ASSESSMENT OF CO PHOTODISSOCIATION EXPERIMENTS BY MODEL SIMULATIONS AND SPECTROSCOPIC MEASUREMENTS. J. R. Lyons[1], G. Stark[2], A. N. Heays[3]. [1]Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095-1567, USA; jimlyons@ucla.edu.;, [2]Physics Department, Wellesley College, Wellesley, MA xxx, USA;, [3]Res. Sch. Phys. Sci. & Eng., ANU, Canberra, CA ACT 0200, Australia

Introduction: CO self-shielding is presently the leading hypothesis for explaining the CAI oxygen isotope mixing line [1]. Preliminary analyses of GENESIS solar wind samples show that solar wind ions have $\Delta^{17}O$ ~ -25 ‰ [2], similar to the isotopically lightest CAIs, supporting a self-shielding scenario for the solar nebula. Recent oxygen isotope measurements of CO_2 produced during CO photodissociation in the laboratory have been interpreted as evidence that self-shielding is not significant during CO photolysis, and is therefore not relevant to understanding solar system formation [3]. One of us (JRL) has argued against this interpretation [4,5], and here we present recent simulations and data relevant to 2 of the 4 (by wavelength) experiments reported in [3].

Simulation of experiments: The photolysis experiments [3] were carried out at the ALS synchrotron using the direct undulator beam (FWHM ~ 2 nm, photon flux ~ $5x10^{15}$ ph s^{-1} from 91-110 nm). The beam entered a phototube containing CO at a column density of 4-$12x10^{17}$ cm^{-2}. CO_2, formed by recombination of O and CO, was collected on cold fingers near the end of the phototube. Experiments were performed with the beam centered at 94.12, 97.03, 105.17 and 107.61 nm. The experiments are continuous flow, with a published flow rate of 1 sccm [6] and a photocell volume ~ 300 cm^3. The units 'sccm' are standard cm^3 min^{-1}, where 'standard' usually means STP, i.e., 1 atmosphere. For experiment pressures of 0.1 to 0.4 torr, 1 sccm implies a CO residence time of 2-10 seconds in the phototube [4]. Chakraborty et al. [6] state that the flow rate is 1 cm^3 min^{-1} at the phototube pressures, yielding a residence time of ~ 300 minutes.

The factor of 10^4 difference in residence times is significant to the interpretation of the experiments. The rate constant for gas-phase CO_2 formation is k_{CO+O} = $1x10^{-35}$ cm^6 s^{-1}. For a gas density of ~10^{16} cm^{-3}, the timescale for loss of O to CO_2 formation is ~ 10^3 seconds. If the residence time of CO is ~2-10 seconds, then most O is lost before it can form CO_2. This could explain the much lower than expected CO_2 yield in the experiments [6].

Simulation of the experiments at 105.17 and 107.61 nm follows [5], but with the addition of a proper spectral beamshape for the ALS synchrotron (Fig. 1). ([5] assumed a Gaussian beamshape, but the ALS beam is asymmetric about the center wavelength. [6]). The timescale of CO_2 condensation is determined by the timescale for radial molecular diffusion, which is << 1 second for a tube of length 10-100 cm, and radius ~ 1-3 cm. The code has been run to ~ 100 seconds for several CO column densities. Longer runshave been made to account for a CO residence time ~ 300 minutes, but formation reactions for CO_2 have not yet been added.

Photodissociation of CO isotopologues is computed using synthetic absorption spectra (Fig. 1) as described in [5]. Isotopologue-dependent uncertainties in band oscillator strengths (i.e., f-values, a measure of the strength of the band) are typically ~ 30 % or less but for some bands can be higher. Here we assume that f-values are identical for all CO isotopologues.

Model Results: Photodissociation rate coefficient profiles, J(z), as a function of depth in a 10 cm phototube demonstrate the CO self-shielding effect for the CO E(0) band at 107.6 nm (Fig. 2). Radiation enters the phototube at z=10 cm, and is rapidly attenuated by $C^{16}O$, yielding J_{17} and J_{18} values ~ 30x J_{16}. For this band $C^{18}O$ is also optically thick, resulting in $J_{17} > J_{18}$. The J profiles are independent of time until a significant fraction of CO is dissociated at > 100 seconds.

Figure 3 shows delta values and slopes for CO and O at the model phototube endwall (i.e., at z=0 in Fig. 2) as a function of time. At short times (<0.1 sec.) O has very large delta values and an abundance < 10 ppm. For the ALS beam at 107.6, O has $\delta^{17}O/\delta^{18}O$ ~ 1.9 (Fig. 3a), and for the beam at 105.17, O has $\delta^{17}O/\delta^{18}O$ ~ 1.2 (Fig. 3b). At later times the delta values decrease (but are still large), and the slope approaches unity. If the CO residence time in the phototube is long (e.g., 300 minutes), self-shielding will produce slopes close to one. If the residence time is very short, or if CO is rapidly converted to CO_2 in wall reactions (not included here), the CO_2 produced from O will have a slope significantly > 1, as is seen in the experiments [3]. Simulations that explicitly include CO_2 formation by gas-phase reactions and by wall reactions are in progress.

Spectroscopic data: Absorption data for a $C^{16}O$-$C^{17}O$ mixture will be used to accurately determine the relative f-values for $C^{16}O$ and $C^{17}O$ (Fig. 4).

Conclusions: Simulations of CO photolysis in a phototube demonstrate fractionation by self-shielding ,

but also show a strong dependence on gas residence time in the phototube.

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References: [1] Clayton, R. N. (2002) *Nature* 415, 860-861. [2] McKeegan et al. (2008) *AGU abstract*, Fall meeting, San Francisco, Dec. 15-19. [3] Chakraborty et al. (2008) *Science* 321, 1328-1331. [4] Lyons, J. R., Lewis, R., Clayton, R. N. (2009) *Science* 324, 1516a. [5] Lyons, J. R. (2009) 40th LPSC, abstract 2377. [6] Chakraborty et al. (2009) *Science*, 324, 1516d.

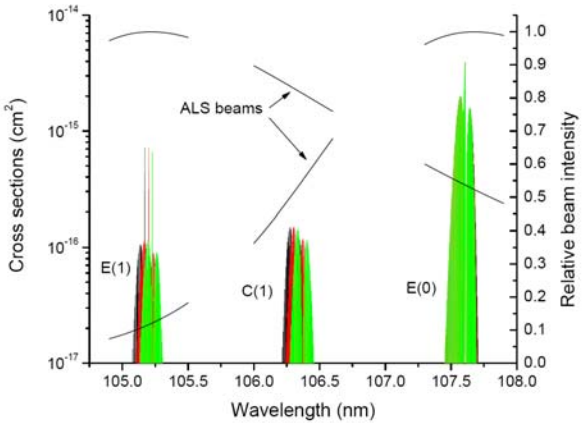

Fig. 1. Computed spectra for CO E(1), C(0) and E(0) bands, with $C^{16}O$ in black, $C^{17}O$ in red and $C^{18}O$ in green. The synchrotron relative beam intensities for the 105.17 nm and 107.61 nm experiments are shown as black piecewise curves.

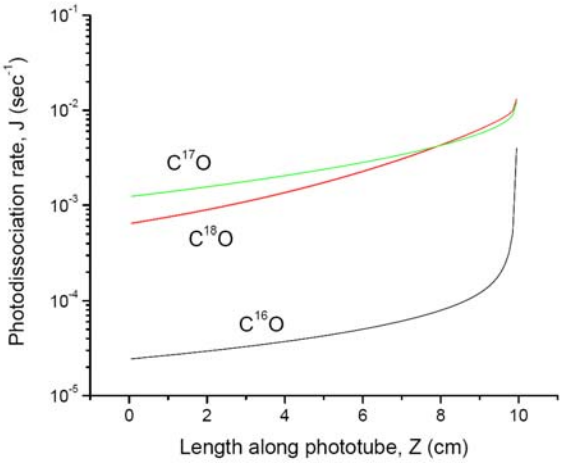

Fig. 2 Photodissociation rate coefficients for CO isotopologues for the ALS synchrotron centered at 107.6 nm (E(0) band). Radiation enters the phototube at z=10 cm. Self-shielding of $C^{16}O$ is readily apparent.

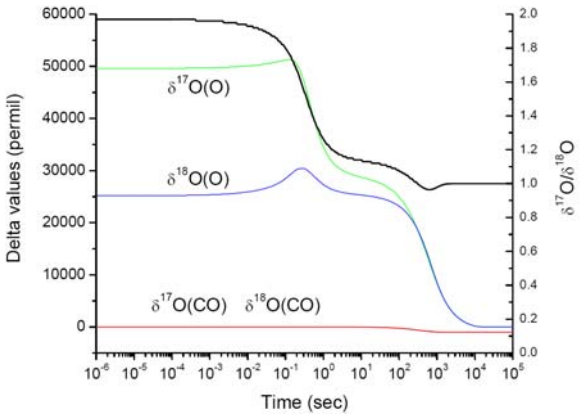

Fig. 3a. Delta values and slope for CO and O at the phototube end wall for the ALS beam centered at 107.6 nm (E(0) band).

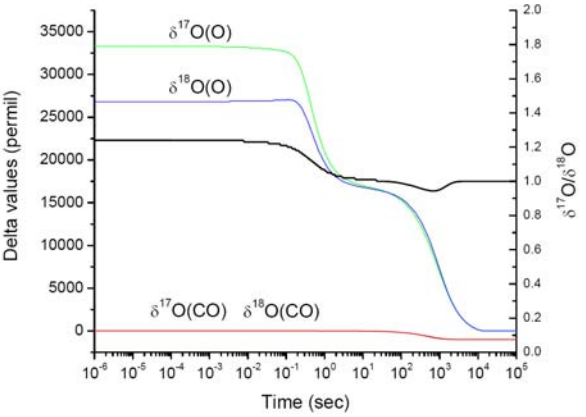

Fig. 3b. Same as Fig. 3a for the ALS beam centeed at 105.17 nm (E(1) band). 50% CO dissociation occurs at ~5000 sec.

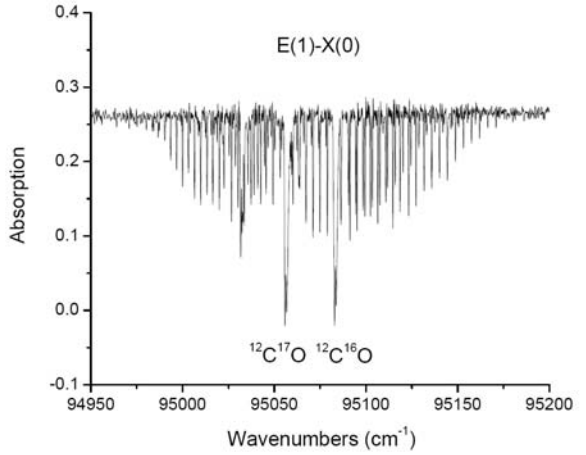

Fig. 4. Preliminary absorption spectra for a mixture of $C^{16}O$ and $C^{17}O$ (plus ~10% $C^{18}O$). This data will be used to reduce the present uncertainty in f-values for CO isotopologues.