

**ISOTOPE SIGNATURES IN ORGANICS DUE TO CO AND N<sub>2</sub> SELF-SHIELDING.** J. R. Lyons<sup>1</sup>,<sup>1</sup>Department of Earth & Space Sciences, UCLA, Los Angeles, CA 90095-1567; jimlyons@ucla.edu

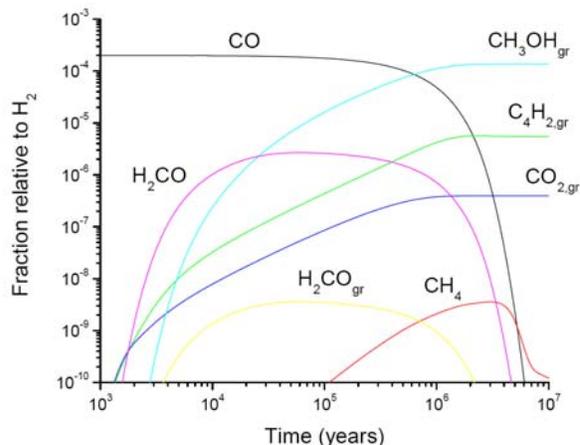
**Introduction:** The remarkable O MIF signatures seen in acid-insoluble organic matter (IOM) from a CR2 meteorite [1] <sup>2</sup>H and <sup>15</sup>N enrichments in the same IOM do not correlate with <sup>17</sup>O and <sup>18</sup>O and/or <sup>13</sup>C enrichments, but do show some correlation with each other [1]. Both N and H isotopes have been shown to be strongly fractionated by ion-molecule reactions in molecular clouds [2, 3]. Here, the question I address is whether these results, particularly those for meteorite IOM [1], are consistent with expected photochemical and ion-molecule processes. As a caveat, I note that the exceedingly difficult measurements of [1] are still in need of confirmation.

**Oxygen isotopes in simple organics:** It is well established that in model calculations CO self-shielding produces large enrichment in product <sup>17</sup>O and <sup>18</sup>O, which are then stored in H<sub>2</sub>O. Isotope signatures will also be stored in O-bearing organic compounds. Preliminary abundances and  $\Delta^{17}\text{O}$  values for grain-bound CO<sub>2</sub>, H<sub>2</sub>CO and CH<sub>3</sub>OH are shown in Figures 1 and 2. CO<sub>2,gr</sub> and H<sub>2</sub>O<sub>gr</sub> have  $\Delta^{17}\text{O} > 0$  due to reactions involving O and OH, but CH<sub>3</sub>OH<sub>gr</sub> and H<sub>2</sub>CO<sub>gr</sub> have  $\Delta^{17}\text{O} < 0$  due to formation from residual (undissociated) CO gas. These results argue that exchange of IOM oxygen with nebula water is necessary to explain the high  $\Delta^{17}\text{O}$  values measured in [1] for IOM from a CR2 meteorite. Or, alternatively, the oxygen in meteorite IOM derived from reactions of O atoms with hydrocarbon ions, which would yield O-containing organics with  $\Delta^{17}\text{O} > 0$ . Some of the latter reactions are already in the model, and so would argue that exchange with nebular water is the more important process.

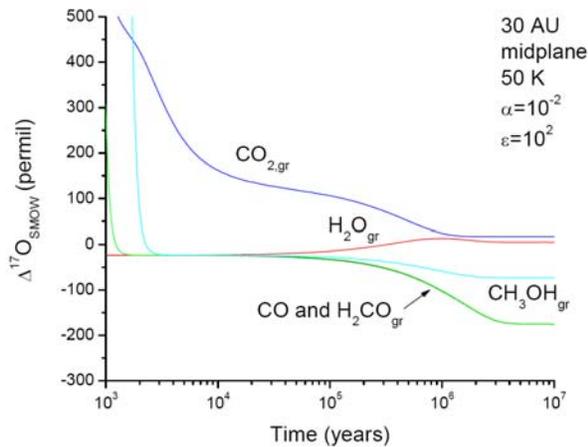
**N<sub>2</sub> self-shielding for different stellar sources:** N<sub>2</sub>, like CO, has a highly structured, band-rich spectrum (Fig. 3). Some stellar sources are dominated by narrow line emission, which, it has been argued [4], will lead to highly source-dependent isotope fractionation during N<sub>2</sub> photolysis. Photodissociation models were run with two source stars: TW Hya, a T Tauri star, and HD 36981, a B5 giant star. The resulting  $\delta^{15}\text{N}_{\text{air}}$  values for N atoms and residual N<sub>2</sub> are shown in Fig 4. Similar behavior with time is seen for all 3 cases. It is also seen that the magnitude of the  $\delta^{15}\text{N}_{\text{air}}$  values increases with decreasing FUV flux. Similar behavior is seen in CO photolysis. A dramatic dependence on the source star is not seen. This implies that the stellar continua are principally responsible for N<sub>2</sub> dissociation.

**Isotope signatures due to N<sub>2</sub> self-shielding:** In a very simple chemical scheme [5], N<sub>2</sub> self-shielding, produces enriched N and N(<sup>2</sup>D), with the N stored in HCN. The N(<sup>2</sup>D) rapidly forms NH, leading to reformation of N<sub>2</sub> by reaction of N and NH, and thus erasing much of the photo-induced fractionation. Large initial <sup>15</sup>N enrichments are possible by N<sub>2</sub> self-shielding, but the total amount of enriched material produced is small. The relatively small <sup>15</sup>N enrichment in HCN, and the large error bars on  $\delta^{15}\text{N}$  of Jupiter, means that N<sub>2</sub> self-shielding cannot be used to rule out CO self-shielding in the outer solar system, based on comparing the Sun and Jupiter. Expanded calculations for N isotopes are in progress (Fig. 5). In particular, the gas-grain and ion-molecule exchange reactions are being updated to include NH<sub>3</sub> formation and exchange between N<sub>2</sub>H<sup>+</sup> and N. The latter has been identified by [2] as particularly important. Results of these updates will be presented.

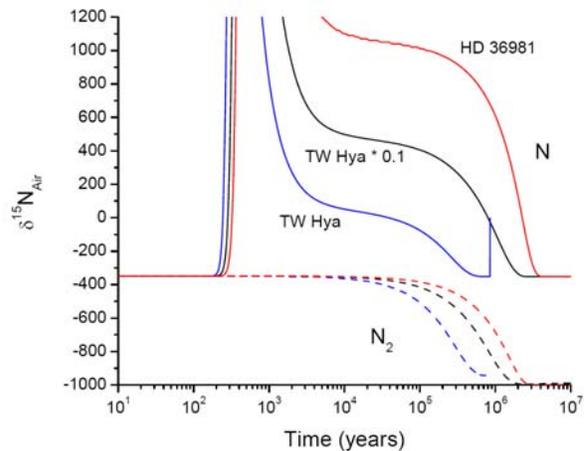
**References:** [1] Hashizume K. et al. 2011. *Nature Geo.* **4**, 165. [2] Rodgers S. D. and Charnley S. B. 2008. *MNRAS* **385**, L48. [3] Aleon J. and Robert F. 2004. *Icarus* **167**, 424. [ ] Muskatel et al. PNAS xx, xx-xx. [5] Lyons J. R. 2010. *73<sup>rd</sup> MetSoc* abstract 5424.



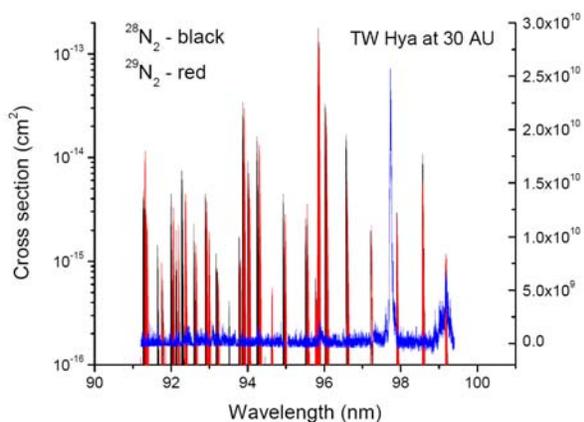
**Fig. 1** Model fractional abundances for several organic species (subscript 'gr' indicates a grain-bound species). Model run at 30 AU (50 K), and results are shown for the midplane.



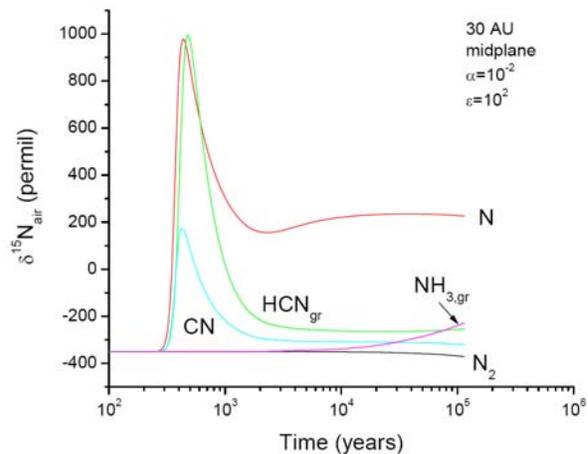
**Fig. 2** Model  $\Delta^{17}\text{O}$  values for several important species.  $\text{CO}_{2,\text{gr}}$  and  $\text{H}_2\text{O}_{\text{gr}}$  are derived from O produced by CO photolysis, and  $\text{H}_2\text{CO}_{\text{gr}}$  and  $\text{CH}_3\text{OH}_{\text{gr}}$  are derived primarily from CO.



**Fig. 4**  $\delta^{15}\text{N}_{\text{air}}$  values for N atoms and residual  $\text{N}_2$  produced by  $\text{N}_2$  photolysis using CSE  $\text{N}_2$  cross sections and two different stellar source spectra.



**Fig. 3.**  $^{28}\text{N}_2$  and  $^{29}\text{N}_2$  cross sections computed from a CSE model (provided by A. Heays and B. Lewis) shown in red. The FUV flux from TW Hya scaled to 30 AU is shown in blue (flux units are  $\text{ph cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ).



**Fig. 5.** Preliminary model results for  $\delta^{15}\text{N}_{\text{air}}$  values of several N-bearing species. This model is presently being updated for gas-grain reactions, and for ion-molecule exchange reactions (e.g.,  $\text{N}_2\text{H}^+$  exchange with N).