Volatile Molecules Produced From Carbides of Iron, Calcium, and Manganese By Laser Pulse

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Studies of the abiogenic synthesis of organic molecules have been performed by laser microprobe/mass spectrometer analyses of carbides. The laser beam interaction with a target produces a plasma plume which is used to simulate the melting and evaporation processes of planetesimal matter caused by high-speed impact (1), and also the high heats and energies associated with the early solar nebula. A plasma plume, produced by laser pulse, contains ionized species, neutral species, and free radicals which may result in the formation of recombination and polymerization biproducts. The gases collected from preselected areas of carbides are extracted and analyzed for volatiles such as O, OH, H_2O, C, C_2H_2, CO, O_2, CO_2, and hydrocarbons like CH_3, C_2H_5, C_3H_7, C_4H_9, etc.

Iron carbide (Fe_3C), calcium carbide (CaC_2), and manganese carbide (Mn_3C-Mn_5C_2) were mounted separately on aluminum disks, using torr seal (a low vapor pressure adhesive) and analyzed with the laser microprobe/mass spectrometer. Elemental abundances of H were determined by gas chromatography for the Fe_3C and Mn_3C-Mn_5C_2 samples and an elemental abundance for N in Fe_3C were determined by similar methods. This was done to determine if enough H was present in the system to account for all the hydrocarbons formed by laser interaction and to know how much N remained in the iron carbide. The values of H in μg/g (error ± 2%) for Fe_3C and Mn_3C-Mn_5C_2 are 132.2 and 1224.7, respectively and the analysis of N for Fe_3C ranged from 2.2 - 9.0 μg/g. Fe_3C was synthesized from Fe_3N and CO and produces molecules such as C, N, O, H_2O, CO (C_2H_4), CO_2 and hydrocarbons C_1 to C_8 groups when subjected to the laser pulse (Fig. 1). Because CaC_2 or Mn_3C-Mn_5C_2 are not formed by reactions with N an elemental analysis of N was not done and since CaC_2 was made from acetylene and is expected to contain plenty of H, an analysis of H was not done. CaC_2 is formed by reacting CaO and acetylene and Mn_3C-Mn_5C_2 is formed by reacting Mn and C. The gases detected from CaC_2 and Mn_3C-Mn_5C_2 after laser interaction contain molecules of C, O, H_2O, CO (C_2H_4), C_2H_2, CO_2 and hydrocarbons C_1 to C_6 from CaC_2 (Fig. 2) and C_1 to C_8 from Mn_3C-Mn_5C_2 (Fig. 3). The most prominant species produced in all analyses is m/z 28 corresponding to CO plus $H_2C{=}CH_2$ followed by a lesser abundance of hydrocarbons C_2 to C_8 and for the aromatic species m/z=78 and 91. In situ analysis of volatile elements and molecules in carbonaceous chondrites using identical techniques produced similar fragmentation patterns (2). The major volatiles are C, O, OH, H_2O, C_2H_2, CO (C_2H_4), CO_2, O_2, H_2S, COS, SO_2, CS_2, hydrocarbons ranging from C_1 to C_5, and aromatic hydrocarbons such as benzene and toluene.

The hydrocarbons produced by laser interaction with Fe_3C, CaC_2, and Mn_3C-Mn_5C_2 are most likely due to the recombination and polymerization of free radicals and ionized species found in the plasma plume. Other analyses (3) have shown that through recombination and polymerization, hydrocarbons are generated from methane at high-temperature. The major components (benzene, naphthtalene, acenaphthylene, phenanthrene, fluoranthene, and pyrene) are identified in a flow system by passing methane through silica gel at 1000°C. The results show that 97 percent of the total weight of the analyzed arenes have even number of carbon atoms and since C_2 species are more stable at high temperatures than C_1 species, the products formed will have an empirical carbon-skeleton of $(C_2)_n$. This data is analogous to the results obtained in our laser pulse experiments in that a recombination process are most likely occuring and the most abundant species are in the C_2 group (C_2H_2, C_2H_4). Polycyclic Aromatic Hydrocarbons (PAH) have been identified in the Allende meteorite probed with two-step laser desorption/laser multiphoton ionization mass spectrometry (4) and in the Murchison meteorite by gas chromatography - mass spectrometry (5). It is interesting to see that some of the fragments detected in Allende (e.g. m/z=119) are also found in the mass spectra of the three carbides. Another analysis using laser pulse was done to collect gases on various ultra-mafic rocks and meteorites and then compared to impact vaporization gases (1). The residual gas mixture desorbed from such samples are composed of CO, CO_2, H_2O, O_2, H_2, N_2, H_2S, COS, CS_2, hydrocarbons, mostly unsaturated, C_1 to C_6, HCN, and CH_3CHO. Based on these results, it was suggested that the hydrocarbons were formed inside a hot and dense vapor cloud and not by pyrolysis of organic matter already present in the sample. Furthermore, since the gas mixture contained saturated, unsaturated and aromatic hydrocarbons, and precursors of organic matter, the possibility exists for enhanced abiogenic synthesis.

Hydrocarbons desorbed from Fe_3C, CaC_2, and Mn_3C-Mn_5C_2 can participate in an abiogenic synthesis and in the presence of ammonia, dilute acid, and hydrogen cyanide are capable of forming amino acids or its precursors. Carbides treated with acid form hydrocarbons very similar to those seen during the laser interaction study. The hydrocarbons, C_1 to C_8, detected in the gas mixture produced by laser interaction with Fe_3C are similar to the hydrocarbons, C_3 to C_7, identified from the reaction of Fe_3C with deuterium labeled hydrochloric acid (DCl) (6). The hydrogenolysis of CaC_2 and Mn_3C-Mn_5C_2 with DCl is in progress and the hydrocarbons, if present, will be compared in the future to the hydrocarbons detected in gas mixtures produced by laser interaction with CaC_2 and Mn_3C-Mn_5C_2.

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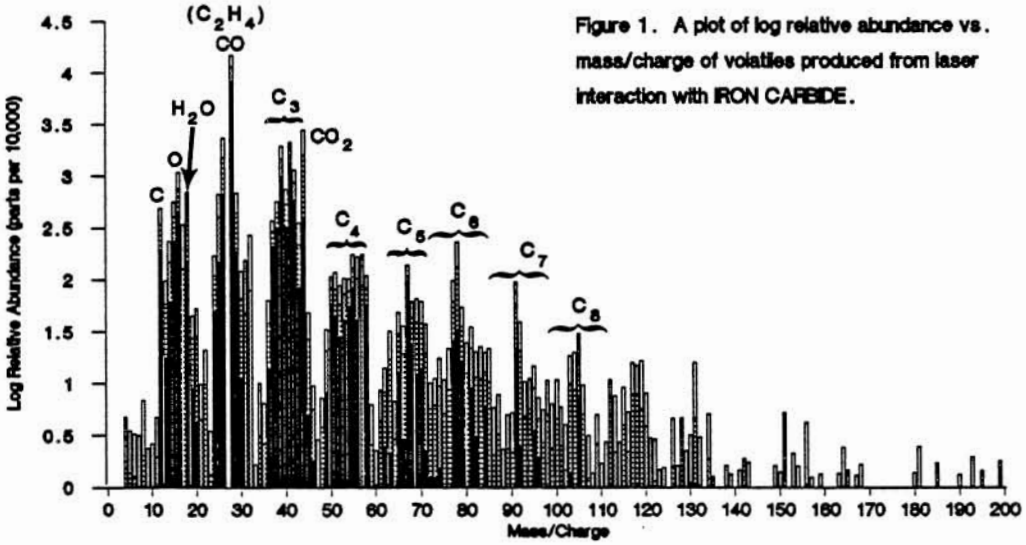

Figure 1. A plot of log relative abundance vs. mass/charge of volatiles produced from laser interaction with IRON CARBIDE.

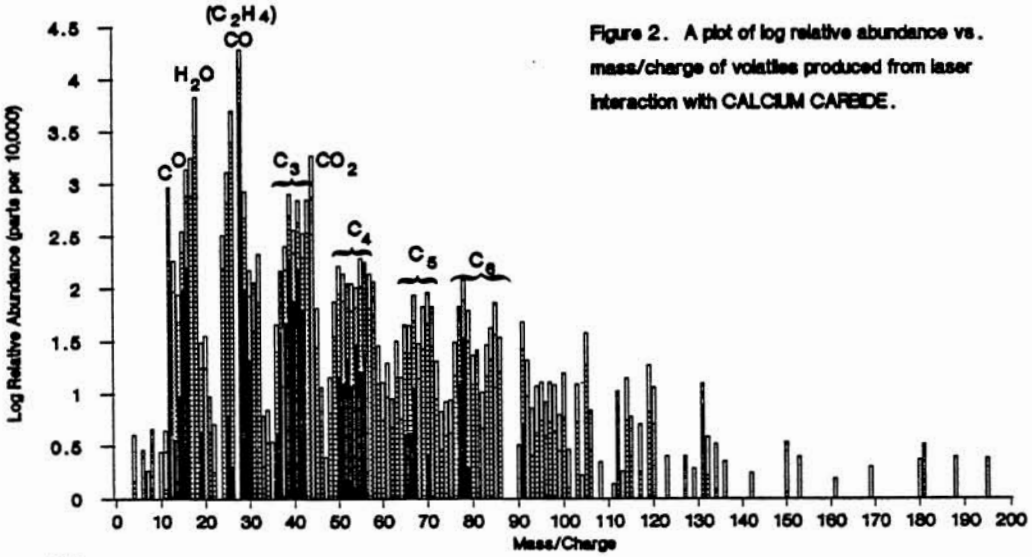

Figure 2. A plot of log relative abundance vs. mass/charge of volatiles produced from laser interaction with CALCIUM CARBIDE.

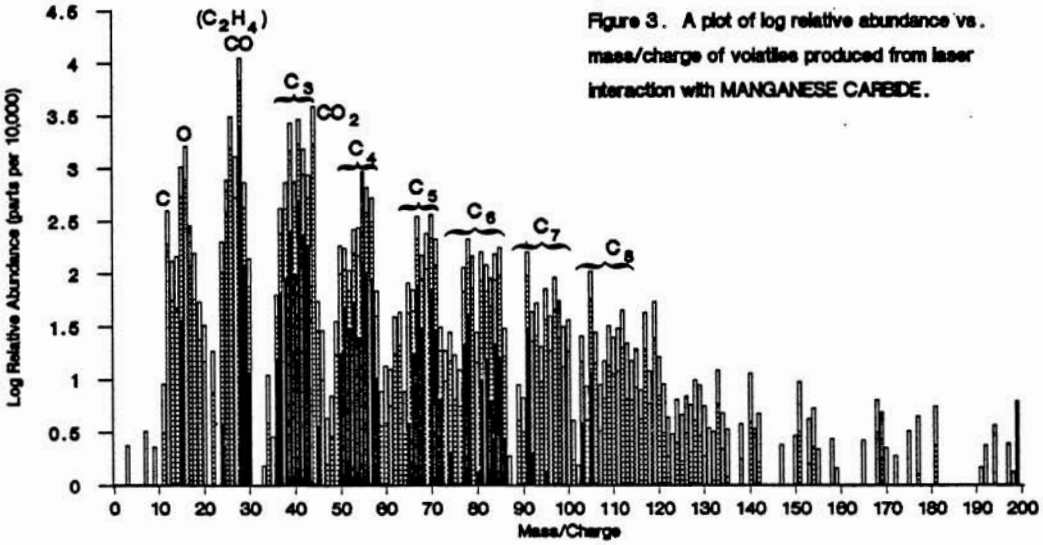

Figure 3. A plot of log relative abundance vs. mass/charge of volatiles produced from laser interaction with MANGANESE CARBIDE.