SURVEY OF LUNAR CARBON COMPOUNDS II: THE CARBON CHEMISTRY OF APOLLO 11, 12, 14 and 15 SAMPLES. P.H. Cadogan, G. Eglinton, J.N.M. Firth, J.R. Maxwell, B.J. Mays and C.T. Pillinger, Organic Geochemistry Unit, School of Chemistry, Bristol University, U.K.

In our previous studies hydrocarbons released from lunar samples by acid dissolution were resolved into indigenous species and reaction products (deuterocarbons) by the use of deuterium-labelled reagents. The quantities of CH$_4$ and CD$_4$ released by DF etch of Apollo 11 and a variety of Apollo 12 fines were correlated with parameters relating to surface exposure. These data, taken with preliminary results from other experiments (shallow etching and analysis of an igneous rock and of size-differentiated fines) indicated that solar wind implantation in the fines plays a major role in the synthesis of endogenous hydrocarbons. Also, a dual extralunar origin (meteorite impact and solar wind implantation) appeared likely for the 'carbides', the presumed source of the deuterocarbons. Further analyses by mass spectrometry and improved gas chromatographic techniques have now provided additional evidence for the origins of these carbon species:

1. Sources of possible contamination and of artefacts. It has been suggested that methane in lunar fines arises by adsorption from the terrestrial environment or by hydrolysis of reactive lunar 'carbides' by adsorbed water. Three experiments taken together indicate to the contrary: (i) Exposure of fines (10086) to CD$_4$ for 24 hours and subsequent dissolution in HF showed that $< 0.2 \mu$g/g of CD$_4$ was not desorbed by standard degassing procedures preceding each analysis. Further, adsorbed terrestrial CH$_4$ has never been observed in standard procedural blanks (activated A1$_2$O$_3$ exposed during sample handling), (ii) immersion of fines (10086) in D$_2$O for 41 days did not generate CD$_4$. HF dissolution after 3 months in D$_2$O also failed to reveal trapped CD$_4$, (iii) DC1 dissolution of freshly-exposed interior chips of breccia 10059 afforded quantities of CH$_4$ and CD$_4$ similar to those observed for fines (10086).

In addition, vigorous heating of DC1 (200°C, 2h.) with fragments of laboratory glass released CO, indicating that the single high value for CO previously reported was artefactual, as suspected. No CO was generated in the normal reaction procedure blank (100°C, 2h.) and quantities of CO released from a variety of All, 12 and 14 samples certainly do not exceed 3 µg/g.

2. Location of carbon compounds in lunar fines. Evidence concerning the location of hydrocarbons and 'carbides' has been obtained by analysis of size-differentiated fines and mineral separates. Our data for the Apollo 11 fines, which suggested that CH$_4$ was concentrated in the finest grains, have been extended to show that both the CH$_4$ and CD$_4$ released by DC1 are directly proportional (surface correlated) to the reciprocal of the mean grain radius for particles 48 to 152µm diameter. However, for particles 152µm to 2mm diameter the surface relationship is no longer valid; there is an additional CH$_4$ and 'carbide' component which may be associated with the microbreccias and glassy aggregates abundant in these coarse fractions. Initial studies of density-
Survey of Lunar Carbon Compounds II:

P.H. Cadogan

separated mineral fractions have not revealed major differences in CH₄ and CD₄ contents, but more information is expected with sieved fractions.

3. Survey of lunar samples. We have shown that quantitation of 'carbide' based on CD₄ released from All fines, is dependent on the nature and strength of the acid; our standard method employs 38% DCI at 100°C. Hydrolysis of coarsely powdered meteoritic cohenite under standard conditions afforded ca 6% CD₄; even this improved dissolution does not permit an accurate determination of lunar 'carbide', for on this basis the All fines should contain 300 µg/g total carbon (measured, ca 180 µg/g). Our survey of the CH₄ and 'carbide' concentrations has been extended to 8 samples from depths between 9.0 cm and 39.8 cm of the A12 double core (12025, 12028), A14 fines 141, 148, 149, 156, 163, 240 and 298, A14 breccias 267, 311, 313 and 321, and A15 fines 031, 041, 231, 261, 431, 471 and 501. CH₄ and CD₄ values range from 0.5 and 1.1 (Cow Crater 14141) for light-coloured fines, to 5.1 (15231) and 23.5 (15041) µg/g, respectively, for dark-coloured fines. The CD₄ to CH₄ ratios fall in the range 2:1 - 12:1, averaging 4:1. There is no systematic variation for CH₄ and CD₄ with depth for the core and correlations with other parameters are difficult to obtain with the existing sample allocations. However, the CH₄ and CD₄ data roughly parallel the available exposure parameters. The A15 fines All give high CH₄ and CD₄ values with no apparent relationship to 'ray' or 'front' material but the most depleted sample (15431) was derived from the pedestal of "genesis" rock. Three A14 breccias, 14267, 14321 and 14311, gave extremely low values for CD₄ and CH₄ in accord with the high temperature origin indicated petrologically for these samples. Figures for total carbon are awaited.

4. Correlation of carbon chemistry and lunar surface exposure history. We have extended our correlations for CH₄ and 'carbide' concentrations with parameters indicative of extended exposure of the fines at the lunar surface:

(i) Extent of solar wind implantation (as 36Ar concentration) correlates with amounts of CH₄ with a 36Ar:CH₄ ratio of 1:18. There is a similar, though less marked relationship with 'carbide', the ratio of 36Ar:CD₄ being 1:81. Relative diffusion losses will need investigation. (ii) CH₄ concentrations correlate with the proportions of grains exhibiting radiation damage as estimated by Maurette et al from the number of amorphous-coated 1-2µm grains and of feldspar grains (<200 mesh) having >10⁵ tracks cm⁻² (A14), and by Arrhenius et al from the pyroxene and feldspar grains (coarse fractipn) having >10⁶ tracks cm⁻² (A1 and A2). Other possible parameters (e.g. δ¹³C values, modal analyses of grains) for exposure and reworking will be reintroduced as data become available from other investigators.

5. Solar wind-carbon chemistry simulation studies. The physical location and correlation studies are in agreement with an extralunar origin for the hydrocarbons and 'carbide' in the fines. We have previously stated the arguments in favour of a hydrocarbon component of solar wind origin and 'carbide' of a solar wind and meteoritic origin. The possible role of solar wind hydrogen and carbon in the synthesis of lunar hydrocarbons and 'carbides' is now demonstrated by laboratory simulations: irradiation of a number of targets, including lunar fines, with ¹³C⁺ and D⁺ at energies similar to those in the solar wind. LRMS analysis of labelled C₁₃ compounds released by acid
dissolution or pyrolysis showed the formation from the irradiating species of hydrocarbons and material reacting as carbide. The simulation only approximates to the effects of the solar wind. For example, (i) higher dose rates were used, (ii) when both $^{13}$C and $^{2}D_{2}$ were used, irradiation was consecutive and not simultaneous, and (iii) $^{2}D_{2}$ was used instead of $^{13}$C to obtain a sufficiently high flux. The data indicate that carbon and hydrogen in the solar wind could implant hydrocarbons and 'carbides' into lunar fines. No $^{13}$CO or $^{13}$CO$_{2}$ were observed when irradiated lunar fines or simulated lunar fines were pyrolysed to 800°C. This suggests that solar wind carbon is not released as CO and CO$_{2}$ when lunar fines are pyrolysed to this temperature. Indeed, others have shown that acid dissolution and stepwise pyrolysis together with $^{13}$C measurements indicate that the carbon is present in more than one form. Treatment of the vacuum-deposited Fe film with deuterated acid afforded $^{13}$CD, which was also released by dissolution of the unirradiated film. FeC originally present in the iron filament evidently deposits 'carbide' with the iron, a possible analogue for the deposition of meteoritic carbide on the lunar surface under impact conditions. Furthermore, for the fines, a trend is evident between concentrations of 'carbide' and the volatile element bismuth considered by Anders et al as indicative of the micrometeorite contribution. The fewer published values for selenium follow the same trend. The addition of elemental material by meteoritic impacts may be partially compensated by redistribution and loss of volatile elements by the resulting melting and vaporisation of lunar material. Thus, metallic iron may be generated and vapour-transported to the surface of the fines possibly generating 'carbide' by interaction with solar-wind implanted carbon. Models of lunar surface exposure history for carbon chemistry will need to take into account the processes mentioned above.

References