EXPERIMENTAL STUDIES ON SULFIDE, CARBIDE AND HYDROCARBON FORMATION IN IDPs.

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Introduction: Sulfides, carbides and organics found in extraterrestrial materials may provide a singular record of low-T evolution as well as information on chemical composition and physical conditions in the early solar system. A considerable amount of work has been addressed towards the identification of organic molecules in carbonaceous chondrites [1], comets [2] and interplanetary dust particles [3], but their origin is not well understood. There are various processes which may partially explain their occurrence, including gas-solid catalytic Fischer-Tropsch (FTT) reactions in the solar nebula [4, and references therein]. Recent experimental studies [5] suggest that the formation of hydrocarbons, carbonaceous deposits and carbides in IDPs takes place simultaneously in the presence of kamacite particles subjected H_2+CO mixtures under typical nebular compositional, temperature and pressure conditions. It is commonly accepted that many sulfide-metal assemblages found in carbonaceous chondrites and IDPs result from reaction between H_2S and Fe,Ni phases in the solar nebula [6]. But sulfur is generally regarded as a catalyst poison which deleteriously affects catalytic function [7], and several authors have pointed out the possibility of catalyst poisoning by sulfur in FTT reactions due to the presence of H_2S in the nebular gas [8]. We have carried out 10^3 hour experiments in order to study the interaction between nanometer-sized model kamacite particles, and different gas mixtures including of H_2:H_2S, H_2:CO and H_2:CO:H_2S under low-P,T (5×10^{-4} atm, 473 K) conditions.

Experimental results: We have observed no specific poisoning effects. In fact, the addition of small amounts (60-70 ppm) of H_2S in the reactant gas (H_2+CO, 250:1) promotes the formation of organic molecules and carbonaceous deposits, and that organic molecules other than hydrocarbons are produced. On the basis of these results, we propose that both sulfide and carbide formation were possible in the solar nebula through interaction of metal with the nebular gas, and that these processes were accompanied by the synthesis of organic molecules and non-graphitic carbon deposition on Fe,Ni metal grains. After reaction with H_2+CO, two different carbon-containing phases develop onto the kamacite particles: The outermost layer consists mainly of carbon, with trace amounts of iron and nickel. In this layer, a broad C 1s peak is recorded which can be deconvoluted into two narrow peaks at 283.1 and 286.8 eV, corresponding to carbidic carbon and organic carbon, respectively. The

associated Fe $2p_{3/2}$ and Ni $2p_{3/2}$ binding energies at 707.5 and 852.7 eV represent a slight increase of 0.2-0.3 eV relative to the corresponding binding energies of reduced iron and nickel in the kamacite particles before reaction and are in accordance with the formation of an iron-nickel carbide [5] The inner carbon-bearing layer, is free from organic carbon and exhibits Fe $2p_{3/2}$, Ni $2p_{3/2}$ and C 1s binding energies at 707.6, 852.8 and 283.2 eV, respectively, which indicate the presence of iron-nickel carbide. The carbide C/(Fe+Ni) atomic ratio found in the area free from carbon diffusion limitations is about 0.5, which indicates that under the conditions used in this work a carbide phase with a stoichiometry consistent with $(Fe,Ni)_xC$, x~2, is formed. On the other hand, a preferred segregation of nickel to the surface followed by an iron enrichment at increasing depth is found in the carbide phase. When the carbon signal is no longer detected as the sputtering proceeds, a Ni/Fe atomic ratio of pure kamacite is found as well as Fe $2p_{3/2}$ and Ni $2p_{3/2}$ binding energies at 707.2 and 852.6 eV, respectively, indicative of a complete reduced state for the metallic atoms. In the three gas mixture experiments (H_2+CO+H_2S), different depth-profile curves are obtained. First, a thick layer containing only sulfur and carbon is encountered. This layer exhibits C 1s binding energies at 283.2 and 286.6 eV and a S 2p binding energy at 162.5 eV, which are attributed to the presence of organic carbon and sulfide and carbide phases on the basis of the values reported previously for the H_2+H_2S and H_2+CO experiments. At increasing depths, broader Fe $2p_{3/2}$ and Ni $2p_{3/2}$ features are encountered, which can be deconvoluted into signals at 711.3 and 707.4 eV for Fe $2p_{3/2}$, and 854.1 and 852.7 eV for Ni $2p_{3/2}$. Binding energies at 711.3 and 854.1 are attributed to the formation of an iron-nickel sulfide, whereas the values at 707.4 and 852.7 eV are assigned to an iron-nickel carbide phase. Furthermore, C 1s binding energy at 283.4 eV and S 2p binding energy at 162.5 eV are also indicative of both carbide and sulfide phases. The Ni/Fe atomic ratio profile indicates a preferred segregation of iron towards the outer part of the iron-nickel sulfide-carbide assemblage, as observed when kamacite particles are exposed to H_2+H_2S atmosphere. Taking into account the stoichiometries for iron-nickel sulfide and carbide obtained in the experiments performed only with binary gaseous mixtures, a ratio of roughly $(Fe,Ni)S:(Fe,Ni)_2C=4:1$ can be obtained from mass balance calculations in the three-gas experiment. At-

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tenuation of both sulfur and carbon signals are simultaneous and coincidental with the shift of Fe $2p_{3/2}$ and Ni $2p_{3/2}$ peaks to 707.2 and 852.6 eV, respectively, which correspond to the unaltered kamacite alloy.

Synthesis of organic molecules and poisoning effects: Carbon incorporation into the kamacite grains in the H_2+CO and H_2+CO+H_2S experiments follows a double exponential kinetic law indicating that the carbonaceous layers deposited onto the particles tend to inhibit subsequent carbon incorporation as the reaction proceeds. Carbon deposition onto metallic particles may thus represent a possible poisoning effect on the FTT reaction under nebular conditions. This poisoning effect is less pronounced when sulfur-containing carbonaceous layers are developed (H_2+CO+H_2S experiment), where carbon incorporation from the gas phase is faster even the mean thickness of the resulting carbonaceous layer is larger with respect to sulfur-free coatings (H_2+CO experiment), 11 and 8 nm respectively. There are in fact a number of reports in the literature which indicate that the presence of trace amounts of sulfur enhances carbon deposition on metal surfaces [9]. Consequently, H_2S may indeed have a promoting effect in carbon incorporation from the gas phase into kamacite particles. The higher conversion to organic compounds together with a high chain growth probability value and higher alkene production is encountered in the experiment performed under the three gas mixture. It is concluded that at nebular concentrations sulfur had no poisoning effects on FTT reactions. Our experimental results [5, this work] demonstrate that such FTT reactions could, at least partially account for the existence of hydrocarbons in primitive bodies. On the other hand, homologous series of alkyl sulfonic acids and a few sulfur-containing heterocyclic compounds have been identified in water extracts of the Murchison meteorite [10, 11, 12]. Seven of the eight possible alkyl sulfonic acids through C_4 have been reported, and their abundances decrease with increasing carbon number as observed for hydrocarbons and other homologous series indigenous to Murchison. Methanethiol undergoes oxidation to methyl sulfonic acid in water, which is know to be the stable end product of a series of oxidation reactions. In our experiments we have obtained methanethiol and ethanethiol from the interaction between H_2+CO+H_2S gaseous mixtures and kamacite particles, and it is probable that longer reaction times could result in chain growth. We propose that the occurrence of sulfonic acids in carbonaceous chondrites may be the result of thermal hydrolysis of the corresponding thiols during aqueous alteration events. Thiols may in turn be produced by reaction between H_2, CO and H_2S over metal Fe,Ni grains in the solar neb-

ula, or incorporated directly from the interstellar medium [13].

Sulfurization of metal: It is commonly accepted that troilite (FeS) is the first sulfur-bearing phase to form by condensation in the solar nebula [e.g. 14 and references therein] and that pyrrhotite ($Fe_{1-x}S$) results from secondary processes. However, there are several reports of pyrrhotite formation as a condensation smoke [15] and during sulfurization of Fe,Ni metal [16]. Compositional gradients of sulfide grains formed in the two-gas (H_2+H_2S) and three-gas runs suggest progressive sulfurization of the kamacite particles. The outer 4 nm of the 8 nm-thick sulfide rims formed under the H_2+H_2S mixture are stoichiometric troilite, but the S content decreases sharply towards the metal-sulfide interface, suggesting that sulfurization starts in fact with the formation of pyrrhotite that converts to troilite as the gas-solid reaction progresses. The same kind of trend is observed in the three-gas mixture experiments, but here the sulfides are mixed with carbides and sandwiched between the metal substrate and an amorphous carbon layer. In this case, no troilite is formed and the maximum sulfur contents correspond to a sulfide phase with a S/(Fe+Ni) atomic ratio of 0.80. These results suggest that under low-P,T conditions and the presence of C-bearing species, pyrrhotite can in fact be a primary product of metal sulfurization in the solar nebula.

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