OXYGEN AND NITROGEN ISOTOPES IN THE EARTH AND THE SUN.

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By analogy with CO, it has been suggested that photochemical self-shielding may have been important for N_2 in the early solar system [1]. Self-shielding in CO has led to an enrichment on Earth, relative to the Sun and solar nebula, in the rare heavy isotopes of oxygen by about 6% [2]. Nitrogen isotope measurements in the Genesis solar wind collectors imply an enrichment of ^{15}N on Earth of about 40%. [3]. A similar enrichment in the heavy nitrogen isotope was not seen in ammonia on Jupiter [4], implying that the photochemical process operated in the inner solar system, and also implying that the young Sun was the source of UV radiation. An obvious question is: why is the nitrogen isotope effect so much larger than that in oxygen? A possible solution lies in the nature of the photolysis products in the two cases:

$CO\ (^1\Sigma) \rightarrow C\ (^3P) + O\ (^3P)$
(both atoms in the ground state) [5] (1)

$N_2\ (^1\Sigma) \rightarrow N\ (^4S) + N\ (^2D)$
(one atom in an excited state) [6]. (2)

The subsequent "trapping reactions" are much faster for the excited N (^2D) than those for the ground-state atoms (C (^3P), O (^3P) and N (^4S)). The first (and rate-limiting) step in trapping is probably reaction with the abundant molecular hydrogen:

$N + H_2 \rightarrow NH + H$ (3)

$O + H_2 \rightarrow OH + H.$ (4)

It was shown [7] that a depletion of about a factor of five in $^{12}C^{17}O/^{12}C^{16}O$ and $^{12}C^{18}O/^{12}C^{16}O$ can be found in a molecular cloud, implying almost complete photodissociation of the rarer isotopologues in the cloud interior. If the same degree of dissociation applies also to $^{14}N^{15}N$ in the solar nebula, then the atom ratio $^{15}N(^2D)/^{17}O$ is near unity. The implication is that the larger "isotopic anomaly" observed for terrestrial nitrogen relative to oxygen is not due to the primary photochemical process, and likely reflects the greater "trapping" reactivity of N (^2D) relative to O (^3P). The observed ratio of isotope effects is consistent with a trapping reaction temperature of about 1400K, and is inconsistent with lower temperatures, due to the large activation energy (and consequent large temperature dependence) for the oxygen trapping reaction.

Note that there is no large isotope effect in carbon, since its lower ionization potential leads to rapid isotope "scrambling":

$C + H^+ \rightarrow C^+ + H$, and (5)

$^{12}C^+ + {}^{13}C \rightarrow {}^{12}C + {}^{13}C^+.$ (6)

There are, of course, many measurements of $^{15}N/^{14}N$ ratios in solar system materials that are greater than the terrestrial atmospheric value, usually associated with high D/H ratios in organic materials. These have been interpreted as the result of low-temperature ion-molecule reactions [8,9] either in the solar nebula or in the precursor molecular cloud.

References: [1] Clayton R. N. 2002. *Nature* 415:860. [2] McKeegan K. D. et al. 2011. *Science* 332: in press. [3] Marty B. et al. 2011. *Science* 332: in press. [4] Owen T. et al. 2001. *Astrophysical Journal* 553:L77. [5] Gaydon A. G. and Penney W. G. 1945. *Proceedings of the Royal Society* 183:374. [6] Walter C. W. et al. *Physical Review A* 50:2930. [7] Sheffer Y. et al. 2002. *Astrophysical Journal* 574:L171. [8] Terzieva R. and Herbst E. 2000. *Monthly Notices Royal Astronomical Society* 317:563. [9] Charnley S. B. and Rodgers S. D. 2002. *Astrophysical Journal* 569:L133.