The interpretation of the mass independent isotope effect in ozone: Possible implications for solar system isotopic anomalies

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A possible origin for the mass independent isotope fractionation factor η observed during the synthesis of ozone [1] was proposed [2] based on the conjecture that the lifetimes of the different isotopomers of the complexes - later stabilized as ozone - cannot be equal if they result from reactions involving dis- or indistinguishable isotopes. Accordingly, η was assigned to the lifetime ratio between these two types of complexes. It was shown that, although predicted by the exclusion principle, this effect can be calculated at a first order, in classical mechanics. A schematic and simple interpretation of this effect will be presented graphically.

In this first attempt [2], η was considered as constant for all the reactions involving the 3 isotopes of oxygen. Here we will show that this assumption is only valid within ±40‰. Indeed, the measured isotopic fractionation factors for O_3 formed only by reactions involving only indistinguishable isotopes (as for example the $^{17}O^{17}O^{17}O/^{16}O^{16}O^{16}O$ ratio) show a systematic departure from unity that is not predicted by the usual mass dependent isotopic fractionation theory. If the isotopic masses are taken into account in the calculation of η, the lifetime ratios reproduce these slight isotopic variations.

The present formalism developed for ozone is extended to other chemical elements and yield theoretical isotopic distribution patterns. Some of these patterns show similarities with those measured in various phases of the carbonaceous meteorites and generally attributed to nuclear effects. It is thus possible that unidentified isotope effects caused by the production of reactive molecular species via photochemistry has played an important role in the formation of the first solids of the solar system.

[1] Thiemens, M.H., Heidenreich, J.E., 1983. *Science* **219**, 1073-1075. [2] Reinhardt, P., Robert, F., 2013. *Earth and Planetary Science Letters* **368**, 195-203.