THE ORIGIN OF LUNAR CARBIDE.
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The concentration of carbide in lunar fines (estimated as CD_4 from DCl dissolution) is related to both solar wind exposure history (1) and Fe^{II} content (2) of the sample. The $CD_4/^{36}Ar$ ratio is proportional to the content of Fe^{II} (calculated as FeO) in fines from the A11, A12, A14, A15 and A16 missions (2). Current results show that carbide in A17, L16 and L20 fines has the same exposure and Fe^{II} dependence. Limited data suggest that the key iron species implicated in the relationship is superparamagnetic iron, $Fe^o sp$ (2). An understanding of the role of $Fe^o sp$ is now being sought by acid dissolution studies and Mössbauer spectroscopic measurements (3) of a variety of soils selected on the basis of Fe^{II} concentrations and solar wind exposure histories.

We have previously suggested that the finest (< 10 μm) soil grains represent the main site for initial synthesis of carbon compounds and that the reactions occurring in these non-aggregated fine grains are important in understanding lunar carbon chemistry (4). Subsequent redistribution of carbon species and any further reactions which occur during the recycling (5) of material via the formation and comminution of complex particles, such as glassy agglutinates and microbreccias, must be considered separately. Primary synthesis of $Fe^o sp$ and carbide in finest fines could be the result of solar wind ion implantation and/or meteorite impact cloud reactions (inter alia, 2,4,6-8). Each of the two basic processes may take place by one or more mechanisms. Solar wind ions could reduce silicate Fe^{II} to Fe^o by (i) preferential sputtering of the more electronegative elements (e.g. oxygen) or (ii) chemical reactions occurring during diffusion of implanted species, particularly hydrogen, with or without heating or other activation. Carbide synthesis might occur in each case from simultaneously implanted carbon atoms. Reduction of silicate Fe^{II} to Fe^o might occur in the hot base surge accompanying a meteorite impact. The reducing gas cloud could be (i) predominantly hydrogen and CO released by pyrolysis of the soil, or (ii) the gas mixture in (i), with a greatly increased proportion of CO, if the meteorite is a carbonaceous chondrite. The presence of carbon species in the gas cloud might be expected to lead to the simultaneous formation of carbide.

The feasibility of each mechanism is being investigated by simulation studies using Fe^{II}-rich glass samples (Fe^{II} in the range 0-20% FeO, supplied by P.S. Irlam, Pilkington Bros. Ltd.) under the appropriate reaction conditions. The DCl dissolution method is used to detect the formation of either Fe^o or Fe^o with associated carbide. In a preliminary study, glass

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containing 4% Fe^{II} and 7% Fe^{III} was implanted with $^{13}C^+$ ions. No conclusive evidence for the formation of Fe^o or carbide was found, even after heating at temperatures up to 1000^oC. However, during the pyrolysis ^{13}CO and $^{13}CO_2$ were released, indicating that ^{13}C-implanted iron-rich glasses exhibit some characteristics of lunar soils (9,10). A suite of samples irradiated by D_2^+ ions is now under investigation.

To simulate the effects of meteorite impact gas clouds, powdered glass samples (average particle size less than 20 μm) have been equilibrated at fixed temperatures (in the range $500^oC - 1000^oC$) in controlled H_2/CO or CO/CO_2 atmospheres. These experimental conditions are probably more favourable for the reduction and carbide synthesis reactions than those prevailing at the lunar surface. However, preliminary results from samples heated in CO/CO_2 at 1000^oC show no measurable Fe^o or carbide. Similarly, neither species has been detected in samples of $^{13}C^+$-implanted glass which had been heated in a stream of H_2 at 500°-700^oC.

After the initial formation of Fe^o in fine lunar grains, carbide could be generated by (i) subsequent implantation of solar wind carbon, or (ii) gas cloud reactions in which CO chemisorbed on exposed metal is catalytically decomposed. Indeed, laboratory studies have already shown both processes to be possible (11,12).

Any Fe^o synthesized in lunar soil by solar wind ion bombardment should be distributed only in the range of penetration of the ions:e.g. $2000 + 500Å$ for hydrogen (13). The proportion of Fe^o exposed at the "very surface" should be small. Conversely, reactions occurring in a gas cloud would be expected to generate only "very surface" material. Housley et al (14) have shown the presence of iron particles (presumably Fe^osp) within the surface region and we are attempting to establish the relationship between these particles and the species which produce CD_4 on DCl dissolution. Preliminary results with a variety of surface-specific reagents suggest that most of the Fe^o and carbide is not directly accessible to these reagents. About 90% of the Fe^o is not attacked without concurrently destroying part of the silicate matrix, implying that solar wind implantation is the major mechanism for Fe^o reduction.

Precise location studies should prove informative in regard to the redistribution processes occurring during the formation of complex particles from finer material. The carbide and CH_4 contents of a series of fractions obtained by disaggregating glassy agglutinates are being measured.

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