

Self-shielding of CO in the Solar Nebula

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Self-shielding of $^{12}\text{C}^{16}\text{O}$ and concomitant depletion of the rare isotopologues of CO (e.g., ^{13}CO , C^{18}O) are well known to occur at the edges of molecular clouds. Self-shielding occurs because the predissociation absorption lines in the more abundant $^{12}\text{C}^{16}\text{O}$ become saturated at shorter pathlengths than for the CO isotopologues. The absorption lines of the isotopologues do not, in general, overlap those of $^{12}\text{C}^{16}\text{O}$, resulting in a higher photodissociation rate coefficient for the former. Recently Clayton (2002) suggested that the same process operated in the inner solar nebula (e.g., near the X-point of the X-wind model) and led to an $^{17,18}\text{O}$ enrichment in primitive solar system material (other than CAI's). I present here preliminary results of a quantitative evaluation of this hypothesis.

The amount of CO photodissociated in the solar nebula is limited by the flux of extreme ultraviolet (EUV) photons from the protosun. In the presence of H_2 , CO photodissociation occurs from 91 to 108 nm (van Dishoeck and Black, 1988). For a protosolar EUV enhancement ~ 10 times modern solar maximum conditions, ~ 4 earth masses of oxygen atoms are produced in $\sim 10^6$ years. Such an estimate of total CO photodissociation must be regarded as highly uncertain, but is probably a lower limit.

In order to quantify the isotopic effects, the ratio of the photodissociation rate coefficients for $^{12}\text{C}^{18}\text{O}$ to $^{12}\text{C}^{16}\text{O}$ must be known. For typical cold molecular cloud conditions, this ratio has a peak value ~ 10 (van Dishoeck and Black, 1988). At the high temperatures and pressures of the inner solar nebula, absorption by H_2 , H_2O , higher vibrational states of these and $^{12}\text{C}^{16}\text{O}$, and overlap of absorption line tails may extinguish the self-shielding effect. A line-by-line assessment of these effects is in progress and will be reported.

For plausible inner solar nebula conditions (1500K and 10 mbar), the self-shielding mechanism produces water with oxygen isotopes above the TF line. The excess $^{17,18}\text{O}$ liberated during CO photolysis is converted to H_2O via the reaction $\text{O} + \text{H}_2$ to produce $\text{OH} + \text{H}$, followed by the reaction $\text{OH} + \text{H}_2$ to produce $\text{H}_2\text{O} + \text{H}$. For a CO mixing ratio $\sim 10^{-4}$, $< 0.1\%$ of O atoms will undergo exchange with CO. Thus, the heavy (i.e., $^{17,18}\text{O} > 0$) component of the photodissociation product of CO self-shielding will reside in H_2O , and the remaining CO will be light. Subsequent reaction of rock-forming elements (e.g., Si, Mg, Fe) with enriched H_2O may result in rocky material enriched in $^{17,18}\text{O}$, but the specific chemical pathways are unknown.

References

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Reduced sulfate concentrations in the Mesoproterozoic ocean

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Our analyses of carbonate-associated sulfate (CAS) from several Mesoproterozoic units (~ 1.7 Ga McNamara Group, NW Queensland; ~ 1.4 Ga Belt Supergroup, Montana; ~ 1.2 Ga Apache Group, Arizona; and ~ 1.2 Ga Bylot Supergroup, NE Canada) consistently show wide $\delta^{34}\text{S}$ variation (10–30‰) over stratigraphic intervals of only 10s to 100s of meters. These trends, which range from scattered to highly systematic, are similar to $\delta^{34}\text{S}$ variation observed for Fe sulfides from several Mesoproterozoic shales and argillites. This sulfide isotopic variation is often systematic and little offset from coeval sulfate. Furthermore, the Bylot Supergroup contains gypsum that follows the $\delta^{34}\text{S}$ of interbedded CAS in dolostones. The consistency observed among systematic S isotope trends from temporally and spatially distinct units defines a style of rapid Mesoproterozoic isotopic variability that may be mirroring sulfate in the world ocean. Such rapid variability in the $\delta^{34}\text{S}$ of marine sulfate, compared to variations spanning $\sim 20\%$ on scales of 10^7 – 10^8 yr for the Phanerozoic (Claypool et al., 1980), suggests a substantially reduced sulfate reservoir in the Mesoproterozoic ocean—as linked to the amount of free oxygen in the ancient biosphere.

The hypothesized low sulfate is further reflected in the abundance of ^{34}S -enriched Mesoproterozoic sedimentary pyrite and the scarcity of bedded gypsum prior to ~ 1.3 Ga. Although extensive deep-water anoxia and associated sulfate reduction and pyrite burial (Canfield, 1998) might have perpetuated low sulfate concentrations, limited initial sulfate availability would have ultimately affected the amount of free sulfide produced within the water column. Our ongoing efforts are focused on a model wherein comparatively short sulfate residence times are estimated from observed rates of $\delta^{34}\text{S}$ variation in CAS and gypsum. From these estimates, the amount of sulfate in the ocean can be bracketed as a function of approximations of input/output terms. Alternatively, trace element concentrations within the Bylot gypsum are being tested as an independent proxy for oceanic sulfate concentration, whereby fluxes—such as weathering inputs and burial within a euxinic deep ocean—can be addressed in a Mesoproterozoic context.

References

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