CO IS CHEMICALLY ACTIVE IN THE SOLAR NEBULA: CO SELF-SHIELDING IS INVALID. J. A. Nuth[1], N. M. Johnson[2] and F. T. Ferguson[2,3]. [1]Solar System Exploration Division, Code 690 NASA-GSFC, Greenbelt MD 20771 USA (joseph.s.nuth@nasa.gov) [2]Astrochemistry Branch, Code 691 NASA-GSFC, Greenbelt MD 20771 [3]Chemistry Department, The Catholic University of America, Washington DC 20064.

Introduction: Oxygen comprises nearly one third of all solids in the solar system including planets, moons, asteroids and comets, yet this gigantic chemical reservoir is non-mass-dependently fractionated [1]. For three decades the meteoritics community believed that this was due to a primordial difference between nebular components that resulted in at least two separate reservoirs that underwent mixing in the solar nebula [2]. Mixing between such reservoirs would naturally yield oxygen distributed along a slope 1 line when the oxygen content of products were plotted as a ratio of $^{17}O/^{16}O$ vs. $^{18}O/^{16}O$. The Reservoir Mixing Model was suddenly replaced in 2002 by the CO Self Shielding Model [3] first proposed nearly two decades earlier [4].

In the Self Shielding model, photolytic destruction of CO depletes the supply of photons that activate $C^{16}O$ while photons capable of cleaving the less abundant $C^{17}O$ and $C^{18}O$ bonds penetrate deeper into the gas and create a region rich in $C^{16}O$ molecules plus atomic ^{17}O and ^{18}O. While the atomic ^{17}O and ^{18}O react to form isotopically heavy solids, the $C^{16}O$ must remain inactive or the isotopic selection effect will be erased. Three separate flavors of the CO Self Shielding Model exist depending on the region where the isotopically selective photolysis of CO is hypothesized to occur: the inner nebula [2], the outer nebula [5] or the presolar cloud from which the nebula was born [6,7]. Yet each of these models depends on the long term stability of $C^{16}O$ and with a bond energy of 13 eV, CO is a very stable gas-phase molecule.

Surface-Mediated CO Reactions: For many years our group has worked to understand the chemical reaction rates and products of surface mediated reactions in the solar nebula [8,9,10]. We have found that, while gas-phase CO is thermodynamically stable, especially at high temperatures (> 750K), that it is also very reactive (see Figure 1). This very high reactivity at temperatures up to ~1000K will lead to rapid O isotopic exchange in the inner solar nebula. Photolytically-produced, and mass-independently-fractionated $C^{16}O$-rich reservoirs will cycle among many different carbonaceous species before they are oxidized back to CO. This will thoroughly erase the effects produced by self shielding in the hot inner solar nebula.

Examining Figure 1 we can identify three separate reaction regimes leading to the destruction of CO. At the lowest temperatures at least two reactions contribute to CO loss: surface-mediated reactions that produce hydrocarbons (e.g., Fischer-Tropsch Type reactions) and "metal dusting" reactions that produce various solid metal carbides plus CO_2. At the conditions used in our experiments CO becomes more stable than CH4 at about 675C; this crossover temperature will decrease at the lower pressures in the solar nebula. In Figure 2 we have overlain our CO rate loss mesurements with data on the rate of metal dusting [11] in a mixture of 50% H_2 and 50% CO. While the absolute rates of these reactions will be dependent on pressure, the relative rates are not.

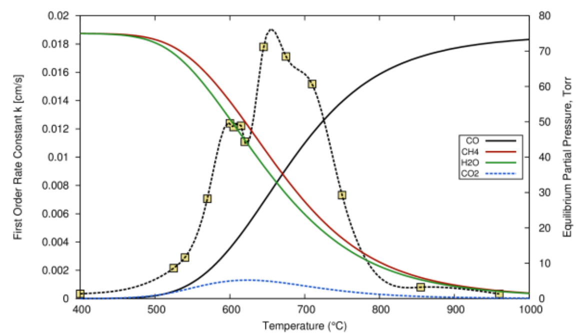

Figure 1. ***CO loss rate (yellow squares) is compared to the equilibrium fraction of CO (black line), CH_4 (red), H_2O (green) & CO_2 (blue) in the same gas mixture as a function of temperature.***

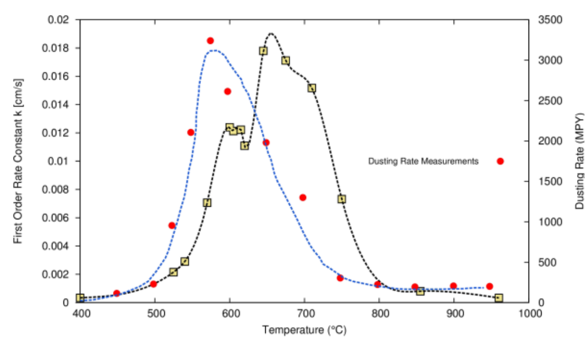

Figure 2. ***CO loss rate compared to the rate of "metal dusting" reactions producing metal carbides plus CO_2 [11].***

At the highest temperatures seen in Figure 1 the rate of CO loss has decreased significantly. However, experiments carried out at temperatures up to 1890K under ionizing conditions have demonstrated that carbonaceous solids, including both single-layer and bi-layer graphine, form on alumina substrates [12]. We note that graphene whiskers have been detected in both CAIs and chondrules in a variety of carbonaceous meteorites [13], demonstrating the applicability of such experiments to conditions in the solar nebula.

Low-Temperature Reactivity of CO: At low temperatures CO is trapped in amorphous water ice and can then spend condiderable time exposed to cosmic rays [14, 15], ultraviolet light [16] or highly reactive atomic hydrogen [17]. These types of cryogenic reactions have been studied for decades as sources for the variety of complex organic molecules found in molecular clouds, comets and meteorites. This general process is illustrated in Figure 3.

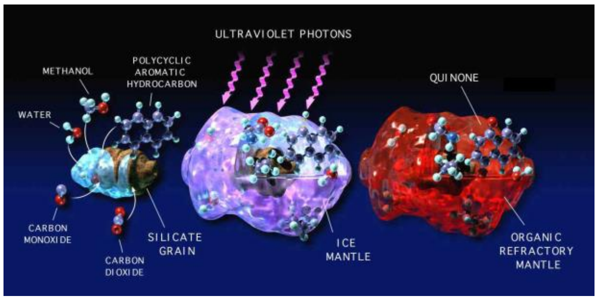

Figure 3. ***Exposure of ice mantles to cosmic rays breaks CO bonds and converts CO into more complex organics that might retain ^{16}O or might exchange it.***

Mixing in the Solar Nebula: Even if we were to assume that CO Self Shielding produces ^{17}O & ^{18}O (that is eventually converted to heavy water ice) together with an excess of $C^{16}O$ in the giant molecular cloud [6, 7] in the inner solar system [3] and/or in the outer solar system [5], we know that strong mixing transports crystalline minerals great distances in the nebula [18, 19]. This was unequivolally demonstrated by analyses of refractory grains returned by the Stardust mission [20] where it was shown that Kuiper-Belt comet (Wild 2) contained CAI fragments that must have been produced in the innermost solar nebula. Strong mixing should transport both dust and gas.

From the Genesis Mission we know that the Sun is ^{16}O-rich [21], yet most solid objects in the solar system are ^{16}O-poor [3]. It has been suggested that the isotopic structure of the nebula was set once Jupiter reached a mass sufficient to isolate the inner from the outer solar system a few hundred thousand years after CAI formation [22]. This implies that the strong mixing observed in Stardust grains must have occurred very early in solar system history and well before the formation of Jupiter's core: A time when the Sun was still accreting disk materials at a significant rate. At such a time, gas and dust from the molecular cloud flows through the outer nebula towards the Sun. Excess $C^{16}O$ produced in the molecular cloud or the outer nebula will be mixed inward to react on grain surfaces, releasing the ^{16}O into the system. Excess $C^{16}O$ produced in the inner nebula will also react on grain surfaces to release the ^{16}O, even at very high temperatures [12].

Summary: CO Self Shielding Models universally rely on the stability of the CO molecule to preserve the excess $C^{16}O$ produced by these models and separate it from the ^{17}O & ^{18}O that is the ultimate source that produces heavy refractory compounds. Unfortunately, while CO has one of the strongest known chemical bonds and is thermodynamically favored at high temperatures under nebular conditions, the CO molecule is very reactive on grain surfaces or in ice mantles. A wide range of Surface Mediated Reactions are therefore available to destroy any excess $C^{16}O$, anywhere in the nebula, releasing the ^{16}O back into the nebular chemical reaction network and negating the isotopically selective reactions that may have initially produced a heavy oxygen excess. Very simple models that do not account for the wealth and variety of chemical reactions that could occur in the solar nebula may "work". However, as originally shown by Navon and Wasserburg [23], once a more complicated chemical system that better represents the natural environment is used, the effect of self shielding disappears into the noise.

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