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CARBON CHEMISTRY OF THE LUNA 16 AND 20 SAMPLES

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CONTENTS

The analysis of CH_4 and CD_4 gases released by DCl from fractions of Luna 16 and 20 samples selected by size, visual appearance, density and magnetic susceptibility, has shown these soils to be typical of mare and highland material respectively. Both samples are shown to be highly mature in that they contain large quantities of hydrolysable carbon and trapped hydrocarbon. Luna 16 is characterized by a high content of glassy reworked material. The CD_4/CH_4 ratios indicate that the formation of CH_4, unlike hydrolysable carbon, is apparently independent of bulk chemistry in fractions < 48 μm. However, the proportion of volatile carbon species lost during the formation of larger aggregated grains may depend on the different melting and sintering temperatures of soils of different chemical compositions.

Introduction

Both Luna 16 and Luna 20 samples have previously been investigated for the presence of volatilizable carbon species by pyrolysis of < 125 μm sieved fractions to 1400 °C (Simoneit *et al.* 1973). Major gaseous products were CO, CO_2 and CH_4; minor components included C_2, C_3 and aromatic hydrocarbons together with fragments indicating a small proportion of polymeric contaminants, Teflon and silicone oil. The high total C contents of the sieved fractions examined 418 and 380 μg/g for Luna 16 and 20 respectively, suggested that both samples had experienced considerable exposure on the lunar surface.

An alternative approach to the study of carbon compounds in lunar soil is to dissolve samples in deuterated mineral acids (Abell *et al.* 1970). This technique has now been applied to a number of fractions of Luna 16 and 20 samples selected according to size, visual appearance, density and magnetic susceptibility. A preliminary communication describing this work has been submitted elsewhere (Eglinton *et al.* 1976).

† Elected F.R.S. 18 March 1976.

Trapped gaseous species are released from lunar samples by destruction of the matrix with DCl; the major carbon compound is CH_4. The concentration of this gas increases in finer size fractions with respect to the exposure history of the sample (Cadogan *et al.* 1972). A number of simulation studies have been conducted which support the hypothesis that low molecular mass hydrocarbons in lunar samples occur as a result of synthetic reactions involving carbon and hydrogen atoms implanted by the solar wind (Pillinger *et al.* 1972; Bibring *et al.* 1974).

In addition to trapped gases, reaction products, particularly the deuterocarbon CD_4, are released by DCl from the decomposition of hydrolysable carbon species within the lunar soil. The distribution of deuterocarbons released, the high yields of CD_4 obtained from acid treatment of magnetic glassy grains (Cadogan, Eglinton, Maxwell & Pillinger 1973*a*; Cadogan *et al.* 1973*b*), and the direct correlation observed between (Pillinger *et al.* 1974) CD_4 and the amount of iron in the range 0.01–1 μm (measured by ferromagnetic resonance) indicate that the carbon is associated with metallic iron. However, the hydrolysable species need not necessarily be some stoichiometric form of iron carbide (Jull *et al.* 1975). The abundance of the iron/carbon species increases with respect to the exposure of the samples on the lunar surface (Cadogan *et al.* 1972) and with the total Fe^{II} content of the soil (Pillinger *et al.* 1973). Thus, hydrolysable carbon formation may involve the reduction of Fe^{II} indigenous to lunar silicates, to free metal (Pillinger *et al.* 1973, 1974). Alkali or alkali-earth metal carbides which give rise to C_2D_2 on DF treatment may also contribute to the hydrolysable carbon, particularly in lunar soils from highland areas (Wszolek & Burlingame 1973).

Trapped and hydrolysable carbon species in lunar soil are important indicators of exposure and reworking, provided that the effects of bulk chemistry are taken into consideration (Pillinger *et al.* 1976). Furthermore, the relative proportion of involatile to volatile species (CD_4/CH_4 ratio) provides information about the thermal history of various particle types (Cadogan *et al.* 1973*a*, *b*).

Experimental

The separation and subdivision of the Luna 16 and 20 samples has been described in an accompanying paper (Pillinger & Gowar 1977). The amounts of CD_4 and CH_4 released by DCl (38 % in D_2O) were measured by gas chromatography according to previously described procedures (Cadogan *et al.* 1972, 1973*b*). The analyses were performed using *ca.* 5 – 10 mg samples, except in the case of magnetic/density separates of the 48–250 μm fraction of L1627 where *ca.* 3 mg aliquots were employed. For these magnetic concentrates only CD_4/CH_4 ratios have been quoted since absolute values of CD_4 and CH_4 are subject to errors of ± 50 % due to inaccuracies in weighing small samples. The absolute amounts of CD_4 and CH_4 for other samples are estimated to be accurate to ± 10 %; CD_4/CH_4 ratios are believed to be ± 2 %. A sample of Apollo 11 bulk fines, analysed as a check on the systematic errors of the analytical procedure, released CD_4 and CH_4 in quantities within ± 10 % of values previously measured for samples of this soil.

Results and discussion

The quantities of CD_4 and CH_4 released from various fractions of L1627 and L2015, together with the measured CD_4/CH_4 ratios, are given in tables 1 and 2. The results may be compared favourably with those obtained from similar fractions of Apollo mare (10086) and highland (60501) soils (Cadogan *et al.* 1973*b*). When the Fe^{II} contents (L1627 FeO = 16.3 %, Vinogradov 1971, and L2015 FeO = 7.0 %, Vinogradov 1973) of the soils are taken into consideration, the amounts of CD_4 released from bulk materials (table 1) confirm that both soils are very mature and have experienced a similar degree of exposure on the lunar surface. For the samples > 10 μm in size, there is a direct relation between the CD_4 concentration and the magnetic susceptibility χ_i (Stephenson, Collinson & Runcorn 1977) indicating that the hydrolysable carbon species in Luna samples is associated with metallic iron (Pillinger *et al.* 1974). The yields of CH_4 from all of the L2015 fractions analysed is comparable with other lunar soils investigated (Cadogan *et al.* 1973*b*). The very high value (*ca.* 25 μg/g) obtained by Simoneit *et al.* (1973) for this sample presumably reflects an additional contribution from CH_4 generated during the pyrolysis.

TABLE 1. CD_4 AND CH_4 RELEASED BY DCl DISSOLUTION OF SELECTED FRACTIONS OF LUNA 16 AND 20 FINES

		L1627			L2015		
sample description	sample daughter no.	CD_4 μg/g as C	CH_4 μg/g as C	CD_4/CH_4	CD_4 μg/g as C	CH_4 μg/g as C	CD_4/CH_4
bulk sample	1	19.3	3.0	6.4	10.9	4.8	2.3
> 250 μm (hand-picked agglutinates)	3	12.1	0.86	14.1	insufficient material available for analysis		
48–250 μm (washed)	8	19.3	2.7	7.1	4.4	1.7	2.6
< 48 μm	7	18.8	5.7	3.3	8.0	5.3	1.5
'finest fines' (< 10 μm)	9	19.2	6.2	3.1	15.9	8.9	1.8

TABLE 2. CD_4 AND CH_4 RELEASED BY DCl DISSOLUTION OF DENSITY AND MAGNETICALLY SEPARATED FRACTIONS OF 48–250 μm OF LUNA 16 AND 20 FINES

sample no.	density g/cm³	h/cm	CD_4 μg/g as C	CH_4 μg/g as C	CD_4/CH_4
L1627,10,2,1	< 2.96	0.25–0.35	not calculated		11.9
L1627,10,2,2	< 2.96	0.05–0.25	not calculated		9.5
L1627,10,2,3	< 2.96	0–0.05	not calculated		10.5
L1627,11,2,1	> 2.96	0.2–0.25	not calculated		5.2
L2015,10,2,1	< 2.78	not separated	7.2	1.6	4.5
L2015,11,2,1	> 2.78	not separated	1.5	0.85	1.8

The analysis of size separated fractions (table 1) shows that for both Luna soils the CH_4 concentration, and for Luna 20 only, the CD_4 concentration increases as particle size decreases, suggesting a surface area relationship in agreement with studies previously carried out on Apollo 11 (Abell *et al.* 1970; Cadogan *et al.* 1972) and Apollo 14 samples (Holland *et al.* 1972). For L1627, the amount of CD_4 released appears to be independent of grain size, suggesting a considerable volume related component. Microscopic examination shows that L1627 is predominantly complex, reworked particles (Pillinger & Gowar 1977; Eglinton *et al.* 1976) and hence, surface concentrations of hydrolysable carbon may be masked by volume-related components contained in welded aggregates of fine, well-exposed grains. DesMarais, Hayes & Meinschein (1973) suggested that an equilibrium situation may be reached in mature samples where the rate of particle aggregation has been rapid relative to the rate of carbon accumulation. The hydrolysable carbon in L1627 may be the result of such an effect.

The ratio (CD_4/CH_4) of involatile (acid-hydrolysable) carbon to volatile carbon (trapped gases) must reflect the rate of formation of hydrolysable carbon species (dependent on Fe^{II} content) and the extent to which CH_4 has been lost during aggregation of fine grains into complex particles. Thus, high CD_4/CH_4 ratios are observed (table 2) for agglutinate rich fractions (the residue after hand picking of L1627 (L1627,3), the low density/magnetic fractions of Luna 16 (L1627,10,2,1–3) and the low density material from Luna 20 (L2015,10,2)). All three low density/magnetic fractions of L1627 gave high CD_4/CH_4 ratios indicative of the presence of glassy grains in keeping with the very high proportion of these observed in the > 250 µm fraction (Pillinger & Gowar 1977; Eglinton *et al.* 1976). Apparently the magnetic separation effects no obvious fractionation which can be determined by carbon chemistry measurements, probably because of the wide particle size range being studied. A similar effect was observed for the 48–250 µm size fraction of Apollo sample 60501 whereas the low density 152–250 µm fraction of 10086 was easily separated into three distinct aliquots according to magnetic susceptibility (Cadogan *et al.* 1973*b*). The high CD_4/CH_4 ratio of 6.4 measured for the bulk sample L1627 suggests that this sample contains a high proportion of glassy welded material. The CD_4/CH_4 ratio of 2.3 from bulk L2015 suggests a much lower quantity of glass in agreement with Mössbauer spectroscopy data (Gibb, Greatrex & Greenwood 1976). The apparent decrease of CH_4 with increasing grain size observed for L1627 could be interpreted in terms of the loss of volume related volatile species during the formation of agglutinates. The high density fractions of both L1627 and L2015 have substantially lower CD_4/CH_4 ratios than the light fractions (table 2). Most of the high density particles are thought to be soil microbreccia which had not been strongly heated during their formation (Cadogan *et al.* 1973*a*, *b*).

Table 3. CD_4 and CH_4 released by DCl dissolution of < 48 µm grains from Apollo samples 10086 and 60501

sample	10086 CD_4 µg/g as C	10086 CH_4 µg/g as C	10086 CD_4/CH_4	60501 CD_4 µg/g as C	60501 CH_4 µg/g as C	60501 CD_4/CH_4
< 48 µm	not measured			7.0	3.1	2.3
‘finest fines’ 0.5–10 µm	42.8	11.2	3.8	14.2	6.4	2.2

For both Luna 16 and 20, the finer fractions (< 48 µm) have lower CD_4/CH_4 ratios and higher absolute amounts of CH_4 than do the fractions which contain larger grains (bulk samples, > 250 and 48–250 µm samples, table 1). High absolute amounts of CH_4 and low CD_4/CH_4 ratios are also observed for fine grained material collected from Apollo samples 10086 and 60501 (table 3). Thus, since the concentrates of small particles have the lowest CD_4/CH_4 ratios, they cannot contain a high proportion of complex particles such as glassy agglutinates which have highly fractionated carbon species. Indeed, over 80 % of the < 48 µm fraction are simple grains (Eglinton *et al.* 1976). Therefore, for the complex particles, either (i) the rate of comminution relative to the rate of aggregation was low, or (ii) the effect of comminution on agglutinated particles has been to regenerate single grains rather than to produce smaller, complex grains. Since the proportion of agglutinates in a sample increases with surface exposure and is considered as a measure of maturity (McKay & Heiken 1973), (i) would appear to be more likely.

Certainly the ultra-fine grains which adhere to larger particles represent the primary site for CH_4 and hydrolysable carbon synthesis (Cadogan *et al.* 1973*a*, *b*). If these grains are indeed relatively simple, then the CD_4/CH_4 ratios observed for them should reflect the relative rates of formation of hydrolysable carbon and CH_4 in the surface of lunar silicates and should be largely unaffected by the sintering and melting processes associated with aggregation by agglutinate formation. Samples having high (*ca.* 16.0% FeO, L1627 and 10086) and low (*ca.* 6.0% FeO, L2015 and 60501) Fe^{II} contents exhibit high concentrations of trapped CH_4. The CD_4/CH_4 ratios are *ca.* 3.3–3.8 and 1.5–2.2 respectively. The differences in the CD_4/CH_4 ratios can be accounted for entirely on the basis that the synthesis of hydrolysable carbon is dependent on Fe^{II} content. Thus, CH_4 formation does not appear to involve the availability of Fe^{II} within the sample, although the scatter observed (Pillinger *et al.* 1974) in a correlation plot of CH_4 content against ^{36}Ar concentration for Apollo 11–17 bulk samples was considerably reduced when the CH_4 concentrations were normalized for Fe^{II} content. To reconcile these two apparently contradictory observations, we suggest the following explanation: the fine grain fractions (< 48 μm) contain only a small proportion of complex grains, whereas bulk samples have abundant complex particles containing fractionated carbon species. In samples of apparently very similar exposure history such as Luna 16 and 20, the proportion of glassy material in the high Fe^{II} sample (L1627) is considerably higher than in the low Fe^{II} sample (L2015). Since the impact history of the samples should be approximately similar, the low abundance of glass in highland material is presumably related to the high melting and sintering temperature of the anorthositic suite of rocks compared to mare basalts (Agrell 1974, personal communication). For example, anorthositic gabbro might be expected to melt at 1200–1400 °C, whereas a mare basalt melts at 1060–1160 °C. Thus, when complex agglutinate particles are formed by impact-produced glass splashed on to highland soil the CH_4 losses due to thermal diffusion from particles incorporated into the glass will be considerably greater due to the increased temperature of the molten material. The increased CH_4 losses are readily apparent from a comparison of hand picked agglutinate samples such that those selected from L1627 (FeO = 16.3%) and from 10086 (FeO = 15.7%) had CD_4/CH_4 ratios of 14.1 and 14.6 (Gardiner 1974) respectively. A similar sample taken from 60501 (FeO = 5.7%) had a CD_4/CH_4 ratio of 8.9 (Cadogan *et al.* 1973*b*); however, allowing for the lower Fe^{II} content by normalizing CD_4 to 16.0% FeO, this ratio increases to *ca.* 25. Thus, the decreased scatter observed for the $CH_4/^{36}Ar$ against FeO plot may indicate that FeO is acting as an indicator of the different melting characteristics involved during the formation of agglutinates. Low concentrations of CH_4 in samples which are low in Fe^{II} could be explained by higher diffusion losses during high temperature agglutination. Therefore, in the $CH_4/^{36}Ar$ against FeO correlation plot for bulk samples, FeO may be acting as a bulk chemistry indicator of the different melting characteristics of the soils involved. Low CH_4 concentrations in low Fe^{II} samples could be due to higher diffusion losses during high-temperature melting. Alternative explanations involving catalytic effects of Fe^{II} or Fe° in the synthesis of CH_4 or production of CH_4 by reduction of carbon in solid solution (Pillinger *et al.* 1974) may be less likely.

Conclusions

Analysis of the gases released by acid dissolution of L1627 and L2015 has confirmed that both are highly mature soils. The carbon chemistry of L1627 is typical of a mare soil, similar to Apollo 11, whereas that of L2015 is similar to highland material collected from the Apollo 16

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site. Fractions from L1627 are characterized by high CD_4/CH_4 ratios in accord with this sample being rich in glassy material, presumably as a reflection of the lower temperatures required to melt mare rocks. The high absolute values of CH_4 in fractions of L2015 which contain the least number of complex, recycled grains (< 48 μm) suggest that the formation of CH_4, unlike that of acid-hydrolysable carbon, is independent of the Fe^{II} content of the silicate. A more complete examination of the effects of bulk chemistry on CH_4 diffusion during agglutination is in progress.

Even with less than 10 mg quantities of lunar sample, the acid dissolution method provides useful carbon chemistry data for investigating the exposure history of the lunar regolith. The method is particularly effective when applied to a sample which has been subdivided by physical separation techniques.

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