

LUNAR SOIL MATURATION, PART II: SYNTHESIS OF CARBON COMPOUNDS IN THE REGOLITH. J.P.Bibring, A.Burlingame⁺, J.Chaumont, M.Maurette, G.Slodzian^{*}, P.Wszolek⁺. Laboratoire René-Bernas, 91406 Orsay; ⁺University of California, Berkeley 94720; ^{*} Laboratoire de Physique du Solide, 91406 Orsay.

I - INTRODUCTION. See Part I.

II-THE ION IMPLANTATION SYNTHESIS OF CARBON COMPOUNDS IN SOLIDS("IIS" PROCESS).

II.1. Analysis of targets artificially exposed to low energy (~ 1 keV/amu) ^{13}C , ^{14}N and D ions. Several lines of evidence previously reported by others have suggested that the implantation of solar wind nuclei could synthesize carbon compounds in the lunar soil. In this chapter we present a study of simulated solar wind implantation synthesis that differs from previous ones in several important aspects : 1. the IIS species were searched for in a great variety of targets including metals with known but different characteristics for radiation damage defects (Al, Au) as well as solids either found in the lunar regolith (glass, pyroxenes, feldspars, ilmenite) or proposed as plausible models for cosmic dust grains (olivine, MgO, SiC, graphite, magnetite) ; 2. the IIS species were analyzed by using, in addition to the mass spectrometric techniques already applied to this problem (acid dissolution and pyrolysis), an ionic analyzer at ONERA which gives the implantation depth profiles of all species released by ion sputtering from the targets with a good mass resolution (~ 7000); 3. the physics of ion implantation phenomena was taken into consideration by directly examining the irradiated targets with a high voltage electron microscope (HVEM), and by carefully choosing the irradiation conditions.

II.2. Preliminary evaluation of the IIS yields. 1. Mass spectrometer: acid dissolution. In plagioclase and quartz implanted with C and D ions, both

Table I	
Species	Relative amounts
$^{13}\text{C}_2\text{H}_2$	10
$^{13}\text{C}_2\text{H}_6$	2.4
$^{13}\text{C}_3\text{H}_6$	1.7
$^{13}\text{CD}_4$	13
$^{13}\text{C}_2\text{D}_4$	16
$^{13}\text{C}_2\text{D}_6$	1.0
$^{13}\text{C}_3\text{D}_6$	3.5

deuterocarbons and hydrocarbons up to C_3D_6 have been detected (Table I) with a total yield which corresponds to several percent of the initial ^{13}C . The deuterio- and hydrocarbons represent species synthesized by implanted ions and reaction products of FH with carbide like material respectively ; 2. mass spectrometer : pyrolysis. In plagioclase implanted with the " C,D,N " mixture, 11% of the ^{13}C was released as ^{13}CO and $^{13}\text{CO}_2$, 0.5% of the ^{13}C and ^{14}N evolved as HCN and 0.25% of the D_2 was recovered as HOD. In aluminium implanted with the same ions no gaseous compounds have so far been detected during pyrolysis; 3. ionic analyzer. The mass spectra obtained with the ionic analyzer is very complex as both gaseous and non gaseous species released from the targets are detected. The light IIS species so far analyzed in the mass range $M < 40$ have been classified in 4 distinct groups (deuterocarbons ; oxygen species ; nitrogen compounds ; carbide and deuterated like material) and we present some of our preliminary results for 3 "oxygen-poor" (Al, Au, graphite) and 2 "oxygen-rich" (olivine ; plagioclase) targets : (a) deuterio-carbon lines. In Al single crystals CD, CD_2 , CD_3 and C_2D lines were detected in a very reproducible way. Furthermore the implantation depth profiles of all CD_n species were strikingly similar to that corresponding to the ^{13}C line. On the other hand with the polycrystalline Al foil the relative yield of these species

CARBON COMPOUNDS IN THE REGOLITH

Bibring, J.P. et al

was extremely variable with some target area only showing the CD line. In all the other targets including gold, only lighter molecular fragments were identified -CD, CD₂ in Au and graphite ; CD in plagioclase and olivine ; CD, C₂D and CD₂ in plagioclase which was pre-irradiated with a high dose ($\sim 10^{12} \text{ cm}^{-2}$) of 3 MeV/amu krypton ions ; (b) oxygen species. Strong OD lines were clearly detected in the oxygen-rich targets, with olivine showing the most intense line; (c) nitrogen compounds. ND and weak CN and DCN lines were detected in Al single crystals and in the pre-irradiated plagioclase; (d) carbide and deuterated like material. A rich variety of D-metal and ¹³C-metal lines (Na-D, Mg-D, Al-D ; Na-C, Mg-C ; Al-C) have been found in the targets where these metals are present.

II.3. Characteristics of the IIS process. From these preliminary results we deduce the following conclusions : 1. the IIS process certainly occurs in solids and its mass yields are astonishingly high ; 2. the IIS yields markedly depend on both the nature of the target and of its pre-implantation history. This is illustrated first by the results obtained with aluminium prepared either as single crystal or as polycrystalline foil, secondly by the marked differences between the oxygen-rich and the oxygen-poor targets and thirdly by the heavier species obtained with the plagioclase containing a high density of krypton tracks ; 3. the IIS process is highly selective and only gives a mixture of small molecules. It should then be considered as a possible contributor for synthesizing lunar carbon compounds as well as the mixture of molecules with up to 3 carbon atoms which are found in interstellar clouds. Indeed the dust grains in such clouds have certainly been exposed to heavy doses of low energy nuclear particles during their history that can both synthesize IIS species and trigger their release into space by ion sputtering.

II.4. The solid state radiation damage chemistry of the IIS process (tentative comments) : 1. the IIS yields are likely to depend on the sputtering rate, S, of the targets. Indeed the "saturation" concentration of the implanted ions are known to vary as S⁻¹, in various targets, including aluminium and graphite. Therefore higher IIS yields can be expected in Al than in gold, as S(Al) ~ 0.1 S(Au), and magnetite and graphite should be the most efficient minerals so far investigated for the IIS process, as they show the lowest S values (see Part I, Chapter II.2) ; 2. after implantation the "D,C,N" reactants possibly undergo a complex redistribution before being trapped at active sites, during which they could possibly precipitate at sinks that discriminate between the D,C,N atoms to form graphite inclusions as well as gas bubbles. Furthermore such a redistribution could be made much easier in the amorphous layers of radiation damaged material which are produced during the ionic implantation of the non-metallic targets (see Part I, Chapter II.2). Then it could as well be argued that the redistributed atoms are lost for the IIS process, thus decreasing the IIS yields, or that the precipitates act in fact as active sites where chemical reactions can proceed ; 3. the HVEM observation of graphite inclusions in aluminium as well as the astonishing rich variety of carbide like material detected in plagioclase with the ionic analyzer, support the view that the active sites for the formation of the C-metal species are indeed graphite inclusions in which knocked-on "hot" target atoms are injected producing "carbides" not limited to Fe and Ca as previously thought; 4. it is more difficult to identify the active sites involved in the formation of the IIS gaseous species. As such sites should show no steric factor hindrance for the growth of molecules up to C₃D₆, they could be "voids"

CARBON COMPOUNDS IN THE REGOLITH

Bibring, J.P. et al

containing an excess of deuterium and with sizes at least comparable to the length of the heaviest IIS deuterocarbons. Then the release of IIS gaseous species upon heating or ion sputtering could be explained by the "bursting" of the voids when they come within a few atomic layers of the target surfaces. However the occurrence of such a "void chemistry" is still problematic as we have so far not searched for small sized ($<50\text{\AA}$) voids with the HVEM in any one of our targets.

III- LUNAR CARBON CHEMISTRY.

III.1. Occurrence of a solar wind implantation synthesis on the Moon. Our combined "mass spectrometer - ionic analyzer" studies of both irradiated targets and lunar dust grains add considerable strength for the occurrence of a solar wind IIS process on the Moon. We first observed up to C_3 molecules as well as similar CH_4/CNH ratios for both types of material during acid dissolution experiments with the mass spectrometer. We then clearly showed that the pyrolysis products obtained for the silicate targets and the lunar soil were similar but very different from those released by the Murray and Murchinson carbonaceous chondrites. Thus the signature of the IIS process looks even more specific than previously thought. On the other hand the meteoritic contamination of the regolith in carbon compounds, which most likely occurs via the deposition of lunar wind vapor phases on the surface of the grains, should inject a "Murchinson" pyrolysis like mixture in the lunar soil, if the micrometeorites impacting the Moon have a carbon compound composition similar to that observed in carbonaceous chondrites. In fact the signature of the IIS process on the Moon is so clear that it is even possible to conclude that natural pyrolysis in the regolith has not noticeably modified the initial load of fossil IIS species in the lunar dust grains.

III.2. Carbon compounds and lunar soil maturity. The concentration, C , of lunar carbon compounds is known to depend on various indices of soil maturity, including the proportion of micron-sized grains showing an ultra-thin amorphous coating, $P(\Delta)$. As we demonstrated that such coatings are solar wind radiation damaged layers and not lunar wind vapor phases, this observation adds strength for the occurrence of the IIS solar wind process and consequently suggests that lunar carbon compounds are possibly trapped in a "void-inclusion" network extending in the amorphous coatings. However HVEM studies as well as ionic analyzer and electron microprobe runs also indicate that in the most mature soil samples, the micron-sized grains are in fact microaggregates of welded particles (see Part I, Chapter II.3) where secondary particles with a peculiar chemical composition are stuck to the amorphous coatings of the central grains. Then the size fraction effect observed on the release of lunar carbon compounds as well as the dependence of C on $P(\Delta)$ could also result from the preferential trapping of the compounds into such secondary particles. Therefore the microaggregates have to be further characterized before either concluding that lunar carbon compounds are localized into solar wind coatings or predicting the amount of solar wind carbon implanted in the finest size fraction of the regolith.