

Article

## CO Self-Shielding as a Mechanism to Make $^{16}\text{O}$ -Enriched Solids in the Solar Nebula

Joseph A. Nuth, III <sup>1,\*</sup>, Natasha M. Johnson <sup>2</sup> and Hugh G. M. Hill <sup>3</sup>

<sup>1</sup> Solar System Exploration Division, NASA's Goddard Space Flight Center, Greenbelt, MD 20771, USA

<sup>2</sup> Astrochemistry Laboratory, NASA's Goddard Space Flight Center, Greenbelt, MD 20771, USA; E-Mail: natasha.m.johnson@nasa.gov

<sup>3</sup> International Space University, Strasbourg Central Campus, 1 Rue Jean-Dominique Cassini, 67400 Illkirch-Graffenstaden, France; E-Mail: hugh.hill@isunet.edu

\* Author to whom correspondence should be addressed; E-Mail: joseph.a.nuth@nasa.gov; Tel.: +1-301-286-9467; Fax: +1-301-286-1683.

Received: 1 April 2014; in revised form: 8 May 2014 / Accepted: 13 May 2014 /

Published: 21 May 2014

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**Abstract:** Photochemical self-shielding of CO has been proposed as a mechanism to produce solids observed in the modern,  $^{16}\text{O}$ -depleted solar system. This is distinct from the relatively  $^{16}\text{O}$ -enriched composition of the solar nebula, as demonstrated by the oxygen isotopic composition of the contemporary sun. While supporting the idea that self-shielding can produce local enhancements in  $^{16}\text{O}$ -depleted solids, we argue that complementary enhancements of  $^{16}\text{O}$ -enriched solids can also be produced via  $\text{C}^{16}\text{O}$ -based, Fischer-Tropsch type (FTT) catalytic processes that could produce much of the carbonaceous feedstock incorporated into accreting planetesimals. Local enhancements could explain observed  $^{16}\text{O}$  enrichment in calcium-aluminum-rich inclusions (CAIs), such as those from the meteorite, Isheyevo (CH/CHb), as well as in chondrules from the meteorite, Acfer 214 (CH3). CO self-shielding results in an overall increase in the  $^{17}\text{O}$  and  $^{18}\text{O}$  content of nebular solids only to the extent that there is a net loss of  $\text{C}^{16}\text{O}$  from the solar nebula. In contrast, if  $\text{C}^{16}\text{O}$  reacts in the nebula to produce organics and water then the net effect of the self-shielding process will be negligible for the average oxygen isotopic content of nebular solids and other mechanisms must be sought to produce the observed dichotomy between oxygen in the Sun and that in meteorites and the terrestrial planets. This illustrates that the formation and metamorphism of rocks and organics need to be considered in tandem rather than as isolated reaction networks.

**Keywords:** Fischer-Tropsch reaction; oxygen isotopic fractionation; nebular chemistry; protostellar nebulae; primitive solar nebula

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## 1. Introduction

Oxygen in minerals found in chondrules and calcium-aluminum-rich inclusions (CAIs) displays a remarkable range in isotopic composition: from rare material that is enriched in  $^{16}\text{O}$  by a few percent [1] to grains well above the terrestrial fractionation line [2]. The original problem after discovery [3] was not only to find a process to distribute oxygen isotopes along a “slope 1” line, but also to find a mechanism that simultaneously increased the  $^{16}\text{O}$  concentration of the dust. This assumed that the oxygen isotopic composition of the Earth, Mars, and most meteorites was representative of the composition of the dust in the protosolar nebula. However, the oxygen isotopic composition of the Sun, as measured by the Genesis mission [4], is considerably enriched in  $^{16}\text{O}$  relative to the composition of Standard Mean Ocean Water (SMOW), a proxy for the oxygen isotopic composition of the Earth. The general consensus is that, as the Sun represents the largest oxygen reservoir in the solar system, then it must also represent the average isotopic composition of the dust and gas in the solar nebula. The problem has therefore been stood on its head and has become one of producing  $^{16}\text{O}$ -depleted oxygen isotopic minerals starting from solar composition [5–8]. Intriguingly, there are some meteoritic materials that are even more enriched in  $^{16}\text{O}$  than the Sun [9–11]. We will show that a combination of CO self-shielding and Fischer-Tropsch type (FTT) organic synthesis reactions could explain such extreme observations.

Before proceeding however, we must take time to explain the nomenclature of oxygen isotopic measurements found in the literature. Oxygen naturally fractionates during chemical reactions along the Terrestrial Fractionation (TF) line, a line of slope 0.52 in a plot of  $^{17}\text{O}/^{16}\text{O}$  versus  $^{18}\text{O}/^{16}\text{O}$  as shown in Figure 1. To anchor this line, the composition of oxygen contained in SMOW is defined as the origin (0.0). Deviations from SMOW along the TF line are due to chemical partitioning of oxygen isotopes during chemical reactions, and can be predicted based on chemical thermodynamics. Deviations from SMOW that do not lie on the TF line were once considered to be possible only as the result of the addition of oxygen from an extra-solar source, such as the addition of pure  $^{16}\text{O}$  from a supernova.

There are thus two different ways to express differences from SMOW. One can simply report the deviation from SMOW in terms of the absolute ratios of ( $^{17}\text{O}/^{16}\text{O}$ ,  $^{18}\text{O}/^{16}\text{O}$ ) reported as ( $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ). The problem with this method is that since normal chemical reactions produce isotopic fractionation, there will always be a range of ( $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ) values for any natural sample and it will not be obvious which samples might contain admixtures of extra-solar materials. The solution to this dilemma is to report oxygen isotopic compositions as  $\Delta^{17}\text{O}$ ; this is the deviation of the sample from the TF line in units of  $\delta^{17}\text{O}$  at the sample's  $\delta^{18}\text{O}$  coordinate. Any terrestrial sample will therefore have a  $\Delta^{17}\text{O}$  value of 0 anywhere along the TF line. Meteoritic samples and samples of other planetary bodies were expected to have slightly different  $\Delta^{17}\text{O}$  values depending on the chemical partitioning of the constituents from which they formed and this is seen in the data shown in Figure 1. In this paper we

will generally use the ( $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ) notation, though we will occasionally refer to the  $\Delta^{17}\text{O}$  values if necessary to avoid misunderstandings.

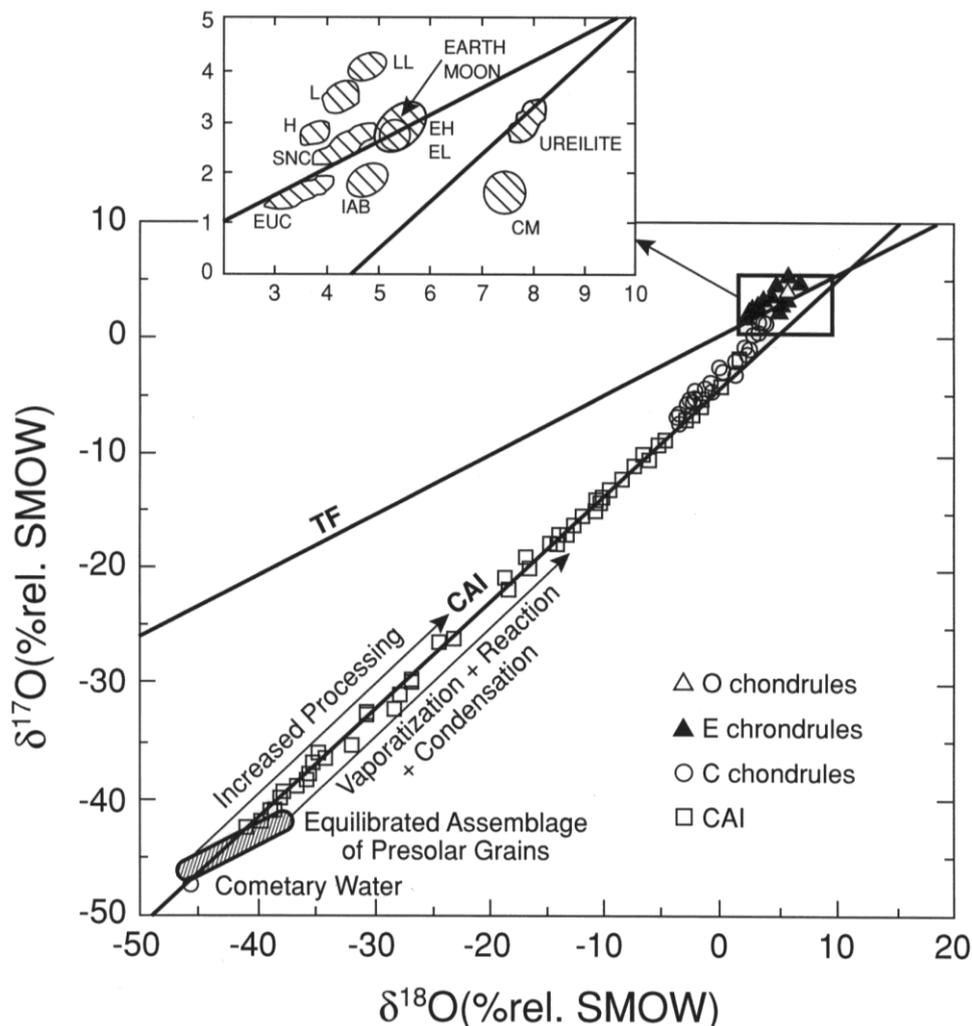
In FTT reactions, CO reacts with hydrogen on grain surfaces to produce methane and water in the idealized case. In reality, the products produced in the solar nebula will include water and a host of organic molecules [12–14]. We have previously argued [15] that FTT reactions could seriously decrease the efficiency of the CO self-shielding mechanism for the production of  $^{16}\text{O}$ -depleted solids in the solar nebula. Specifically, if the isotopically-heavy water and  $^{16}\text{O}$ -rich CO do not separate completely and the CO undergoes FTT reactions that release  $^{16}\text{O}$ -rich water back into the system, then the effects of the self-shielding reactions will be diminished. If separation occurs, then isotopically-heavy water can react to produce  $^{16}\text{O}$ -depleted silicates. However, the converse can also occur when  $^{16}\text{O}$ -rich CO is separated from the heavier water and is not lost from the nebula, but instead undergoes FTT reactions that release  $^{16}\text{O}$ -rich water into the nebula.

For nearly three decades following discovery of the mass independent fractionation of oxygen in solids from the early history of the solar system, the Reservoir Mixing Model [2] dominated alternative explanations for this phenomenon. This model assumed that nearly pure  $^{16}\text{O}$ -rich solids, derived from a nearby supernova, seeded the early nebula and formed a mixing line with “normal” nebular solids. The model predicted the existence of extremely  $^{16}\text{O}$ -enriched presolar grains, possibly corundum ( $\text{Al}_2\text{O}_3$ ) or hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ) dust synthesized in the supernova that had survived processing in the nebula. While many other presolar grains have been observed in meteorites [16],  $^{16}\text{O}$ -rich presolar grains are rare and are not present in sufficient numbers to validate this prediction.

As an alternative to the Reservoir Mixing Model, and still under the prevailing assumption that an oxygen isotopic composition near that of Standard Mean Ocean Water (SMOW) constituted the average composition of nebular materials, Marcus [17] proposed a quantum chemical model for the condensation of solids with mass-independent oxygen isotopic fractionation that drove solids to more  $^{16}\text{O}$ -rich compositions while the surrounding gas became depleted in  $^{16}\text{O}$ . To date, this is the only published mechanism for processing solids which results in a more  $^{16}\text{O}$ -rich solid end product. The modern versions of the Chemical Self-Shielding Model [5–8] all result in  $^{16}\text{O}$ -depleted solids compared to the starting compositions in keeping with the assumed necessity of going from a solar oxygen isotopic composition [4] near  $(-40, -40)$  up to SMOW, defined to be at  $(0,0)$ .

However, the oxygen isotopic composition of the sun is not an end-member on the mixing line that runs from SMOW through the anomalous CAI and chondrule compositions towards the pure  $^{16}\text{O}$ -rich solid compositions once predicted by the Reservoir Mixing Model. In fact, there are CAIs from the meteorite Isheyevo (CH/CBb) [11], as well as chondrules from the meteorite Acfer 214 (CH3) [9], that plot nearly as far below the sun (at  $-70, -70$ ) as SMOW is above the solar oxygen isotopic composition (Note that in  $\Delta^{17}\text{O}$  notation the composition of the sun is at  $-28$  per mil while Acfer and Isheyevo are at  $-34$ ). These meteoritic components are much too large to represent the average composition of an early population of nebular dust [18] injected by a nearby supernova. Furthermore, if nebular solids gradually migrated towards more  $^{16}\text{O}$ -depleted compositions with time, then these solids must have been produced very early in nebular history in order to buck the prevailing trend towards  $^{16}\text{O}$ -depletion. Are these the  $^{16}\text{O}$ -enriched condensates that were predicted by Marcus [17]?

**Figure 1.** A typical three-isotope plot of oxygen isotopes in calcium-aluminum-rich inclusions (CAIs) and chondrules, and in various meteorite types (note that the label “O chondrules” refers to chondrules from ordinary chondrites, “E chondrules” from enstatite chondrites, “C chondrules” from carbonaceous chondrites and TF is the Terrestrial Fractionation line). The CAI line delineates the evolution of oxygen in solids either by evaporation + exchange + recondensation or by photodissociation. Any mineral phase on the CAI line can react and fractionate along slope 0.52 lines to broaden the CAI line. Finally, if the oxygen isotopic composition of the gas and dust were originally the same, then cometary water (representing the nebular gas) would evolve to more negative values as processing proceeded to increase the dust in  $^{17}\text{O}$  and  $^{18}\text{O}$ . However, since there is 20–30 times more gas than dust, the effect on the isotopic composition of the gas is much less dramatic than on the composition of the solids.



## 2. Interactions between Organic Synthesis and Oxygen Isotopic Fractionation

Most modelers assume that the  $^{17}\text{O}$  and  $^{18}\text{O}$  isotopes freed by CO self-shielding are incorporated into ice grains, but that the left over  $\text{C}^{16}\text{O}$  remains in the gas phase until it is lost from the nebula or the protosolar cloud from which it collapsed. To preserve the full effect of this fractionation process, the icy grains must become completely separated from the  $\text{C}^{16}\text{O}$  gas or the  $\text{C}^{16}\text{O}$  must remain forever inert.

Unfortunately, nebular CO is far from inert. Both Fischer-Tropsch type reactions [13] as well as radiation-induced icy grain chemistry [19] can convert CO into organic materials, freeing  $^{16}\text{O}$  back into the nebula, typically as water. This leads to three possible long-term outcomes for the CO self-shielding models depending upon the degree of separation of the  $^{16}\text{O}$ -rich CO and  $^{16}\text{O}$ -depleted water produced in the model.

In Scenario 1, the CO remains inert and is eventually lost from the nebula. In Scenario 2, the CO remains with the water as it descends to higher temperature environments and reacts with silicates, while those silicates act as catalysts for the FTT process and release water from the CO. In Scenario 3,  $^{16}\text{O}$ -depleted water separates from  $^{16}\text{O}$ -enriched CO, but both remain in the nebula and participate in subsequent chemical reactions, though in different, localized, nebular regions. Scenario 1 is the typical self-shielding model producing  $^{16}\text{O}$ -depleted water that is eventually transferred into increasingly  $^{16}\text{O}$ -depleted nebular solids. Scenario 2 is the antithesis of Scenario 1, as nebular chemistry converts the  $^{16}\text{O}$ -rich CO into organics releasing the  $^{16}\text{O}$  back into the nebula as water and largely cancels the effects of the self-shielding process. Scenario 3 has an interesting and complicated outcome depending on whether it is examined on a local scale or on a global scale.

On a global scale, the outcome for the average oxygen isotopic composition of nebular dust in Scenario 3 is exactly the same as for Scenario 2: there is no net effect on the average oxygen isotopic composition of nebular dust. The  $^{16}\text{O}$ -depleted water reacts to form  $^{16}\text{O}$ -depleted dust in one region while the  $^{16}\text{O}$ -rich CO reacts via FTT processes or radiation-induced chemistry within icy grains to form  $^{16}\text{O}$ -enriched solids. The net global average oxygen isotopic composition of nebular dust remains unchanged as, proportionally, just as much  $^{16}\text{O}$ -rich water was released from the CO via FTT or other processes as was required to compensate for the  $^{16}\text{O}$ -depleted water produced via self-shielding earlier. Of course, there is an entire spectrum of possibilities between Scenarios 1 and 2, depending on the degree to which  $\text{C}^{16}\text{O}$  is actually lost from the nebula (or incorporated into organic compounds) rather than just spatially separated from the  $^{16}\text{O}$ -depleted water produced via the self-shielding process.

On a local scale, the results can be much more varied. FTT-produced,  $^{16}\text{O}$ -enriched water could react during either the CAI or chondrule formation process to produce CAIs or chondrules that are more  $^{16}\text{O}$ -rich than the average dust composition at that time in the nebula. If this occurs late in nebular history, after the oxygen isotopic composition of the dust has become more  $^{16}\text{O}$ -depleted than the sun, it will be difficult to tell such CAIs and chondrules from those produced earlier in nebular history when the dust was more  $^{16}\text{O}$ -rich. However, if such processes occur quite early in nebular history it may be possible to drive the composition of temporarily isolated nebular regions to significantly  $^{16}\text{O}$ -enriched levels compared to solar [4] and to leave a record of such extraordinary regions as relatively durable CAIs and chondrules such as those found in Isheyevo (CH/CBb) [11] and Acfer 214 (CH3) [9]. Such materials will be exceedingly rare given that they must survive all further nebular events as well as processing that might occur in a meteorite parent body and they should represent some of the oldest surviving materials produced in the formation of our solar system. It might be possible that this hypothesis could be tested by measurements of the absolute ages of these unique materials.

### 3. Conclusions

We have argued that chemical processes in the solar nebula that result in non-mass-dependent oxygen isotopic fractionation could be intimately coupled to processes that form organic materials: processes that have previously been considered to be completely independent of one another. Not only can organic synthesis totally erase the oxygen isotopic signature of self-shielding on nebular dust globally, but the combination of organic synthesis releasing CO back into the nebula as water, with the isotopic fractionation due to self-shielding, can potentially lead to separate regions that are respectively enriched and depleted in  $^{16}\text{O}$  in a complementary fashion. Furthermore, given the large degree of mixing that can occur in the solar nebula, it is possible that the oxygen isotopic composition of specific dust populations does not change monotonically from solar towards SMOW. Unfortunately, it might be very difficult to distinguish solids that have become more  $^{16}\text{O}$ -rich from those that may have become  $^{16}\text{O}$  depleted less rapidly than average, except at the very earliest times in nebular history when these processes would result in solids that are more  $^{16}\text{O}$ -rich than the Sun, such as those measured in Isheyevo and Acfer 214.

### Acknowledgments

JAN and NMJ acknowledge the support of NASA's Exobiology R&A program as well as the Goddard Center for Astrobiology for supporting this research.

### Author Contributions

The ideas in this manuscript arose as the result of many conversations among the authors and have been presented and discussed at several scientific meetings. JAN wrote the first draft of the manuscript that was then extensively improved by the co-authors and as the result of comments from our reviewers.

### Conflict of Interests

The authors declare no conflict of interest.

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