

WILL ORGANIC SYNTHESIS WITHIN ICY GRAINS OR ON DUST SURFACES IN THE PRIMITIVE SOLAR NEBULA COMPLETELY ERASE THE EFFECTS OF PHOTOCHEMICAL SELF SHIELDING ?

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Introduction: There are at least 3 separate photochemical self-shielding models with different degrees of commonality. All of these models rely on the selective absorption of $^{12}\text{C}^{16}\text{O}$ dissociative photons as the radiation source penetrates through the gas allowing the production of reactive ^{17}O and ^{18}O atoms within a specific volume. Each model also assumes that the undissociated C^{16}O is stable and does not participate in the chemistry of nebular dust grains. In what follows we will argue that this last, very important assumption is simply not true despite the very high energy of the CO molecular bond.

Self-Shielding Models: Stellar radiation penetrating into the natal cloud from which the solar system collapsed produces a gas enriched with ^{17}O and ^{18}O towards the interior of the cloud (1) that could be transferred into the silicates during grain processing events such as shocks. Such a model produces regions within the cloud where, on average, the oxygen isotopic composition of the dust would be distinctly heavier than the oxygen isotopic composition of the gas. In particular the model assumes that most of the heavy oxygen combines with abundant hydrogen to produce water or ice and that the CO in these regions would be significantly enriched in C^{16}O . (Note that this CO could be trapped in icy grain coatings.) If dust does not separate from gas during collapse, then this would represent the starting composition of the nebular material.

In the other two versions of the self-shielding model, the source of the C^{16}O dissociative photons is the energetic young sun. In one model (2) the radiation preferentially dissociates C^{17}O and C^{18}O at the margins of the flared nebular disk. The resulting oxygen atoms react with hydrogen to produce water or ice that must then react with dust grains following convection deeper into the nebula. As in the first model, the gas is enriched in C^{16}O that should remain with or could be trapped in coatings on the solids, barring a mechanism for dust-gas separation. In the second model (3), solar radiation penetrates directly into the disk near the midplane producing heavy oxygen atoms that could react directly with under-oxidized dust that might form via the vaporization and recondensation of refractory materials (4) in the high temperature regions near the sun. As in the previous versions, the gas is enriched in C^{16}O that is implicitly assumed to be an extremely stable long-term reservoir for ^{16}O .

Fischer-Tropsch-Type Reactions: CO is not stable in a dusty, hydrogen-rich environment such as the solar

nebula. In fact, such environments present ideal conditions for the Fischer-Tropsch type reactions that will convert CO into hydrocarbons, releasing the enriched ^{16}O back into the gas phase as water (see Figure 1).

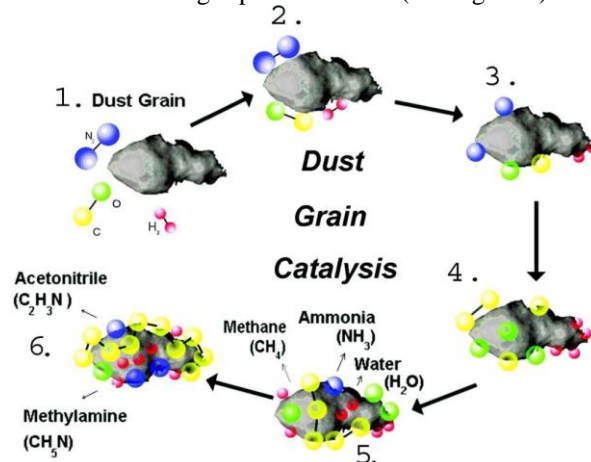


Figure 1: These reactions are often generalized as the production of hydrocarbons and nitrogen compounds but the specific “name-brand” reactions are as follows:
Fischer-Tropsch Reaction: $\text{CO} + 3\text{H}_2 (+\text{grain}) \Rightarrow \text{CH}_4 + \text{H}_2\text{O}$
Haber-Bosch Reaction: $\text{N}_2 + 3\text{H}_2 (+\text{grain}) \Rightarrow 2\text{NH}_3$

The Fischer-Tropsch mechanism has long been seen as a potential route to meteoritic organics (see, e.g.5) and such surface mediated reactions are still under active experimental investigation (6,7). A series of papers (8,9) has recently shown that **any** solid surface (not just iron grains) can promote Fischer-Tropsch Type (FTT) reactions, even graphite (10). A more interesting finding is that the FTT reactions appear to leave an organic film on the grain surface that is a more effective catalyst than the original material, thus greatly increasing the efficiency of FTT reactions in converting CO and H₂ into organics.

Organic Synthesis in Irradiated Ice: Ciesla and Sandford (11) demonstrated that the thermal and radiation environment in the outer solar system is ideal for the conversion of CO trapped in ices into complex organics. Such CO-rich ice coatings could form on the outer edge of the solar nebula and be transported outward for processing or they may have formed in the pre-collapse molecular cloud. The organics thus formed would eventually filter back into the inner nebula where the organic coated grains would be incorporated into growing planetesimals. As the planetesimals evolve due to internal heating or collisional processes, the organics will react with oxidized metals to produce CO that will be released back into the gas.

A Carbon Cycle in the Inner Nebula: From the above we can deduce that there should be a significant carbon cycle operating in the inner nebula. Organic coated grains incorporated into larger planetesimals can react with silicates after radiogenic heating to generate copious quantities of CO or CO₂ that escapes back to the nebula. Once back in the gas phase these oxides have at least two paths (FTT or irradiated ice synthesis) that can reform organics on grain surfaces to start the cycle over again. The C¹⁶O left intact by the photochemical self shielding mechanism should mix with CO generated by planetesimal evolution that is recycled back into organics via FTT or reactions in irradiated ices, greatly diminishing the effectiveness of the self shielding process in altering the isotopic composition of nebular dust.

Summary: Operation of the photochemical self shielding mechanism in CO allows the production of two distinct reservoirs. The first is the CO that is not photodissociated and which contains highly enriched C¹⁶O. The second reservoir is generally water or ice that is enriched in ¹⁷O and ¹⁸O. Even ice-coated dust grains are small enough that they remain with the gas, thus ensuring that the two reservoirs remain intimately mixed as they fall into the nebula where an unspecified series of chemical reactions might occur to incorporate the ¹⁷O and ¹⁸O into the dust. During these reactions, the C¹⁶O is generally assumed to remain unreactive in the gas phase.

Unfortunately, CO will not remain unreactive in the gas phase in the presence of dust, and will not remain unreactive even when buried in ice subject to cosmic radiation processing in the outer nebula. In both cases the CO is converted to hydrocarbons plus water, thus returning the ¹⁶O back to the gas phase to react with the dust in exactly the same form as the heavier ¹⁷O and ¹⁸O produced earlier by photochemical self shielding. While the conversion of CO into organics might erase all traces of the oxygen isotopic fractionation caused by photochemical self shielding, the devil is indeed in the details. While there is little doubt that the CO will be cycled into organics plus water, the question comes down to the potential separation of dust from gas in the solar nebula. Separation of dust from gas will mean the existence of heavy oxygen rich volumes in dust rich zones, together with volumes rich in ¹⁶O where organic molecules are forming, whether via FTT processes or as the result of radiation processing in ice.

The remaining question is the relative size of the isotopically fractionated reservoir of CO compared to the size of the unfractionated reservoir participating in the larger carbon cycle. It has been hypothesized that all interstellar dust has an organic coating, yet only some meteorites contain as much as a few percent carbon. This implies the loss of carbon – probably as CO

or CO₂ – from planetesimals following the accretion of such grains during heating events.

Did the CO generated from heated planetesimals constitute a larger or smaller reservoir of CO than the CO that participated in photochemical self shielding at any given time? By how much would the isotopic effects of converting C¹⁶O into organics and water be diluted by the presence of normal planetesimal CO? Does any trace of C¹⁶O generated via photochemical self shielding survive in the inner solar nebula? These questions must be addressed quantitatively before we can estimate the effect of photochemical self shielding on the oxygen isotopic composition of dust in the primitive solar nebula.

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