

Carbon Isotopic Fractionation in Fischer-Tropsch Type Reactions and Relevance to Meteorite Organics

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ABSTRACT

Fischer-Tropsch-Type (FTT) reactions have been hypothesized to contribute to the formation of organic compounds in the early solar system, but it has been difficult to identify a signature of such reactions in meteoritic organics. The work reported here examined whether temperature-dependent carbon isotopic fractionation of FTT reactions might provide such a signature. Analyses of bulk organic deposits resulting from FTT experiments show a slight trend towards lighter carbon isotopic ratios with increasing temperature. It is unlikely, however, that these carbon isotopic signatures could provide definitive provenance for organic compounds in solar system materials produced through FTT reactions, because of the small scale of the observed fractionations and the possibility that signatures from many different temperatures may be present in any specific grain.

INTRODUCTION

Stable isotope analysis can be used to determine the origins or histories of various materials. Carbon isotopic fractionation of meteoritic organic compounds may provide diagnostic information about the environments and mechanisms responsible for their formation. For example, work comparing the bulk isotopic ratios of insoluble organic matter (IOM) from over 75 carbonaceous, ordinary, and enstatite chondrites showed distinct trends with petrologic type (Alexander et al. 2007); in particular, comparisons of C, H, and N isotopic compositions showed that chondrite classes tended to form discrete groupings. Carbon and nitrogen isotopic studies of different classes of meteoritic organic matter (free, labile, or refractory) have also been used to infer aqueous and thermal alteration processes on the meteoritic parent body; both aqueous alteration in type 1 and 2 chondrites and oxidation in type 3 chondrites appear to reduce ¹³C and ¹⁵N enrichments in chondritic macromolecular material (Sephton et al. 2004). Compound-specific isotopic analysis of individual meteoritic organic compounds, such as amino and carboxylic acids, has revealed carbon isotopic ratios that correlate with compound structures and presumed formation pathways (e.g., Pizzarello et al. 2004; Huang et al. 2005; Yuen et al. 1984). These examples illustrate that the carbon isotopic ratio of meteoritic organics depend on the total pathway followed from the source carbon to the final product — a path often not readily discernible after 4.5 billion years.

One possible mechanism for forming meteoritic organic compounds in the solar nebula is through Fischer-Tropsch-type (FTT) reactions. The Fischer-Tropsch reaction is a common chemical engineering method to hydrogenate carbon monoxide via a catalytic reaction to form methane (Schulz 1999). FTT reactions can also be combined with the Haber-Bosch reaction to include hydrogenation of both carbon monoxide and nitrogen to create more complex organic

molecules (e.g., Hill and Nuth 2003). FTT reactions were first seriously addressed as a mechanism to form organics in the early solar nebula over four decades ago (e.g., Studier et al. 1968). It was suggested that a great variety of complex hydrocarbons could be generated by FTT reactions in the solar nebula because of the wide range of available catalysts (Lancet and Anders 1970). Reviews of possible mechanisms for generating meteoritic organics concluded that FTT reactions were feasible and consistent with known solar nebula conditions such as the abundance of molecular hydrogen and carbon monoxide, the presence of suitable catalysts, and the temperature and pressure ranges (e.g., Kress and Tielens 2001; Llorca and Casanova 2000; Fegley 1999). It has been difficult, however, to find evidence of FTT-produced meteoritic organics, and no conclusive signature of FTT production has been identified or detected. Several arguments have been made against FTT reactions as a primary source of meteoritic organics (e.g., Alexander et al. 2007). The straight-chain alkanes typically produced by FTT reactions are not the predominant molecules found in meteoritic material (Cronin and Pizzarello 1990; Sephton et al. 2001). Meteoritic IOM is highly aromatic, while the products of low-temperature FTT reactions are typically aliphatic; however, there is evidence for the production of aromatic material through FTT synthesis at higher temperatures (Johnson et al. 2004) or through the reheating of low temperature FTT products (Studier et al. 1972). The efficiency of FTT reactions under nebular conditions has also been questioned, with measured experimental values lower than those predicted by models (Sekine et al. 2006), although reaction rates were dependent on catalyst type and on reaction pressures. Even if FTT reactions were not the primary source of meteoritic organics, however, they still may have contributed to the inventory of organic material, and further studies are needed to examine their potential role.

FTT reactions are catalytic, and the nature of the catalyst can be an important variable in the efficiency of organic production. Many starting materials, including amorphous iron and magnesium silicates, pure silica smokes, graphite, metals, and 'natural' samples such as iron meteorite powder, have been shown to serve as suitable catalysts for FTT reactions with varying degrees of efficiency (e.g., Studier et al. 1968; Brown and Lawless 1974; Hill and Nuth 2003; Johnson et al. 2005; Nuth et al. 2010). As FTT reactions progress, an organic coating is formed on the initial catalyst surface. Rather than 'poisoning' the catalytic surface and reducing production efficiency, recent studies have instead shown that this organic coating is itself a more efficient FTT catalyst, improving efficiency of organic production as reaction time increases (Nuth et al. 2008). The organic coating consists of solvent-insoluble organic phases. Analysis of the IOM remaining after demineralization of organic-coated FTT catalysts showed similarities with the insoluble organic fractions of Murchison (Johnson et al. 2004). It has been suggested that one signature of FTT organic production in meteorites would be the association of IOM with mineral catalysts. To date, there have not been any consistent petrologic relationships found between IOM and iron-nickel catalysts or other minerals (Alexander et al. 2007). However, if such a wide range of materials can catalyze FTT reactions, and if organic macromolecular material can itself serve as a catalyst, it is possible that no such petrologic relationship would exist.

The carbon isotopic fractionation of hydrocarbons produced by FTT reactions in laboratories has been studied with varying results. A kinetic isotope fractionation that is consistent with meteoritic organics was initially observed, supporting the potential role of FTT reactions in the solar nebula (Lancet and Anders 1970). A subsequent study showed that kinetic isotope effects produce saturated hydrocarbons that are isotopically lighter than the initial CO, with no systematic carbon isotopic variation with carbon number observed (Yuen et al. 1990).

More recent work observed that for volatile hydrocarbons, such as ethane, propane, and butane, an inverse trend with carbon number is observed under kinetic conditions, with a greater $^{12}\text{C}/^{13}\text{C}$ ratio (lighter carbon) corresponding with longer chains (Hu et al. 1998). Such a trend has also been observed in low-molecular weight hydrocarbons and carboxylic acids in the Murchison meteorite (Yuen et al. 1984). However, that same analysis of Murchison revealed that the CO in the meteorite was isotopically lighter than the hydrocarbons; in a FTT synthesis, the opposite would be true (Lancet and Anders 1970). Other laboratory studies of isotopic fractionation in FTT reactions have been performed under hydrothermal conditions, relevant to geothermal systems on the early Earth but not to the solar nebula; these reactions show no clear isotopic fractionation pattern between hydrocarbons (McCollom and Seewald 2006). A review of previous work suggests that differences in isotopic fractionation of hydrocarbons may be related to initial conditions, catalytic material, degree of completion of the reaction, and type of system (open vs. closed; Taran et al. 2007).

Many of these previous measurements of FTT-produced isotopic fractionation attempted to determine whether FTT processes played a role in the formation of hydrocarbons in the early solar nebula. Although these studies specifically analyzed the volatile compounds generated by FTT for carbon fractionation, there have been almost no analyses of the heavier IOM produced, and those analyses that do exist did not focus on the solid residue (*e.g.*, Lancet and Anders 1970). In this work, we analyzed the bulk carbon isotopic ratio of the organic coating produced in laboratory FTT reactions. We investigated the role of temperature in carbon isotopic fractionation in order to determine whether a measurable and recognizable fractionation signature was produced that could serve as a tool for studying the origin of early carbonaceous materials. This work appears to be the first to systematically address FTT carbon isotope fractionation within the IOM as a function of temperature.

MATERIALS AND METHODS

Fischer-Tropsch experiments were performed at specific temperatures in a closed gas-circulating system using iron silicate grains as the catalyst. The stable carbon isotopic composition of the organic coating formed on these grains was then analyzed via isotope ratio mass spectrometry.

The experiments reported here used amorphous iron silicate grains where each grain is 20 to 50 nm in diameter. The process of producing these grains and their characterization is described in Rietmeijer et al. (1999) and in Hill and Nuth (2003). These grains are considered analogs to dust condensates formed in many astrophysical environments including the primitive solar nebula (*e.g.*, Nuth et al. 2002; Ferrante et al. 2000).

A schematic diagram of the closed gas circulating system is shown in Fig. 1. Following evacuation at room temperature, the system is filled with a standard gas composition of 75 torr of instrument grade CO, 75 torr of ultrahigh purity N_2 and 550 torr of ultrahigh purity H_2 to create an initial total pressure of 700 torr. Gas circulation is begun, and the catalyst ($\sim 25\text{cm}^3$) is brought to its working temperature. The initial heating rate depends on the intended temperature of the run. In this study, we carried out FTT reactions at temperatures of 573K, 673K, 773K, 823K, and 873K. Individual reactions proceed until $\sim 90\%$ of the CO is depleted, as determined by real-time monitoring using a Fourier transform infrared spectrometer (FTIR). The reactants are then pumped away, the system is refilled with the aforementioned standard gas mixture and another heating cycle at the same temperature is carried out while maintaining the initial solid sample in its original position. In this manner, the starting material builds up a coating of organic material

with each successive run. The time required to reach ~90% CO depletion increases with decreasing temperature, and ranges from about three days at 873K to more than a month at 573K. Between fifteen and twenty such runs are performed at each reaction temperature, resulting in coated iron silicate grains ~10% by mass carbon and 0.2% nitrogen (Gilmour et al. 2002). This number of runs strikes a balance between prohibitively long experiment times and the production of enough material for analysis.

Both the initial CO gas and the reacted grains with their organic coatings were then analyzed for carbon isotopic composition. Carbon isotopic data was measured on a Costech ECS 4010 combustion elemental analyzer (EA) connected through a Thermo ConFlo III interface to a Thermo MAT 253 isotope ratio mass spectrometer (IRMS). For measurement of the CO gas, the gas cylinder was attached to an evacuated glass manifold. Gas was introduced into the manifold from the cylinder and allowed to equilibrate for ten minutes. A gas-tight syringe was then used to sample 1 mL aliquots of the gas. These aliquots were injected into the EA through a direct injection device. The $\delta^{13}\text{C}$ value was computed by comparison with pulses of CO_2 ($\delta^{13}\text{C} = -24.23 \pm 0.02$) that had been precalibrated against commercial reference gas (Oztech Corporation). A ~1M aqueous solution of L-alanine of known isotopic composition ($\delta^{13}\text{C} = -23.33\%$, Iso-Analytical) injected in 10 μL aliquots through the direct injection device into the EA was also used for daily calibration.

To measure the isotopic values of the carbonaceous material produced in the FTT reactions, solid samples of the coated grains were weighed into tin cups, which were then sealed and placed in the zero-blank autosampler of the EA. Uncoated grains were also analyzed to determine if there was any carbon contribution from the starting materials. Samples were then introduced from the autosampler into the EA, where they were combusted to CO_2 gas, which was then separated on a gas chromatographic column before passing into the IRMS for isotopic measurement. Solid L-alanine (isotopic value described above) was weighed into separate tin cups and used as a working standard, referenced against the same laboratory reference CO_2 described above.

RESULTS AND DISCUSSION

Table 1 shows the isotopic values measured for the initial CO and the FTT products at the various temperatures. The $\delta^{13}\text{C}$ value for the CO gas (the initial source of carbon in the reaction) was $-42.4 \pm 0.3\%$; all values reported here are of triplicate measurements with their standard deviation. Measurements of uncoated grains (starting catalyst) showed that the grains did not contain any detectable carbon. The $\delta^{13}\text{C}$ values for the coated grains were temperature dependent, with lighter carbonaceous residues produced at higher temperatures and heavier residues produced at lower temperatures (Fig. 2). The largest fractionation measured ($-49.9 \pm 0.2\%$) was less than 7‰ lighter than the starting CO and occurred for the highest temperature experiments (873K). The experiment at 573K produced a residue with carbon isotopic ratio of $-42.2 \pm 1.8\%$, identical to or perhaps slightly heavier than the starting gas. The Student's t-test indicates that the differences between the 573K and 673K, and between the 673K and 773K $\delta^{13}\text{C}$ values are not statistically significant; however, the observed fractionations between 773K and 873K and over the whole temperature range (573K compared to 873K) are statistically significant.

The temperatures used for these experiments are higher than those expected in the outer solar nebula. This is necessary in order for the laboratory experiments to be carried out in a reasonable time frame; for example, experiments at 373K take about 24 weeks per cycle. In

order to produce an equivalent amount of material as in our current setup, a full experiment at 373K would require eight years to complete. Considering that actual nebular temperatures can range as low as 20K in the outer regions (see discussion in Lodders and Fegley 2011), it is clear that laboratory experiments at these lower temperatures are not practicable. However, it is reasonable to extrapolate these higher temperature experiments to the lower nebula temperatures because it is explicitly assumed that the rate-controlling step of these reactions is determined by the collision frequency of H_2 with the surface-bound CO as described by Kress and Tielens (2001). Therefore, in order to avoid effects caused by changes in total pressure or relative partial pressures of the reactants, all experiments were performed with the same starting pressure and gas mixture so that any observed changes would relate directly to temperature.

The values that we measure are noticeably different from that previously reported for carbon isotopic fractionation in FTT-produced solid residue (Lancet and Anders 1970). That previous work showed a fractionation in the “wax” residue of -33.6 ‰ relative to the initial CO. The difference in our values is most likely caused by the variations in experimental setups. The Lancet and Anders work used a semi-open system where the initial source of carbon (CO) was continuously depleted and volatile reactant products (particularly CO_2) were removed during the course of the experiment until completion. In contrast, our experimental setup is essentially a semi-closed system where the source carbon (CO) is replenished at the beginning of each cycle, *i.e.*, a series of closed experiments. The most significant difference between the experimental conditions is that in our system, the resulting carbon-bearing gases continuously circulated with the catalyst until the end of a cycle, thus allowing any potential reactions with the evolving gases to occur. As has been previously reported (Taran et al., 2007), isotopic fractionation in FTT reactions is strongly influenced by experimental factors such as the nature of the system (open vs. closed) and the degree of reaction completeness. The nature of the catalyst is not expected to alter the results of this experiment, as an organic coating quickly builds up on the sample surface catalyst and serves as the catalytic material for the majority of the experimental runs. Moreover, the oxidation states of these materials (Rietmeijer et al. 2006) are not expected to alter the results of this particular study for the same reason.

The goal of this work, however, was not to measure an absolute fractionation for FTT reactions in the solar nebula, but to determine its temperature dependence and the utility of this dependence as a reaction signature. The results of this work indicate that fractionation is only slightly affected by changes in temperature. The measured weak effect of temperature indicates that temperature does not need to be regarded as a major factor when considering isotopic fractionation during FTT reactions in the laboratory. This finding suggests that future investigations into FTT isotopic fractionation may be carried out at higher temperatures, allowing for faster work.

The small magnitude of this fractionation indicates that an isotopic signature for FTT-produced organics preserved in meteorites or other solar systems materials would be difficult to detect. Additionally, any small fractionation that is produced may not be preserved. Even if organics produced at $T < 600K$ are heavier in carbon than those produced at $T > 600K$, these organics are likely to move through different temperature regions in the solar nebula. Organic grain coatings on silicates at $T > 600K$ will oxidize to reform CO at some rate if brought to regions of significantly higher ambient temperature, potentially restarting the FTT process. “Cold” heavy organics could thus be made lighter as reactions occur closer to the sun or could be destroyed and reformed altogether in the innermost nebula. Similarly, “light” organics produced in the inner nebula could mix outward and act as the catalyst to produce heavier layers on their

surfaces. Due to the tiny magnitude of the fractionation, the wide range in possible formation temperatures within the solar nebula, and the possibility of overwriting pre-existing fractionation effects, FTT synthesis is unlikely to produce any distinctive carbon isotopic signature in bulk carbon analysis. The ultimate $^{13}\text{C}/^{12}\text{C}$ ratio depends on the relative quantity of material deposited over the full range of temperatures - essentially the organic coating's formation path through the solar nebula - and not just where an individual grain ceased accumulating organics.

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Table 1. The $\delta^{13}\text{C}$ value of the source CO and coated grains.

Material	$\delta^{13}\text{C}$ value (‰ VPDB)^a
Source CO	-42.5 ± 0.3
573 K	-42.2 ± 1.8
673 K	-45.1 ± 1.7
773 K	-47.9 ± 1.1
873 K	-49.9 ± 0.2

^aErrors are the standard deviation of three measurements.

VPDB: Vienna-PeeDee Belemnite standard

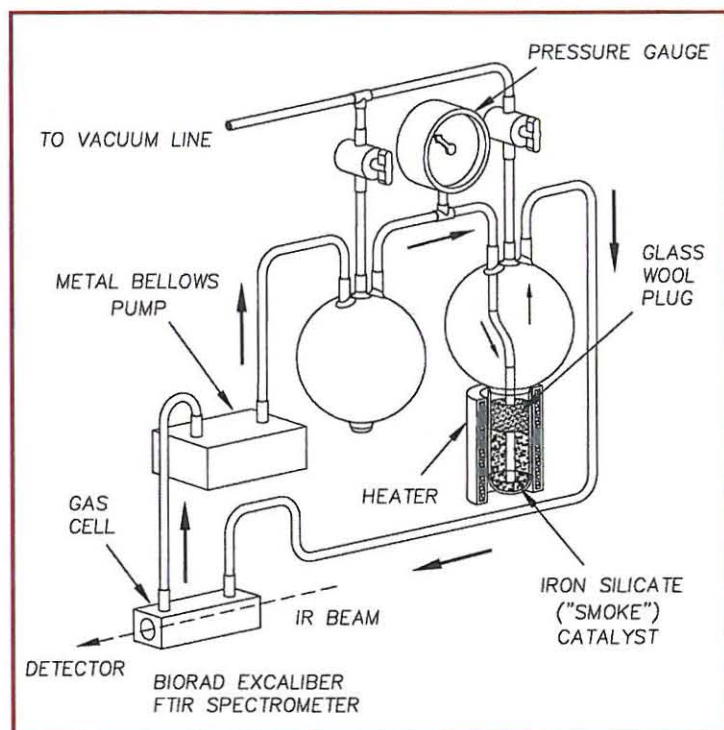


Figure 1. Schematic drawing of the closed gas-circulating system used for the Fischer-Tropsch Type reaction experiments.

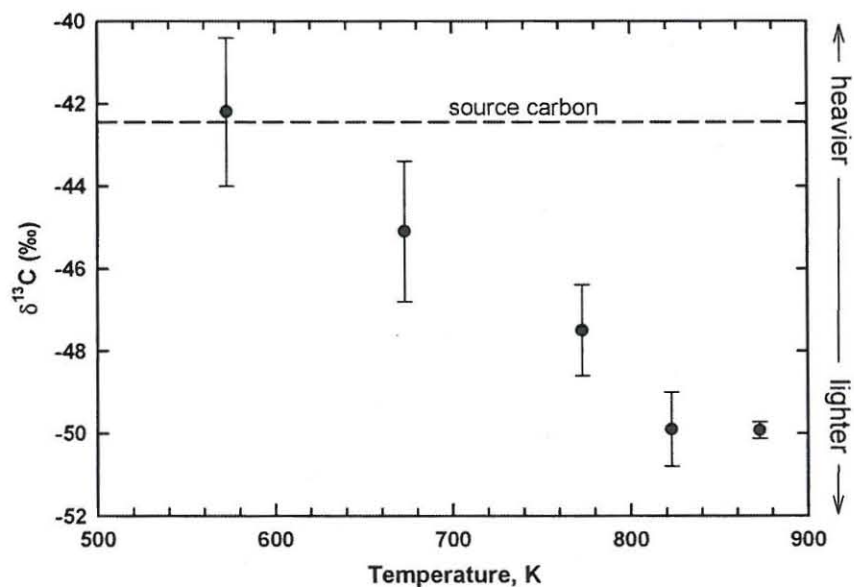


Figure 2. Stable carbon isotopic composition of the insoluble organic coating after FTT reactions at temperatures ranging from 573–873K (300–600°C) compared to the initial CO gas (dashed line). The error bars are the standard deviation of three measurements for each produced organic coating.