



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 (~ 10 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 (1-0.2 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 $d_{33}S > 0$ and $d_{34}S > 0$ 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 ~ 91 -108 nm show very large NMD effects in oxygen (Chakraborty et al. 2008). Because the measured NMD signatures are wavelength dependent, and differ in delta-values (i.e., $d_{17}O/d_{18}O$ 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 $d_{17}O/d_{18}O$ values result primarily from self-shielding effects in both C₁₆O and C₁₈O. Also, model results indicate that the non-unity $d_{17}O/d_{18}O$ values only arise for low CO dissociation fraction (<10 %). When a larger fraction of CO is dissociated (>10 %), $d_{17}O/d_{18}O$ approaches unity. This is consistent with self-shielding models and with the CAI fractionation line.