favourable.

Meteorites, apart from any carbon they supply, must play an important role in the lunar carbon cycle; they (i) erode and comminute grains to expose fresh surfaces to the solar wind and continuously stir or 'garden' the lunar surface, (ii) aggregate small lunar grains into larger, complex soil breccias and glassy agglutinates by sintering and melting processes, and (iii) contribute energy in the form of heat to initiate and maintain chemical reactions.

Other fluxes, such as solar ultra violet and cosmic rays, which could also contribute energy to drive chemical reactions, are included in figure 1.

3. EXPERIMENTAL METHODS

The procedures used by rare gas analysts to detect solar wind gases in both lunar samples and meteorites are most unsuitable for the measurement of carbon compounds. In fact, during rare gas determinations, special precautions are taken to destroy any carbon species which might interfere in the analyses. Consequently, a number of new methods, suited specifically to carbon containing molecules, have had to be developed.

Combustion in oxygen (Moore 1974) has been used to measure total carbon content of lunar soils. Pyrolysis *in vacuo* (Holland, Simoneit, Wszolek & Burlingame 1972*a*; Gibson & Moore 1972) or in helium (DesMarais, Hayes & Meinschein 1973) releases most of the carbon if high enough temperatures are employed. Neither method provides much information about the chemical nature of the carbon in the lunar regolith. Gas trapped in the silicate matrix may be liberated by *in vacuo* crushing but the yield is low due to the inefficiency of the process (Abell *et al.* 1970*c*, 1971).

Most detailed information about the carbon chemistry of lunar soils has come from a method Abell *et al.* 1970*c*, 1971) in which concentrated deuterated acids have been used to dissolve the mineral matrix, thereby releasing trapped gases and deuterium labelled reaction products. The isotopic ratio ($^{13}C/^{12}C$) of a particular carbon species should provide information about how that species was formed. However, because of the large quantities of sample required, most isotope data have been obtained from mixtures of carbon gases released by pyrolysis from bulk samples. (A discussion of carbon isotope data is beyond the scope of this review; the reader is referred to work by Kerridge, Kaplan & Lesley (1974) and Epstein & Taylor (1975).)

As information has been gleaned from the samples, it has been possible to postulate various mechanisms to account for the carbon compounds observed. Thus, laboratory simulation studies designed to evaluate the feasibility of hypotheses and to examine the relative efficiency of proposed lunar processes, have been developed (Pillinger *et al.* 1972; Chang, Mack, Gibson & Moore 1973; Bibring *et al.* 1974*a*, *b*; Davis *et al.* 1975; Chang & Lennon 1975). Most simulations have been directed towards examining the role of the solar wind by the implantation into minerals and glasses of hydrogen, carbon and nitrogen atoms at approximately solar wind energies and doses.

TABLE 2. SPECIES RELEASED FROM LUNAR FINES BY DEUTERATED ACID

species	carbon precursor	proportion of total C (approx. %)
CH_4, C_2H_4, C_2H_6	trapped gases	4
CD_4, C_2D_4, C_2D_6	hydrolysable C in iron	7–20
C_2D_2	ionic carbides	1–2
DCN	cyanides	2
CS_2	C in FeS	< 1
total		15–27

4. CARBON COMPOUNDS IDENTIFIED BY THE DEUTERATED ACID TECHNIQUE

The deuterated acid dissolution method (Abell *et al.* 1970*c*, 1971) was originally conceived to distinguish between conflicting interpretations based on the independent observation by two groups (Abell *et al.* 1970*a*, *b*, Chang *et al.* 1970) that low molecular mass hydrocarbons were released from lunar soils by protonated acids. Abell *et al.* had proposed that the hydrocarbons were indigenous and of solar wind origin, while Chang *et al.* had assumed that they were derived by the hydrolysis of meteoritic metal carbides, mainly cohenite, $(FeNi)_3C$. Both interpretations proved to be partially correct. Four main types of carbon have now been recognized by gas chromatographic and mass spectrometric analysis of the gases released from lunar soils by deuterated acid dissolution. The species identified, together with the proposed precursors for reaction products and an estimate of the proportion of the total lunar carbon accounted for, are listed in table 2. Each type of carbon will be considered in turn.

(*a*) *Trapped hydrocarbons*

The existence of CH_4, C_2H_4 and C_2H_6 trapped in the mineral matrix of Apollo 11 fines (Abell *et al.* 1970*c*) and in a number of Apollo 12 soils (Abell *et al.* 1971) was confirmed by releasing these gases with deuterated acid to allow distinction between trapped gases and reaction products. The considerable weight of evidence which has accrued to suggest that CH_4 is a solar wind product has been reviewed by Cadogan *et al.* (1972). Important factors considered were: (i) the location of CH_4 at particle surfaces or in complex grains such as glassy agglutinates and microbreccias, themselves aggregates of finer particles of high surface area, and (ii) the direct correlations between CH_4 and other measures of surface exposure. More recently, it has been shown that when samples from all missions are used for correlation studies, the composition of the individual materials studied must be taken into consideration. The scatter in a plot of CH_4 against ^{36}Ar is considerably reduced by introducing a parameter (FeO content) representative of bulk chemistry (Pillinger *et al.* 1974). This does not necessarily require that CH_4 synthesis is dependent on sample composition. It may be interpreted to mean that losses of the volatile carbon species during the formation of aggregated grains are governed by the different melting and sintering temperatures of soils of varying chemistry (Pillinger *et al.* 1975).

(*b*) *Carbon in solid solution in iron*

The deuterated acid dissolution method resolved that the hydrocarbons arising from protonated acid treatment had a mixed origin. In addition to trapped hydrocarbons Abell *et al.* (1970*c*, 1971) were able to recognize a hydrolysable phase which gave a series of deuterocarbons (CD_4, C_2D_4, C_2D_6) and both saturated and unsaturated C_3 and C_4 compounds. The original interpretation of these results by Abell *et al.* (1970*c*) (after Chang *et al.* 1970) was that the hydrolysable phase was the meteoritic carbide, cohenite. As the evidence grew that hydrolysable carbon (like CH_4) was located at particle surfaces and correlated with other parameters measuring surface exposure, alternatives to the addition of meteoritic carbide were suggested (see Cadogan *et al.* 1973 for a review). Finally, the idea of a direct contribution of meteorite material had to be discarded altogether when it was found that the correlation plot of CD_4 against ^{36}Ar depended on the ferrous iron content of the silicates (Pillinger *et al.* 1973, 1974). All the currently favoured mechanisms for hydrolysable carbon formation have been reviewed by Pillinger *et al.* (1974). Metallic iron may be formed from Fe^{II} in the silicate by shock (Cisowski *et al.* 1974) or by a reduction mechanism which involves either solar wind hydrogen (Housley, Grant & Paton 1973) or a meteorite impact cloud (Pearce, William & McKay 1972) as the reducing agent. Solar wind carbon implanted into the silicate or solar wind and meteorite carbon in an impact cloud could be incorporated, by a chemical process, into iron (Pillinger *et al.* 1974). The hydrolysable carbon phase could be supplemented by further implantation of carbon into exposed metal.

Since the conception of the DCl method, the species in the lunar soil giving rise to CD_4 and deuterocarbons other than C_2D_2, has been referred to in the literature as carbide, 'carbide', carbide-like, or material reacting as carbide. Recent work has shown that this nomenclature is erroneous and that the only grains of true carbide which have been recognized in the lunar fines are those whch have been identified microscopically (e.g. by Frondel, Klein, Ito & Drake 1970).

Deuterated acid dissolution studies of a series of synthetically produced carbon-containing iron phases have shown that iron carbide is essentially inert to acid attack and that the hydrolysable component in lunar samples is more likely to be correctly identified as carbon in solid solution in α-Fe (Jull *et al.* 1975, 1976). This observation is consistent with electron diffraction data obtained from the finely-divided iron droplets in the 10–15 nm size range in glassy agglutinates (Pillinger *et al.* 1976). The deuterocarbon yields from synthetic samples suggest that a quantitative estimation of the carbon present associated with iron in lunar samples may be obtained by summing the carbon released by DCl as CD_4, C_2D_4 and C_2D_6. Previously, it had been considered that an absolute yield of the hydrolysable carbon phase was not obtained from the acid dissolution method (Cadogan *et al.* 1972).

(*c*) *Ionic carbide*

Of the deuterocarbons released from lunar soil by DCl, one, C_2D_2, cannot be rationalized as being a product deriving from carbon in iron (Chang *et al.* 1970). This deuterocarbon must arise from dissolution of an ionic carbide or acetylide (Evered 1963). The most likely metals to exist as acetylides in the lunar fines would be calcium or aluminium (Wszolek & Burlingame 1973). Indeed, highland soils which contain increased quantities of Ca and Al, due to a greater abundance of plagioclase, do appear to be enriched in the C_2D_2 precursor (Wszolek & Burlingame 1973; Carter 1975). No systematic study has been carried out, however, into the relationship between C_2D_2, exposure and bulk chemistry. Likewise, there has been no complete survey of well-characterized mineral or particle separates. Such an investigation could be frustrated in the case of agglutinates, because C_2D_2 from acetylides may be reduced *in situ* to more saturated deuterocarbons by D_2 arising from the abundant free iron (Carter 1975).

(*d*) *Other reactive forms of carbon*

Two other carbon species, namely DCN and CS_2, are frequently released by DCl acid dissolution of lunar fines (Holland, Simoneit, Wszolek & Burlingame 1972*b*). DCN presumably arises from the decomposition of cyanides. The yield of this species increases with decreasing grain size and a solar wind origin is indicated, illustrating that quite complex chemistry can be induced in the lunar surface. The CS_2 may derive from implantation of solar wind C into troilite, FeS.

On several occasions, various investigators have discussed the possibility that CO and CO_2 are among the products of acid dissolution (Burlingame *et al.* 1970; Abell *et al.* 1971; Chang, Lennon & Gibson 1974). Small amounts of trapped CO might be expected as a solar wind product, and various phases, including carbonate, have been suggested as the precursor of CO_2. However, since both CO and CO_2 are ubiquitous contaminants of mass spectrometers, and atmospheric CO_2 could be adsorbed on the samples or in the acid reagents, considerable caution has been exercised over the interpretation of these results. Perhaps the most significant observation with respect to a portion of the CO_2 released being derived from solar wind implantation, comes from a simulation study. Bibring *et al.* (1974*a*) observed $^{13}CO_2$ from an acid treatment of ^{13}C implanted plagioclase. This result is likely to stimulate new efforts to establish the indigenous component of the CO and CO_2 observed from lunar fines.

5. Solar wind carbon in the silicate matrix

As stated earlier, pyrolysis of the lunar fines *in vacuo* or in helium is able to release the majority of the carbon in the samples as either CO or CO_2. Experiments have been carried out, either by temperature programming at a pre-determined rate or by increasing the heating in a series of steps, and a profile of carbon species against temperature is obtained. There has been considerable speculation concerning the nature of the carbon precursors leading to the various maxima in this release pattern. By using stepwise heating, followed by dissolution of the pyrolysed residue, it has been possible to resolve which peak in the profile is due to the hydrolysable carbon phase (Billetop *et al.* 1976). Although pyrolysis to 900 °C releases greater than 70 % of the carbon trapped in the Apollo 11 lunar soil, DCl treatment of the residue still affords substantial amounts of CD_4 suggesting that the hydrolysable carbon phase is not decomposed up to this temperature. The carbon released up to 900 °C is probably solar wind carbon which is implanted into the silicate matrix, as suggested by Gibson & Moore (1973). How this species is chemically bound to the silicate, if at all, is still a major issue for investigation. The identification of a precursor in the lunar soil giving rise to CO_2 (see §4*d*) may be very important.

6. Simulation studies

Simulation studies designed to understand effects which might occur on the lunar surface as a result of particle bombardment began, in fact, long before any lunar samples had been obtained (Wehner, Kenkright & Rosenberg 1963; Zeller, Ronca & Levy 1966). The first studies specifically directed towards a clearly defined chemical problem, however, were made in an effort to establish that trapped hydrocarbons, particularly CH_4, could be derived from solar wind hydrogen and carbon (Pillinger *et al.* 1972). A series of targets including terrestrial minerals, lunar fines and a powdered lunar rock, were implanted with ^{13}C and D at energies approximating to the solar wind and at a total dose equivalent to about 10^3 years of surface exposure. Treatment of these samples with protonated acid released $^{13}CD_4$ which must have been synthesized from the implanted atoms. The result was confirmed by Bibring *et al.* (1974*a*) by using similar techniques but a more specific detection system. In addition, Bibring *et al.* (1974*a*) showed that a species liberating $^{13}C_2D_2$ on DF treatment could be formed from implantation of ^{13}C into the calcium and aluminium-rich mineral plagioclase.

A number of attempts have been made to form a hydrolysable ^{13}C carbon phase associated with iron produced from Fe^{II} by implanted H or D atoms. Although hydrolysable ^{13}C species have been produced, the amounts generated are so small (usually less than 0.05 % of the implanted ^{13}C) that it is unlikely that the laboratory experiments duplicate the procedure which takes place on the Moon (Davis *et al.* 1975). The failure of the simulations may result from an inability to produce the necessary iron metal from the silicate or some difficulty in getting carbon and the metal in close proximity. In either case, the problem could be that the experiments which have been performed are not an appropriate representation of lunar conditions. Recently, Yin, Tsang & Adler (1975) reported on the basis of e.s.c.a. data that a flux of He ions of solar wind energy is able to preferentially sputter oxygen atoms from the surface of fayalite to reduce Fe^{II} to Fe^0. Similarly, Gold (this volume) by using Auger suggested that a species of iron is enriched relative to oxygen in fines by sputtering with H. Both experiments were performed in vacuum systems and analysed *in situ*. The failure to produce iron metal in association with carbon may be due to re-oxidation of reduced surface layers when the samples implanted with ^{13}C and H were exposed to the atmosphere for processing before analysis by the DCl method (Davis *et al.* 1975).

If reduced surface layers are formed by preferential sputtering on the lunar surface, then the aggregation of agglutinates and microbreccias may be implicated in ensuring that the iron survives for measurement on Earth. It is difficult to envisage how transient impact gas clouds could reach equilibrium and produce iron as suggested by Pearce *et al.* 1972, or hydrolysable carbon (Cadogan *et al.* 1972). Indeed, attempts to simulate this process have been unsuccessful (Jull *et al.* 1975). However, very thin layers of active iron produced by sputtering on the exterior of fine grained material would be highly susceptible to carburization by C species, even in a transient gas cloud. The carburized iron would be incorporated into the glassy matrix of agglutinates as finely divided spheres. Thermally induced migration of solar wind implanted carbon and growth of the iron could also contribute to the synthesis of hydrolysable carbon.

7. Conclusions

Carbon in the lunar regolith appears to derive mainly from extralunar sources, predominently the solar wind. An as yet indeterminate proportion of the carbon present as hydrolysable carbon in association with iron may have been retained from impacting micrometeorites. The large excess of hydrogen in the solar wind has played an important role in determining the chemical nature of carbon. Hydrocarbons are presumably a direct result of chemical reactions involving solar protons. The hydrolysable carbon phase appears to owe its origin to the ability of hydrogen atoms to preferentially sputter oxygen.

Some carbon containing entities, determined by the DCl acid dissolution method, have been readily accepted as indigenous to the samples. Others, particularly a species which may liberate CO_2, require further study. The chemistry of a major proportion of the solar wind implanted carbon remains to be determined. Acid dissolution experiments may still have a part to play in studies of this portion of the carbon.

A full knowledge of the physico-chemical processes involving hydrogen, carbon and nitrogen in the lunar regolith, is expected to enhance the understanding of exposure effects due to the solar wind and micrometeorite impact.

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