

THE EFFECT OF ISOTOPIIC ABUNDANCE ON NoMaDic Chemistry; J. E. Heidenreich III¹ and M. H. Thiemens², ¹IBM T. J. Watson Res. Cntr., P.O. Box 218, Yorktown Heights, N. Y. 10598, ²Dept. of Chem., B-017, Univ. of Calif., San Diego, La Jolla, California 92093.

Recently we have demonstrated (1) a chemical process which produces non-mass-dependent (NoMaDic) oxygen isotopic compositions similar to those observed in Allende "high temperature" inclusions (2). The proposed effect is rather general (3-5) and may be observable in other elements. It has been shown that the mass independent fractionation occurs in variable high frequency plasmas (1,6) UV light (5) and in the microwave region (7). The mechanism for the production of the fractionation (3-5) describes the effect as arising during the actual O₃ formation process and is essentially due to an accelerated formation rate for the isotopically substituted molecules with differing symmetry. Ozone containing only ¹⁶O has C_{2v} symmetry, whereas substitution of ¹⁷O or ¹⁸O may have either C_{2v}(XYX) or C_s(YXX) symmetry. The isotopic fractionation is due to the extended lifetimes for the C_s symmetry species (3-5). Lifetime enhancement occurs due to an increase in the rovibrational level densities for C_s species in the transitory O₃^{*} species. The effect of isotopic abundance is investigated for two reasons. First, at the natural ¹⁷O,¹⁸O abundances, species such as ¹⁷O¹⁷O¹⁶O and ¹⁸O¹⁸O¹⁶O are insignificant. However, at higher abundances, these species will become important, thus altering the C_s/C_{2v} species ratio and in turn the fractionation pattern. Secondly, the model is important for extrapolation to other cosmochemically interesting elements of differing isotopic abundances.

For the model calculations, the fractionation magnitude is determined based on the lifetime differences for the excited O₃ which is given by:

$$\delta x_0 = \left[\frac{(\tau^x / \tau^{16})}{R^x} - 1 \right] \times 1000 \quad (1)$$

where x is 17 or 18 and τ^x , τ^{16} are the lifetimes. Note that τ^{16} represents ¹⁶O¹⁶O¹⁶O and e.g. τ^{17} may be ¹⁷O¹⁶O¹⁶O or ¹⁷O¹⁷O¹⁶O. R^x is the initial isotopic composition ratio (natural abundance); e.g. R¹⁷ is the initial ¹⁷O/¹⁶O ratio.

The lifetime ratios were taken to be a simple function of the relative proportions of the product O₃ symmetries which are:

$$\frac{\tau^x}{\tau^{16}} = \phi_{2v}^x + (\chi \phi_s^x) \quad (2)$$

where the ϕ terms represent the statistical proportion of ozone molecules of either C_{2v} or C_s symmetry which contain isotope x. χ is a constant which is determined by the difference in lifetime for the different symmetry species. The value of ϕ is determined from the statistical probability of forming an O₃^{*} species of a specific symmetry and possessing at least one of the minor isotopes relative to the total number of O₃^{*} species formed containing that same isotope. The numerical value may be determined from:

$$\phi_{2v} = \frac{(R^2 + 2/3R^4 + R^6)}{(3R + 3R^2 + R^3)} \quad (3)$$

$$\phi_s = \frac{(2R^2 + 4/3R^4 + R^6)}{(3R + 3R^2 + R^3)} \quad (4)$$

where, as in equation (1), R is the initial isotopic abundance ratio. χ is an intricate function of the chemical reaction dynamics and is dependent upon

the specific reaction parameters. Its value has been approximated from experimental data (3). In (3), the largest observed extent of isotopic fractionation is 50%, which, using equations (1)-(4) yields $\chi = 1.075$ which physical means that the C_s symmetry O_3^* lifetime is $\sim 7.5\%$ longer than C_{2v} ozone.

In the table, the effect of varying the O_2 isotopic abundance on the final O_3 composition is given. At 1% ^{18}O abundance, the $\delta^{17}O = \delta^{18}O$ fractionation is no longer observed, and by 5% the $\delta^{18}O$ of the product O_3 is negative. For ^{17}O at 1% abundance, the $\delta^{17}O = \delta^{18}O$ effect is not observed, and at 5% the $\delta^{17}O$ of O_3 is negative. The $\delta^{18}O$ varies because isobaric $^{17}O^{17}O$ contribution to the measurement is significant.

The calculation results clearly indicate that isotopic abundance is an important parameter for the proposed mechanism for mass independent isotopic fractionations based on molecular symmetry. The dependency is due to the statistical dependence of the C_{2v}/C_s ratio of the O_3^* , since at abundances in excess of 1% for ^{17}O and ^{18}O significant amounts of species such as $^{17}O^{17}O^{16}O$ and $^{18}O^{18}O^{16}O$. The slope one fractionations observed experimentally are partially due to the rarity of the heavy isotopes as well as the symmetry. The experiments, mechanism and calculations suggest that similar processes may occur in other elements but with differing fractionation patterns.

References:

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Initial O_2 Isotopic Abundances			Ozone Composition			$\delta^{17}O/\delta^{18}O$	
N16	N17	N18	$\delta^{17}O$	$\delta^{18}O$			
0.9976	0.0004	0.0020	49.6	47.9	1.03) ^{18}O Abundance Variation	
0.9896	0.0004	0.0100	49.6	39.5	1.25		
0.9796	0.0004	0.0200	49.6	29.1	1.70		
0.9496	0.0004	0.0500	49.6	- 1.6	-32.0		
0.7996	0.0004	0.2000	49.5	-137.3	- 0.36) ^{17}O Abundance Variation	
0.9960	0.0020	0.0020	47.9	48.0	1.00		
0.9880	0.0100	0.0020	39.5	48.7	0.81		
0.9480	0.0500	0.0020	- 1.63	27.51	- 0.06		
0.7980	0.2000	0.0020	-137.5	-283.7	0.59		