

 Open access • Journal Article • DOI:10.1126/SCIENCE.170.3961.980

Carbon isotope fractionation in the Fischer-tropsch synthesis and in meteorites.

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Published on: 27 Nov 1970 - Science (American Association for the Advancement of Science)

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NGL-14-001-010

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Carbon Isotope Fractionation in the
Fischer-Tropsch Synthesis and in Meteorites

N70-41098

(ACCESSION NUMBER)

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(CODE)

CR-113871

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(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

FACILITY FORM 602



Abstract. Carbon dioxide and organic compounds made by a Fischer-Tropsch reaction at 400°K show a kinetic isotope fractionation of 50 to 100 per mille, similar to that observed in carbonaceous chondrites. This supports the view that organic compounds in meteorites were produced by catalytic reactions in the solar nebula.

Most of the carbon in carbonaceous chondrites exists in reduced form: largely as an aromatic polymer and to a lesser extent as extractable organic compounds (1). A minor part (~3 to 5%) exists in oxidized form, as the carbonates breunnerite [(Mg,Fe)CO₃] and dolomite [MgCa(CO₃)₂] (2).

These two types of carbon differ greatly in their isotopic composition. The polymeric carbon is light, $\delta C^{13} = -15$ to -17 ‰ in both Type I and Type II carbonaceous chondrites (3). The carbonate carbon is much heavier: $\delta C^{13} = +60$ to $+70$ ‰ in Type I and $+40$ to $+50$ ‰ in Type II carbonaceous chondrites (3,4), for a total difference of 83 to 87 ‰ and 57 to 67 ‰. For comparison, terrestrial organic matter and carbonates (including that formed cogenetically, e.g. by shellfish) generally differ by only about 25 ‰, typical values being -25 to -30 ‰ for organic carbon and $+0$ ‰ for carbonates. The meteoritic carbonates fall well outside the range of terrestrial carbon, -80 to $+25$ ‰ (5).

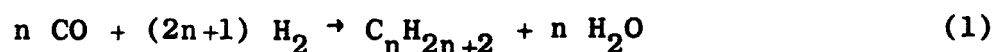
Clayton (4) has considered four possible origins of the meteoritic carbon isotope fractionation. Single-stage equilibrium fractionation can, in principle, give an effect of the right sign and magnitude. Data for organic molecules of appropriate complexity are unavailable, but if calculations for CH₄ and CO₂ (6) are used as a first-order approximation, temperatures of 265 to 335°K would seem to be required for the observed fractionations in Type I and II carbonaceous chondrites. However, no mechanisms

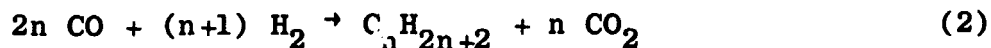
are known on earth that would establish equilibrium at the lower of these temperatures. Kinetic isotope effects are a second alternative, but in the reactions studied thus far, the fractionation was too small (20 to 40 ‰) and in the wrong direction, the oxidized carbon becoming lighter rather than heavier (7).

Biological activity produces fractionations of the right sign, but of insufficient magnitude (25 ‰). Finally, it is conceivable that the differences reflect nuclear processes, the two types of carbon having had different histories of nucleosynthesis. This alternative was favored by Urey (8). However, all work to date has failed to bring to light any isotopic differences that might be attributed to incomplete mixing in the solar nebula.

The origin of the organic compounds is of course pertinent to this problem. Studier et al. (9) have shown that nearly all compounds identified in meteorites can be produced by a Fischer-Tropsch-type reaction between CO, H₂, and NH₃ in the presence of a nickel-iron or magnetite catalyst. They proposed that the organic compounds in meteorites were made by such reactions, catalyzed by dust grains in the solar nebula.

The Fischer-Tropsch reaction produces both oxidized and reduced carbon. Much of the oxygen from CO usually ends up as H₂O (eq. 1), but a variable proportion is converted to CO₂ (eq. 2):





Nothing is known about carbon isotope fractionation in this reaction, however. We therefore decided to investigate it.

A difficulty encountered in our experiments was the tendency of any CO_2 formed to disappear by secondary reactions. [Hydrogenation of CO_2 to hydrocarbons is thermodynamically feasible (10).] We circumvented this problem by collecting CO_2 as fast as it was formed, using a $\text{Ba}(\text{OH})_2$ absorbent.

For our syntheses, we heated 0.8 l of an equimolar CO-H_2 mixture, initially at 1 atm, to $400 \pm 10^\circ \text{K}$ in a Vycor flask in the presence of 1.5 g cobalt catalyst (11). (Cobalt was chosen because it is effective at lower temperatures than iron catalysts; otherwise there is little difference between the two.) As the reaction progressed, CO_2 was removed continuously by 5 ml saturated $\text{Ba}(\text{OH})_2$ solution in a 35 ml sampling tube, connected to the reaction vessel by a side arm. The sampling tube remained at room temperature throughout the reaction. It was removed from time to time, and the gas phase separated into three fractions: CO , CH_4 , and heavier hydrocarbons (C_{2+}). Those components that remained gaseous at -196°C (CO , H_2 , and CH_4) were passed over CuO at 150°C . This converted CO to CO_2 and H_2 to H_2O , which were frozen out. The CH_4 remaining was oxidized to CO_2 by CuO at 850°C . Trial runs showed that this procedure separated CO from CH_4 with 99.1 to 99.5% efficiency.

The fraction condensed at -196°C (" C_{2+} fraction") consisted of hydrocarbons heavier than CH_4 . It was oxidized to CO_2 over CuO at 850°C . Finally, the original CO_2 fraction was recovered from the BaCO_3 - $\text{Ba}(\text{OH})_2$ suspension by adding 85% H_3PO_4 to the sampling tube. The volume of each fraction was determined on a mercury manometer.

Because of the nature of our sampling procedure, the CO_2 fraction was not quite comparable to the other three fractions. It was removed continuously from the entire reaction volume, and thus represents the incremental yield between successive samplings. The other three fractions were isolated from small aliquots of the gas phase, and thus represent cumulative yields. We cannot be sure that the CO_2 was not slightly fractionated owing to slow diffusion and incomplete absorption. However, with sampling intervals of several hours to days, the effect should be nominal. Moreover, the CO - CO_2 fractionation remained constant throughout the experiment, as sampling times increased.

Isotopic compositions were measured on a 15 cm, 60° sector double-collecting mass spectrometer (12). All results are given relative to the PDB standard. The isotopic measurement itself is usually accurate to $\pm 0.1\%$, except for samples smaller than 40 μmoles which had to be diluted with standard CO_2 before measurement.

The results reported here are based on two runs under nominally identical conditions, comprising a total of 8 fractions (Table 1). The catalyst in the second run seems to have been slightly less active, judging from the slower rate of reaction. In combining the results on a single graph, we have therefore used degree of conversion rather than time as the abscissa (Fig. 1).

A strikingly large fractionation ($\sim 100\%$) between CH_4 and CO_2 appears in the early stages of the reaction. The equilibrium fractionation at 400°K is only 45% (6), and so this is clearly a kinetic isotope effect.

As the reaction progresses, methane becomes isotopically heavier. This is due in part to material balance: as CH_4 becomes the dominant product, it must, of necessity, approach the isotopic composition of the starting material. This trend seems to be further enhanced by isotopic equilibration. The CH_4 -CO fractionation approaches the equilibrium value of 15% in the latter stages of the reaction. Apparently the CH_4 -CO exchange is fairly rapid under our experimental conditions.

The C_{2+} fraction is perhaps more pertinent to the meteorite problem, because the bulk of the reduced carbon in meteorites consists of polymeric material and molecules of 10 or more carbon atoms. This fraction remains $\sim 50\%$ lighter than the CO_2 throughout the reaction, as its amount increases from $\sim 0.5\%$ to $\sim 3\%$. Apparently its rate of exchange with CO is much slower than that of CH_4 .

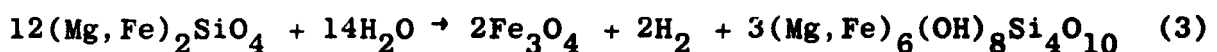
Because of the nature of our experiment, the C_{2+} fraction was not truly representative of all heavy hydrocarbons produced. Only those that were volatile at 400°K found their way into the sampling tube. Compounds of high molecular weight remained on the catalyst in the reaction vessel, and were recovered only after the end of the run. The fractionation between this "wax" fraction and CO_2 was 61% in the first run, some 10% greater than the C_{2+} - CO_2 fractionation. Unfortunately the wax fraction in the second run was too small for isotopic analysis.

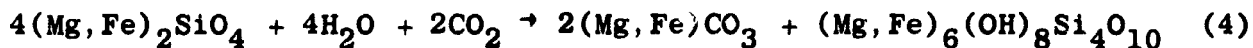
It thus appears that the Fischer-Tropsch reaction gives a carbon isotope fractionation of the same sign and magnitude as that observed in meteorites. Though our results thus strengthen the case for catalytic synthesis of the organic compounds in meteorites, they also place additional constraints on the model.

Judging from the observed fractionation between "wax" and CO_2 at 400°K , the organic compounds in Type I and II carbonaceous chondrites may have formed at $\sim 350^\circ\text{K}$ and $\sim 400^\circ\text{K}$. These values agree well with previous estimates (13), based on trace element content and the formation temperatures of certain minerals in carbonaceous chondrites (Fe_3O_4 , 400°K ; hydrated silicates, $\sim 350^\circ\text{K}$). However, in a cooling solar nebula it may be difficult to keep most of the carbon in the form of CO down to such low temperatures. Though CO is the stable form of carbon at high temperatures, it becomes unstable with respect to hydrogenation (= Fischer-Tropsch) reactions at lower temperatures. Thermodynamically, the most favored product is CH_4 , followed by ethane, benzene, and other hydrocarbons. Thus, if equilibrium were maintained, most of the CO would be converted to CH_4 before formation of heavier hydrocarbons became possible. (Their formation temperatures lie some 100° to 150° below those of methane.) At total pressures of 10^{-4} and 10^{-5} atm, only 1% of the carbon would remain in the form of CO by the time the temperature had dropped to 570°K and 520°K . Essentially no CO would be left at 400°K .

This dilemma does not seem to be insoluble. Hydrogenation of CO is known to be very slow in the absence of a suitable catalyst. The fact that carbon compounds are abundant only in meteorites containing magnetite and hydrated silicates raises the possibility that these compounds themselves were the required catalysts. Above their formation thresholds (400°K and ~350°K), lack of a catalyst may have permitted the survival of CO. In support of this suggestion, there is some evidence that the solar nebula cooled rapidly from high temperatures down to the accretion range of meteorites, and then much more gradually (14). For the ordinary chondrites, the accretion range was a 100-degree interval centered on 510_{-60}^{+80} °K (15). For the carbonaceous chondrites, this range seems to have been ~300 to ~400°K (13). No carbonaceous chondrites without magnetite are known, which suggests that accretion in the source region of carbonaceous chondrites commenced only below 400°K. Presumably the range above 400°K was traversed too rapidly for any significant accretion to take place.

Formation of hydrated silicates may also have provided the cations needed for the carbonate. These silicates, though mineralogically ill-defined (16), have a distinctly lower cation-to-silicon ratio than the olivine from which they seem to be derived (2,13). The following equation schematically represents the process:





Just as in terrestrial serpentinization reactions (17), some basic cations are left over. The excess cations can appear either as magnetite (eq. 3) or carbonate (eq. 4). Basic oxides react rapidly with CO_2 , and would thus remove it from the gas phase fast enough to prevent secondary reactions or isotopic equilibration.

Alternatively, the organic polymer in meteorites may have a formation temperature close to that of methane. Thermodynamic calculations (18) have shown that aromatic polymers may become the favored product under a variety of conditions. Moreover, an essential first step in the Fischer-Tropsch synthesis is adsorption of CO on the surface of the catalyst. At the low partial pressures of CO expected in the solar nebula (10^{-7} to 10^{-8} atm), effective adsorption may not commence until temperatures have fallen low enough to permit the formation of products other than methane.

Our experiments also provide a very tentative clue to the initial isotopic composition of the carbon in the nebula. Comparing the CO_2 -CO-wax fractionation in our experiments with the polymer-carbonate fractionation in Type II carbonaceous chondrites, we would estimate an initial carbon composition of +15‰ on the PDB scale. This is remarkably close to the isotopic composition of carbon in lunar soil (19), which is a mixture of indigenous, meteoritic, and solar-wind carbon (20).

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20. We are indebted to Prof. R. N. Clayton for the use of his mass spectrometer, and valuable criticism. Mrs. T. Mayeda kindly provided advice and assistance. This work was supported in part by NASA Grant NGL 14-001-010.

Table 1. Carbon Isotope Fractionation
in Fischer-Tropsch Synthesis

CO:H₂ = 1:1; T = 400°K; P = 1 atm; cobalt catalyst

Run	Time hr	Percent of Total*				δC^{13} (‰) [†]			
		CO	CH ₄	C ₂₊	CO ₂	CO	CH ₄	C ₂₊	CO ₂
1	7	90.2	8.2	0.5	0.05	-37.6	-81.2	-30±30	0±9
1	31	30.5	68.6	0	0.05	-46.8	-38.5	-	-8±6
1	58	15.8	80.7	1.5	0.10	-47.7	-35.1	-61±3	-11.5±3
1	320	8.1	87.9	3.3	0.68	-48.0	-35.3	-62.2	-11.1
2	4	95.6	1.9	1.5	0.05	-37.3	-100±4	-62±3	-1±5
2	15	93.8	3.5	1.7	0.05	-37.4	-94±3	-55±2	-
2	30	64.7	29.4	2.3	0.18	-33.1	-50.2	-61.2	-5.3
2	217	24.1	63.0	3.0	0.20	-47.2	-37.1	-63.1	-11.1

* Values for the first three gases were determined on a 1/20th aliquot, and reflect the composition of the gas phase at the time of sampling. Carbon dioxide, on the other hand, was removed continuously from the entire reaction mixture. The amounts given in the table are 1/20 the amount actually collected, and refer to the CO₂ formed between consecutive sampling intervals.

[†] Initial CO: -38.6 ‰. Errors are 0.1 ‰, unless otherwise indicated. A "wax" fraction was recovered from the catalyst in run 1 at the end of the reaction. It comprised 1.5% of the total carbon and had a δC^{13} of -72.2 ‰.

Figure Caption

Fig. 1. In the early stages of the reaction, CH_4 shows a fractionation as large as 100 % relative to CO_2 . Higher-molecular-weight hydrocarbons (C_{2+} , "wax") show smaller fractionations (50-60 %) which, however, persist throughout the reaction.

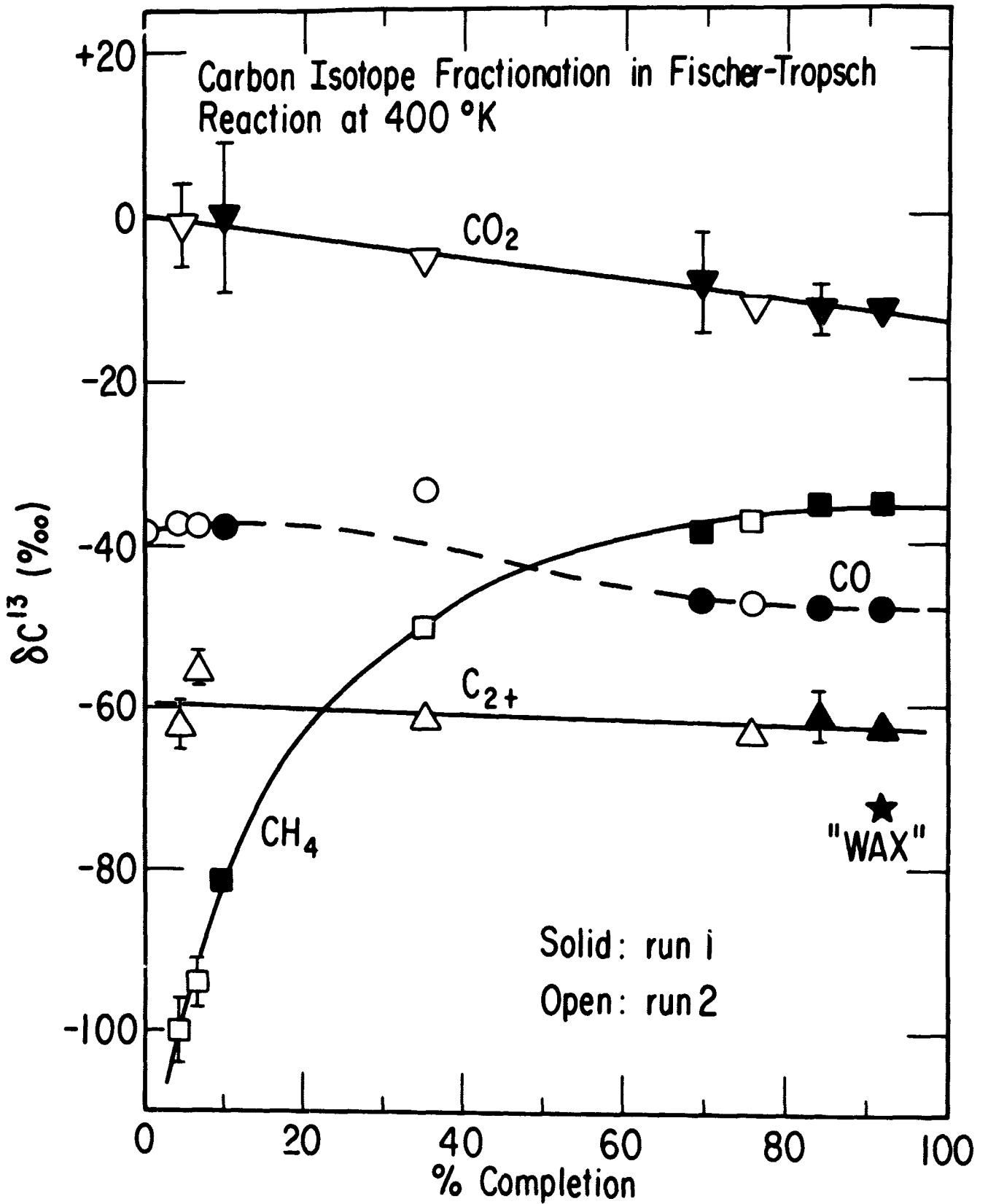


Fig.1