ANALYSIS OF ORGANOGENIC COMPOUNDS IN APOLLO 11, 12, AND 14 LUNAR SAMPLES.
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In our work we have placed particular emphasis on obtaining information to allow us to identify which source(s) is the principal contributor for the compounds evolved by thermal and acid treatment. Quadrupole mass spectrometry (QMS) and gas chromatography-mass spectrometry (GC-MS) were used to analyze gases released by thermal treatment. Gases released by acid treatment were analyzed by GC-MS. Sample 14003 was also extracted with benzene-methanol and the extract analyzed by GC-MS with no extractables found at the 10^-9 g/g level.

ACIDOLYSIS. The gases generated upon treatment of the samples with acid were swept into and separated in a Porapak Q (2.5 mm I.D. x 2 m) packed column following our previously described method. DC1 was used in order to distinguish hydrocarbons generated by reaction between the acid and the sample from hydrocarbons present as such in the sample. At the time of injection the column temperature was maintained at -50°C for 6 min. and then programmed at a rate of 8°C/min. to 150°C. These conditions proved to give a better separation of the different components evolved from the samples than did our previous work, although separation of all components was not achieved. Samples examined by this technique were solid and crushed aliquots of Apollo 11 breccia 10059, solid and crushed aliquots of Apollo 14 clastic rock 14311, Apollo 12 fines samples 12023 and Apollo 14 fines 14422. In order to distinguish between deuterated and undeuterated hydrocarbons, to resolve C2H2 from C2H6, and to resolve C3H6 from C3H8, semicontinuous mass scans were recorded to provide mass spectrometric evidence for the presence of the different species. Multiple ion plots were then constructed to improve the gas chromatographic separation as reported earlier.

The DC1 treatment released H2, N2, CO, CO2, CH4, C2H6, C3H8, C2H4, C2H6 and H2S from all samples. Incomplete GC separation precluded any quantitation of the H2, N2 and CO. CO2 ranged from about 2 ppm in sample 14311 to 50 ppm in 10059. CH4 ranged from about 0.1 ppm in 14311 to 40 ppm in 10059. Total hydrocarbons released ranged from about 1 ppm in 14311 to 55 ppm in 10059. CO2 generally correlated with total (deuterated included) hydrocarbons. The ratio of deuterated to nondeuterated hydrocarbons ranged from 2.1 in 10059 to 5.4 in 14311 and generally increased with decreasing hydrocarbon content. Evidence was obtained by multiple ion plotting for CH4, CH3D, CH2D2, CHD3 and CD4 in the methane GC peak of samples 14003 and 10059. Results of a DC1-CH4 methane exchange experiment ruled out any significant D-H exchange during the sample runs.

The deuterated hydrocarbons produced by acid treatment can be considered reaction products with active or "carbide like" carbon atoms in the lunar material while the nondeuterated species evolved should be present as such in
the sample if there is no significant D-H exchange during the times involved in the procedure. The nondeuterated species can then be truly indigenous to the sample or contamination from terrestrial exposure. The deuterated: nondeuterated ratio does not allow one to distinguish between these two sources, but the higher amounts of nondeuterated hydrocarbons found in the older, more exposed samples suggest contamination may be a factor. This ratio, along with the amounts detected, does indicate that there are substantially less hydrocarbons present as such in Apollo 14 samples than in earlier samples. The presence of the several deuterated species of methane may be interpreted as evidence for the presence of some partially hydrogenated carbon atoms which react with the DC1 to produce partially deuterated methane. Alternately the hydrogen evolving from the sample could be competing with the deuterium from the DC1 for the active sites.

VOLATILIZATION-GC-MS. The experimental procedure for GC-MS analysis of volatiles released by stepwise heating of the sample to 980°C was similar to that described in our previous analyses of Apollo 11 and 12 samples. The procedure involves the use of a quartz pyrolysis tube (4 mm I.D. x 25 cm) that can be heated to 980°C which is connected in line to a modified LKB-9000. The physical construction of the system and the gas chromatographic conditions have been improved to give a better separation of the different components evolved. Several samples (14003, 14240, 14311 crushed, and 14422) of both fines and rocks from Apollo 14 have been analyzed by this volatilization GC-MS system. Sample 14240 (SESC, fines) which should be the cleanest and driest sample provided to us was given special handling. This sample was loaded into the volatilization apparatus in a dry nitrogen cabinet at the NASA Manned Spacecraft Center, exposed to D2O vapors for 72 hours and then volatilized into the GC-MS in a way which excluded any exposure to the terrestrial atmosphere. The special handling of this sample was intended to aid in determining amounts of light hydrocarbons which may be produced by hydrolysis of indigenous material due to terrestrial atmospheric exposure. A duplicate run on 14240 was made according to this same procedure. This sample was also rerun after several exposure to atmosphere.

The volatilization-GC-MS technique provided evidence for the presence of N2, CO, CO2, CH4, C2H4, C2H6, C3H6, C3H8 and H2O (or D2O in 14240) in all samples. A duplicate run of sample 14422 under evacuated (He carrier gas pumped away between heating steps) conditions produced only about 10 percent of the amounts of all volatiles, with the exception of H2O, compared to the pressurized (He carrier gas remaining at 40 psi between heating steps) conditions used for the other runs. Methane evolved ranged from a trace in 14311 crushed to 10 ppm in 14422 and generally correlated with CO2 content. The maximum for hydrocarbon release occurred in the 500-700°C range for all samples. Sample 14422 produced nine times more total hydrocarbons compared to acidolysis while 14311 crushed produced approximately the same total hydrocarbons as did acidolysis. The total water evolved by the samples not intentionally exposed to D2O ranged from 50-150 ppm with 10-20% being released at temperatures above 700°C. CO was evolved in the 200-600°C range in several samples but the greatest portion came off in the 800-1000°C range. Sample 14240 gave unique results compared to other fines samples in that 10-100 times less vola-
tiles were released even though qualitatively the release pattern was very similar. No Cd₄ was detected up to 200°C and only a trace at higher temperatures. The second volatilization after exposure released several times larger amounts of CO₂ and H₂O at 200°C. Trace amounts of methane, ethylene, propane and propylene were released at higher temperatures but the mass spectra intensities indicated the hydrocarbons released at all temperatures were significantly lower than for the unexposed sample.

The results obtained for sample 14240 indicate that hydrolysis of active "carbide-like" substances by terrestrial water does not contribute significantly to the amounts of methane found as such in the DC1 treatment. The very low amounts of volatiles, especially methane and the other hydrocarbons, can be attributed to either true differences in the sample or the effects of exposure to the terrestrial environment. The data from the second run of the already pyrolyzed sample 14240, the general observation of increased hydrocarbons at higher temperatures, and the increased yields under pressurized conditions indicate that synthesis (such as Fischer-Tropsch type) could be an important factor in pyrolysis. The presence of CO at the lower temperatures is probably not due to reaction of indigenous minerals (e.g. Fe₂O₃ + 3C → 2Fe + 3CO) as occurs at higher temperatures and may represent a product of reaction between "active carbon" and terrestrial atmospheric components.

VOLATILIZATION-QMS. Direct quadrupole mass spectrometry of gases released by heating to 950°C has been carried out in a manner similar to that described in our previous work with the addition of controlled heating to slowly increase the temperature of the sample. Sensitivity was also increased by approximately 50 as a result of ion source modification. Samples 10086, 12023, 14003, 14156, 14311, and 14422 were analyzed by this technique.

Overall the results were similar to those obtained in our previous work. The presence of water, carbon monoxide, nitrogen, carbon dioxide and argon was confirmed in all of the samples. The temperatures of maximum evolution of the various gases was found to vary considerably from sample to sample. In some cases the release patterns for Apollo 14 samples bear a closer resemblance to samples from earlier missions than to other Apollo 14 samples. The outstanding feature of these results is the absence of hydrocarbons with the one exception of methane in sample 14003. Two samples evolved compounds which we feel represent lunar module exhaust contamination. Sample 14003, a sample of fines collected very near to the LM gave mass spectra for CH₂CO, C₃H₃, HCN, and HNCO which have been reported as lunar exhaust products. A crushed sample of rock 14311 also gave mass spectral evidence for CH₂CO and C₃H₃. Two other samples of fines collected at 50 and 1200 meters from the lunar module did not contain any detectable amounts of these compounds. Evidence was obtained which indicates most of the H₂O and CO₂ evolved is terrestrial contamination. Nitrogen ions found to be evolved in conjunction with CO at 800-1000°C perhaps indicate the rupturing of closed vesicles or traps of some type. Terrestrial N₂ is not significant at such high temperatures in exposed prepyrolyzed samples.