



Photochemical self-shielding as a source of non-mass-dependent isotope fractionation

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Very large isotopic enrichments occur in the photolysis products of molecules that have line-type absorption spectra. Abundance-dependent line saturation, a process termed photochemical self-shielding, yields large non-mass-dependent (NMD) isotope effects, and has been proposed to have occurred in CO in the solar nebula (Clayton 2002) and SO₂ in the early Earth atmosphere (Lyons 2007). The NMD signatures derived from photolysis of CO and SO₂ are believed to be recorded in primitive meteorites inclusions (CAIs) and in Archean/Paleoproterozoic sulfur sediments, respectively. Comparison of theory and experiment can be used to distinguish self-shielding from other NMD processes.

Recent low-resolution ($\sim 10 \text{ cm}^{-1}$) measurements of isotopic SO₂ cross sections (Danielache et al. 2008) exhibit NMD effects when included in photochemical models (Ueno et al. 2009), but not as a result of self-shielding. Higher resolution measurements ($1\text{--}0.2 \text{ cm}^{-1}$) of isotopic cross sections are in progress at Imperial College. Inclusion of preliminary 1 cm^{-1} resolution cross sections in a photochemical model for Earth's early atmosphere clearly demonstrates that isotopic self-shielding is present, yielding $d^{33}\text{S} > 0$ and $d^{34}\text{S} > 0$ in photoproduct SO. However, uncertainties in the measured cross sections also introduce NMD signatures. We are presently working to remove these uncertainties.

Recent experiments on CO photodissociation at wavelengths $\sim 91\text{--}108 \text{ nm}$ show very large NMD effects in oxygen (Chakraborty et al. 2008). Because the measured NMD signatures are wavelength dependent, and differ in δ -values (i.e., $d^{17}\text{O}/d^{18}\text{O}$ not equal unity), Chakraborty et al. claim that their experiments rule out CO self-shielding as the mechanism for the meteorite CAI slope-1 line. Here we show via model simulation of the experiments that the non-unity $d^{17}\text{O}/d^{18}\text{O}$ values result primarily from self-shielding effects in both C¹⁶O and C¹⁸O. Also, model results indicate that the non-unity $d^{17}\text{O}/d^{18}\text{O}$ values only arise for low CO dissociation fraction ($< 10 \%$). When a larger fraction of CO is dissociated ($> 10 \%$), $d^{17}\text{O}/d^{18}\text{O}$ approaches unity. This is consistent with self-shielding models and with the CAI fractionation line.