

CARBON ISOTOPIC FRACTIONATION DURING FORMATION OF MACROMOLECULAR ORGANIC GRAIN COATINGS VIA FTT REACTIONS. J. A. Nuth¹ N. M. Johnson¹ J. Elsila-Cook¹ and M. Kopstein^{1,2}, ¹NASA's Goddard Space Flight Center, Solar System Exploration Division, Code 690, Greenbelt MD 20771 U.S.A. (joseph.a.nuth@nasa.gov) ²Department of Biology, College of William and Mary, Williamsburg, VA 23185.

Introduction: Observations of carbon isotopic fractionation of various organic compounds found in meteorites may provide useful diagnostic information concerning the environments and mechanisms that were responsible for their formation. Unfortunately, carbon has only two stable isotopes, making interpretation of such observations quite problematic. Chemical reactions can increase or decrease the $^{13}\text{C}/^{12}\text{C}$ ratio by various amounts, but the final ratio will depend on the total reaction pathway followed from the source carbon to the final product, a path not readily discernable after 4.5 billion years.

In 1970 Libby [1] showed that the $^{13}\text{C}/^{12}\text{C}$ ratios of terrestrial and meteoritic carbon were similar by comparing carbon from the Murchison meteorite to that of terrestrial sediments. More recent studies have shown that the $^{13}\text{C}/^{12}\text{C}$ ratio of the Earth and meteorites may be considerably enriched in ^{13}C compared to the ratio observed in the solar wind [2], possibly suggesting that carbon produced via ion-molecule reactions in cold dark clouds could be an important source of terrestrial and meteoritic carbon. However, meteoritic carbon has been subjected to parent body processing that could have resulted in significant changes to the $^{13}\text{C}/^{12}\text{C}$ ratio originally present [3] while significant variation has been observed in the $^{13}\text{C}/^{12}\text{C}$ ratio of the same molecule extracted from different terrestrial sources [4]. Again we must conclude that understanding the $^{13}\text{C}/^{12}\text{C}$ ratio found in meteorites may be difficult.

Fischer-Tropsch Type (FTT) Reactions: FTT reactions are well known in the Chemical Engineering literature as the preferred mechanism to convert CO and H_2 into more complex hydrocarbons [5] and it is understood that the chain length of the hydrocarbon product increases as the reaction time increases [6,7]. In the simplest case CO reacts with H_2 to produce CH_4 and H_2O , but such reactions generally produce a mix of products under controlled conditions and the product distribution using catalytic materials likely to be found in the Solar Nebula is much wider [8]. A review of possible mechanisms to make meteoritic organics concluded that FTT reactions were consistent with all known constraints [9]. A more recent study [10] concluded that it was possible to make sufficient quantities of reduced carbon (CH_4) from nebular CO via the FTT process during infall to 3 A.U. to account for all of the organics found in meteorites. In addition, a study by Llorca and Cassanove [11] demonstrated that FTT reactions are viable even at low nebular pressures.

A recent study [12] of simultaneous FTT and the analogous Haber-Bosch reactions [$\text{N}_2 + \text{H}_2 \Rightarrow 2\text{NH}_3$] showed the production of both straight and branched alkanes, single ring and multi-ring aromatics (including some with hydrocarbon side chains), ammonia, methyl amine, methyl cyanide and N-methyl methylene imine. A followon study demonstrated that the macromolecular hydrocarbon coating that was deposited on the original catalytic material was an excellent FTT catalyst itself, and was better than most of the surfaces upon which it was deposited [13]. While one of the chief worries in the study of Kress and Tielens [10] was deactivation of the catalyst via hydrocarbon deposition, this study [13] demonstrated that deposition could actually increase the efficiency of the catalytic material.

An important difference in evaluating the potential for FTT reactions to produce a large mass of organics, compared to the assumptions of Kress and Tielens [10] is the certainty of mixing grains from the inner solar nebula outwards that was first suggested [14, 15] based on the presence of crystalline silicate minerals in comets and later confirmed by the recovery of CAI grains from the coma of comet Wild2 by the Stardust mission [16]. Kress and Tielens [10] assumed that all organics must have been made from CO during infall to ~ 3 A.U. However, if gas could circulate outward, then not only would more time be available to synthesize organic materials as they fell towards the sun, but FTT reactions themselves are much more efficient at the higher temperatures and pressures of the inner solar nebula.

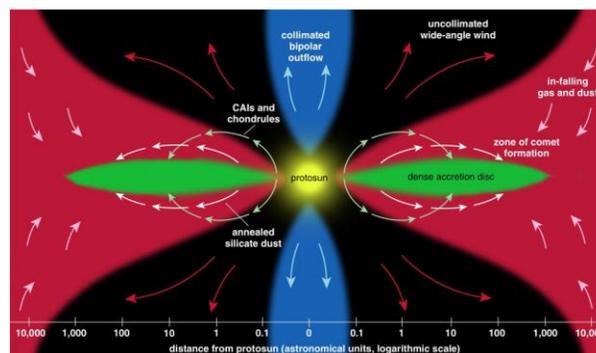


Figure 1. Circulation in the Solar Nebula will bring materials that were annealed or freshly formed in the inner nebula back out to regions where asteroids and comets accrete [17].

The wide range in temperatures over which FTT reactions could be important require understanding both the rates and changes that occur in the reaction products as a function of temperature. Reaction rates

for the loss of CO appear to double for each 100K increment in temperature. However, in this submission we report the carbon isotopic fractionation that occurs in the formation of the macromolecular carbonaceous grain coating compared to the starting composition of the CO used in the FTT synthesis.

Experimental Procedure: Experiments were done in the simple system shown in Figure 2 using 75 torr of CO, 75 torr of N₂ and 550 torr of H₂ as the standard starting composition. Individual reactions proceed until ~90% of the CO is depleted. The reactants are then pumped away, the bulb is refilled and another reaction using the same catalyst is carried out. 15 – 20 such runs are done at each reaction temperature and this results in coated iron silicate grains ~10% by mass carbon & 0.2% nitrogen. A complete description of the experiments can be found in previous publications [12, 13].

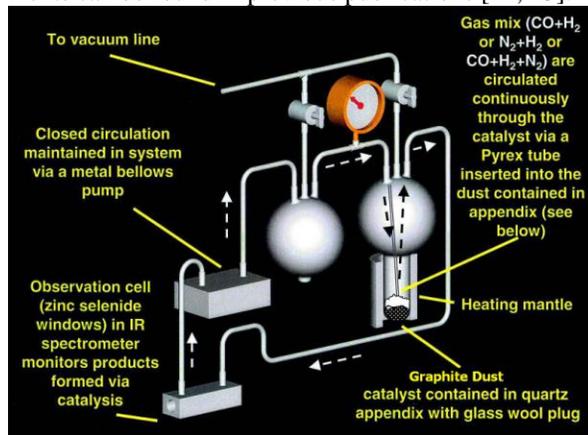


Figure 2. Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures uses infrared spectroscopy to monitor changes.

The isotopic composition of the carbon coated dust from several different experiments done over a range of temperatures was analyzed via IRMS (Isotope Resolved Mass Spectroscopy) using the procedures described in previous publications [e.g.,18] from the GSFC Astrobiology Analytical Laboratory. The results of the analysis are shown in Figure 3.

Results: All fractionation in this study is reported with respect to the composition of the starting CO gas. As can be seen in Figure 3, the fractionations measured are temperature dependent with lighter carbonaceous residues produced at higher temperatures and heavier residues produced at lower temperatures. The largest fractionation measured was less than 7 per mil lighter than the starting CO and occurred for the sample made at 873K, the highest temperature we have ever used. The experiments run at 573K may just begin to show fractionation producing residues heavier than the starting gas. If we extrapolate our data to 300K, and possibly to lower temperatures more representative of the

outer nebula, we might expect residues 5 – 10 per mil heavier than the initial CO. Is this extrapolation valid?

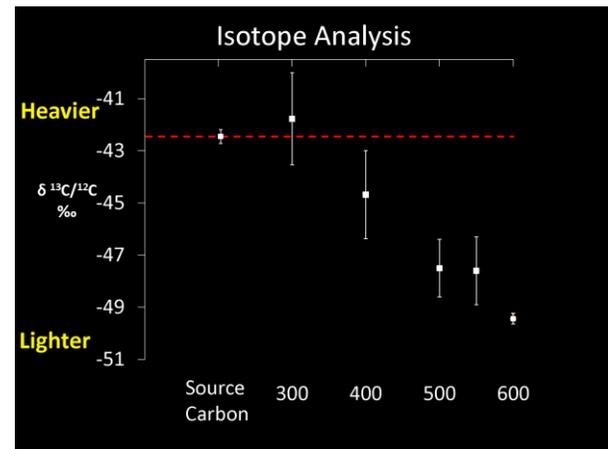


Figure 3. Carbon isotopic composition of the residue left on grains after FTT reactions at temperatures ranging from 300–600°C (573 – 873K) compared to the initial CO gas.

Even if the extrapolation is valid, the case is never going to be simply that heavy organics are produced at T<600K and light organics at T>600K because organic grain coatings on silicates at T>600K will oxidize to reform CO at some rate and potentially start the FTT process all over again. So “cold” heavy organics can be made lighter as reactions occur closer to the sun or could be destroyed and reformed altogether in the inner nebula. Similarly, “light” organics produced in the inner nebula could mix outward and act as the catalyst to produce heavier layers on their surfaces. The ultimate ¹³C/¹²C ratio would depend on the relative quantity of material deposited over the full range of temperature.

References: [1] Libby, W.F. 1971 Proc. Nat. Acad. Sci. 68, 377. [2] Hashizumi, K., Chaussidon, M., Marty, B. & Tereda, K. 2004 Ap.J. 600, 480. [3] Sephton, M.A., Verchovsky, A.B. & Wright, I.P. 2004 Astrobiology 3, 221. [4] Kim, K. & Yang, Y. 1998 J. Astron. Space Sci. 15, 1. [5] Schulz, H., *Appl. Catal. A*, **186**, 1999, 3-12. [6] Dijk, Henricus A.J. van, Ph.D. Dissertation, Technische Universiteit Eindhoven, 2001. [7] Taran, Y., Kliger, G. & Sevastyanov, V. 2006 AGU #V43D-02. [8] Lancet, M.S. & Anders, E. 1970 Sci. 170, 980. [9] Anders, E. Hayatsu, R. & Studier, M. H. 1973 Sci. 182, 781. [10] Kress, M. E., & Tielens, A. G. G. M. 2001, *Meteoritics Planet. Sci.*, 36, 75. [11] Llorca, J., & Casanova, I. 2000, *Meteoritics Planet. Sci.*, 35, 841. [12] Hill, H. G. M., & Nuth, J. A. 2003, *Astrobiology*, 3, 291. [13] Nuth, J. A., Johnson, N. M. & Manning, S., 2008 Ap.J. Lett. 673 L225. [14] Nuth, J. A. 1999, *Lunar Planet. Sci. Conf.*, 30, 1726. [15] Nuth, J. A., Hill, H. G. M., & Kletetschka, G. 2001, *Nature*, 406, 275. [16] Zolensky, M. E., et al. 2006, *Science*, 314, 1735. [17] Hill, H. G. M., Grady, C. A., Nuth, J. A., Hallenbeck, S. L., & Sitko, M. L. 2001, *Proc. Natl. Acad. Sci.*, 98, 2182. [18] Elsila, J., Glavin, D.P. & Dworkin, J.P. 2009 MAPS 44, 1323.