OXYGEN ISOTOPE EFFECT DOMINATED BY VUV PHOTODISSOCIATION DYNAMICS OF CO: IMPLICATIONS FOR NEBULAR CO PHOTOLYSIS.

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Introduction: A large number of absorption bands exist for carbon monoxide (CO) in the VUV region (91 – 108 nm) [1]. All bands contribute towards CO photodissociation in the solar nebula. Experimental measurements of isotopic fractionation through the entire VUV region are needed to determine the oxygen isotope effect through CO photolysis in solar nebula since modeling efforts are insufficient in providing the needed resolution. The oxygen isotopic fractionation due to VUV photodissociation of CO in some bands was previously reported [2-3]. Experimental runs have been performed to cover the entire VUV region by scanning the undulator [4] at the Chemical Dynamics Beamline at the synchrotron facility at ALS, which delivers photons in a wavelength window of ~ 2 nm with a flux of ~ 5 x 10^{14} s^{-1}. Here we report new results and discuss the implications.

Results and Discussions: We investigated the wavelength dependent isotopic fractionation in CO photodissociation for the synchrotron bands centered at: 91.3, 92.6, 94.12, 97.03, 105.17, and 107.61 nm, which together cover the entire relevant VUV regime. We observed that the relative fractionation between ^{17}O and ^{18}O (reflected in the slope value in the oxygen three-isotope plot) depends on the VUV wavelength in the O-atom pool of the CO dissociation product. The synchrotron VUV bands excite CO to different excited electronic states, some which are self shielding, some not. The types of pre-dissociation dynamics associated with the excited states are intrinsically different and depend on the nature and the structure of the electronic states [5] and therefore result in different relative isotopic fractionation between ^{17}O and ^{18}O (slope ranging between 0.55 to 1.3 and 0.55 to 1.1 for 23 and -91^{o}C, respectively for different upper electronic states in the entire VUV region).

The meteoritic CAI-line has a very tight slope of ~1 in oxygen three-isotope plot [6] and the self-shielding models [7-8] require this slope during nebular CO photodissociation with the un supported assumption that there is no isotope effect in the actual photodissociation. Our now extensive experimental results show that this assumption is not valid and a strong dissociation dynamics dependent isotope effect is present. From our low temperature (-91^{o}C) data we deduce the effective slope of 0.7 for O-atom pool generated by CO photodissociation for the entire VUV bands and is inadequate to explain meteoritic oxygen isotope data.

References: [1] vanDishoeck E. F. and Black J. H. 1988. *Astrophysical Journal* 334:32. [2] Chakraborty S. et al. 2008. *Science* 321:1328-1331. [3] Chakraborty S. et al. 2009. *Science* 324:4. [4] Heimann P. A. et al. 1997. *Review of Scientific Instruments* 68:1945-1951. [5] Lefebvre-Brion H. et al. 2010. *The Journal of Chemical Physics* 132:024311. [6] Clayton R. N. 2007. *Annual Review of Earth and Planetary Sciences* 35:1-19. [7] Clayton R. N. 2002. *Nature* 415:860-861. [8] Lyons J. R. and Young E. D. 2005. *Nature* 435:317-320. [9] The work is funded through NASA's Origins program. MA and the ALS are supported by the Director, Office of Energy Res., U. S. Dept. of Energy (Contract No. DE-AC02-05CH11231).