

EVALUATION OF CO SELF-SHIELDING AS A POSSIBLE MECHANISM FOR ANOMALOUS OXYGEN ISOTOPIC COMPOSITION OF EARLY SOLAR SYSTEM MATERIALS. Subrata Chakraborty¹ and M. H. Thiemens², ^{1,2}Department of Chemistry, UCSD, La Jolla, CA 92093-0356 (¹subrata@chem.ucsd.edu, ²mthiemens@ucsd.edu).

Introduction: Oxygen is the most abundant element in the solid phases that formed early in the solar system. Prior to condensation, oxygen was contained in the gas phase molecules CO, SiO, and H₂O in the (solar) nebula (temperatures in excess of 1500 K). For the last three decades it has been well documented from different meteoritic materials that the abundance ratios of its three stable isotopes of oxygen (i.e. ¹⁸O/¹⁶O and ¹⁷O/¹⁶O) deviate significantly from the traditional thermodynamic or kinetically governed fractionation pattern (mass dependent) which is defined by the relation: $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ (where $\delta^{18 \text{ or } 17}\text{O} = (^{18 \text{ or } 17}\text{R}_{\text{sample}} / ^{18 \text{ or } 17}\text{R}_{\text{std}} - 1) \times 1000$ ‰, which is a measure of the deviation of the abundance ratio from a standard material (SMOW for O-isotopes), expressed in parts per thousand variation). The meteorite data falls in a slope of nearly unity in the three oxygen isotope plot (see for example extensive reviews: [1, 2, 3]).

Following the discovery by Thiemens and Heidenreich [4] of a chemically produced mass independent isotope effect that identically reproduces that observed in meteorites, the possibility that these meteoritic anomalies arise from chemical processes became possible. This is a major issue given that the observed anomalies are large and oxygen is the major element; therefore, the source of these anomalies is a major process in the formation of the solar system.

The concept of self shielding in the solar nebula was introduced to explain the enhanced ¹³C and ¹⁸O signatures observed by radio astronomers at the edges of interstellar molecular clouds in CO [4, 5, 6]. Thiemens and Heidenreich [4] also suggested that self shielding of nitrogen might account for observed meteoritic heavy isotope enrichments. Recently, self-shielding of CO has been revitalized to explain the O-isotopic anomalies in meteorites [7].

The photochemical and chemical scheme proposed for production of the meteoritic oxygen isotope anomaly related to CO self-shielding is as follows:

The line corresponding to the most abundant isotopomer C¹⁶O is attenuated at the surface layer of the nebular gas and the line corresponding to C¹⁷O and C¹⁸O are slightly shifted (due to difference in vibration-rotation energy levels) and thus attenuation is much less due to the much lower nuclidic abundances. As a result, C¹⁷O and C¹⁸O are preferentially dissociated by FUV photons in the deeper regions, a process depending upon *abundance* and not *mass*. This proc-

ess generates O-atoms in the inner regions enriched in the heavier nuclides (¹⁷O and ¹⁸O). Once O-atoms formed they may react with H₂ or H₂* (vibrationally excited H₂) to form OH. Subsequent reaction sequences with H₂ or H₂* to form H₂O which will possess signatures of heavy oxygen formed due to CO self-shielding. Once H₂O was formed, O-atoms may become incorporated into the silicate grains through surface reactions. A major issue with respect to self shielding, as discussed in detail by Navon and Wasserburg [8], is that the rapidity of oxygen atom exchange with other molecules may effectively erase the isotopic signature produced by optical self shielding.

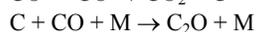
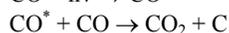
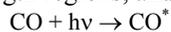
Though self shielding has been hypothesized as a main mechanism in the nebula, the astronomical site of the event is not certain. Three different sites have been proposed [7, 9, 10] starting from the close vicinity of the young Sun [7] in the inner solar nebula (known as ‘X’ point), where the product enriched oxygen atoms are ejected to the outer nebula by an ‘X-wind’ [11] and then are incorporated into grains. In this scenario all the solar system material should be processed through the ‘X’-point. In an alternative site suggestion, Young and Lyons [9] suggested that the region high above the mid plane at large R might be a suitable region. Yurimoto and Kuramoto [10] even have proposed that self shielding of CO occurred in the molecular cloud itself and the left-over CO preserved the isotopically depleted O-signature and water-ice preserved the enriched O-composition and tried to build up the solar system oxygen map through a mixing of these components.

All scenarios to date are strictly theoretical. Historically, there have been theoretical kinetic constraints against self shielding but there have been no experimental studies of the process due to the requisite short wavelength UV light. Models are limited as well because of the lack of kinetic data for many key reaction steps. Here we discuss the possibilities of CO self shielding in the light of new theoretical calculations on CO photodissociation (within 90 to 110 nm). We also evaluate the possibilities of CO photochemistry in the higher wavelength region (~ 150 nm) and its isotopic consequences based on some preliminary experimental data.

CO Photodissociation and Self-shielding: CO is the second most abundant molecule in the solar nebula after H₂ and is the predominant carrier of oxygen prior to condensation into silicates. It has one of the strongest bonds among nebular molecules (11.14 eV or 111.3

nm). High resolution spectroscopic laboratory studies demonstrate that CO Photodissociation occurs primarily via predissociating resonances of the CO molecule and as a consequence, the photodissociation cross sections are quite frequency selective and only photodissociation in narrow frequency bands (within 91 to 111 nm) are capable of dissociating CO. Thus it is effected by self-shielding due to overlapping of the sharp absorption profiles of its own isotopomers. Under nebular conditions, the situation is more complex due to the presence of line coincidence with H and H₂ [5, 6, 12, 13]. Moreover, the amount of self-shielding depends on many factors (interstellar radiation field, cloud density, temperature and pressure.) but if it can be assumed that the resonances of different isotopomers do not overlap, the rarer isotopomers will be subject to less self shielding than the common C¹⁶O [14]. However, the assumption of non-overlapping absorption profiles of the various isotopomers depends on the nature of the predissociating resonances. Some recent calculations show that due to tunneling through a potential barrier, low lying resonances are sufficiently narrow and thus no overlap of the resonances of different isotopomers may be expected (below 94000 cm⁻¹, i.e., above 106 nm). However, for the higher resonances, due to non adiabatic coupling between discrete and the dissociating continuum state, most of the absorption profiles are much wider (~ 1000 cm⁻¹) and a considerable overlap of the resonances of different isotopomers may be expected [14]. In summary, these calculations permit self-shielding within only a very narrow wavelength region; 106 to 111 nm. In the nebular environment, after filtering of lines by abundant H and H₂, four lines (92.3, 93.3, 94.9, and 97.7 nm) are available for CO dissociation [15]. Thus, the result is that CO self-shielding effect is highly restricted, even without consideration of the kinetic issues discussed in [8].

CO photochemistry at higher wavelength region (~ 150 nm). There is a relatively strong absorption band in CO corresponding to a 4th positive system at around 150 nm. The absorption cross section (~ 3 x 10⁻¹⁸ cm²) at these wavelength is about ½ the crosssection at the dissociating wavelengths. An interesting photochemistry occurs due to absorption of light in these wavelength regions, and leads to product formation:



Solar Spectra: In this discussion, it is important to address the solar flux and its variation with wavelength in the early stages of the Sun (e.g , the T tauri phase). The solar UV luminosity was reconstructed based on astronomical observations in [16]. The reconstructed

spectra show slightly intensified fluxes at 150 nm as compared to the FUV region. Thus the combined factor (flux x absorption cross section) at 150 nm is about 3 to 4 times more than that of 100 nm, the region where self shielding may occur.

As a result of the convolution of the cross section and the solar actinic flux, this may be an important region for photochemistry in the early solar system and it potentially may dominate the early solar system chemistry of oxygen, including self shielding.

Preliminary Experimental Result: We have carried out some preliminary CO photodissociation experiments in 147 to 152 nm wavelength region using the synchrotron radiation from Advanced Light Source (ALS) of Lawrence Berkeley Laboratory. These experiments clearly demonstrate that there is a large mass independent isotopic fractionation in this spectral region and will be presented in the conference.

Conclusion: Based on the recent calculations, CO self-shielding below 100 nm due to cross sections, UV fluxes, and competing photochemistry, as well as isotope exchange is likely a very modest process. The convolution of solar actinic flux and the cross section produce a photochemistry of 3 to 4 times in the 150 nm region over the FUV in the early stages of the Sun. The preliminary experimental results show large mass independent effect in the photochemistry of CO at around 150 nm. Given the fact that photons in the longer wavelength UV energy range were readily available in the nebula, and these lines were not totally shielded as compared to the shorter wavelengths, excited state chemistry (without reaching dissociation level) of CO may play an important role in the early solar system process and dominate shielding. More experiments in the entire wavelength zone of 105 to 150 nm are in progress.

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