THE SINGLE-STAGE, MASS INDEPENDENT FRACTIONATION FACTOR IN OZONE;
Mark H. Thiemens and Teresa Jackson, Chemistry Department, B-017, University of California, San Diego, La Jolla, California 92093.

Previous experiments in ozone formation demonstrated that as a function of gas pressure the magnitude of the isotopic fractionation and the $\delta^{17}O/\delta^{18}O$ ratio varies (1),(2). It was suggested that this results from the presence of fractionation processes, each with differing $\delta^{17}O/\delta^{18}O$ (2). One of the end members may be due to a pure mass independent component with $\delta^{17}O \cong \delta^{18}O \cong 90‰$ and which is dominant above ~ 20 torr pressure. At lower pressures (< 6 torr), a mass-dependent component becomes significant, and O_3 is produced with $\delta^{18}O \cong -55‰$, $\delta^{17}O \cong -27.5‰$, presumably due to isotopically selective diffusion to the wall by oxygen atoms with subsequent heterogenous O_3 formation. Wall O_3 production should then be mass-dependent since the rotation states which determine the lifetime differences for the symmetric and asymmetric states of O_3, as required by the symmetry selection model of Heidenreich and Thiemens (1), would then be absent.

If a pressure dependency for the fractionation process does exist, documentation is extremely important for determination of the relevance of such processes in nature where pressures may be variable. To significantly reduce wall effects, a 5L spherical glass photolysis chamber was constructed with a 1" diameter MgF_2 window on the side and an ~ 1.5 x 4.5 in. cold trap at the bottom. Three microwave driven light sources were employed for O_2 dissociation: Kr (130-170nm), Xe (155-200nm) and Hg (~180nm). The O_2 gas pressure was accurately measured with a Barotron pressure gauge. As in previous experiments, the O_3 is cryogenically removed immediately following its production to reduce secondary fractionations. Following reaction termination, the residual O_2 is removed and the trapped O_3 warmed, then converted to O_2 on a molecular sieve, and its isotopic composition determined. In all experiments, the depletion of the O_2 reservoir, due to O_3 production, was insignificant.

The results of the experiments are given in the Table. It may be seen that for the pressures investigated the fractionations are all ~104‰, as compared to photolysis experiments in a smaller metallic reaction vessel (same lamps) where the $\delta^{18}O$ for a 2.9 torr photolysis was + 37.2‰. A modest amount of scatter (± 5‰ in $\delta^{18}O$) exists, which may be due to a variety of processes such as O_3 photolysis, variable amounts of trapped O_2 or catalytically surface enhanced $O_3 + O_2$ isotopic exchange (3). From the data, it appears that the mass independent fractionation process produces a single-stage fractionation with $\delta^{18}O \cong 104‰$. The small degree of secondary effects adds some uncertainty to the $\delta^{17}O/\delta^{18}O$ ratio, though the fractionation remains essentially at $\delta^{17}O \cong \delta^{18}O$. It is also important to note that the fractionation is essentially identical for all three lamps, even though different O_2 quantum dissociative mechanisms occur for the individual sources.

In summary, ozone formation experiments performed in a large volume reaction vessel designed to reduce secondary fractionations indicate that the mass independent fractionation processes in O_3 are pressure independent and have a fractionation factor with $\delta^{18}O \cong 104‰$ and $\delta^{17}O \cong 96‰$. The demonstration that heterogenous (wall) O_3 formation is mass-dependent is further support for the symmetry model of Heidenreich and Thiemens (1), since that particular mechanism requires that the formation processes occur strictly in the gas phase.

Single-stage, Mass Independent Fractionation Factor

Mark H. Thiemens and Teresa Jackson

Experiment Number	Lamp Employed	Ozone $\delta^{18}O$(‰)	Ozone $\delta^{17}O$ (‰)	Pressure (Torr)
1	Hg	110.3	106.8	22.0
2	Hg	101.4	96.6	159.7
3	Hg	110.4	106.5	11.8
4	Xe	99.5	94.5	11.8
5	Xe	102.0	95.0	4.9
6	Xe	100.0	85.0	159.2
7	Kr	113.5	98.7	2.05
8	Kr	108.7	95.5	2.05
9	Kr	98.7	93.4	66.8
10	Kr	98.7	87.3	160.0
	$\bar{x}$	104.3 ± 5.7	95.9 ± 7.0	

Ozone isotopic composition has been normalized to starting O_2 composition $\delta^{18}O = \delta^{17}O = 0$.

REFERENCES:

(1) J. E. Heidenreich and M. H. Thiemens (1986). J. Chem. Phys. 84, 2129.

(2) M. H. Thiemens and T. Jackson (1987). Geophys. Res. Lett. 14, 624.

(3) S. M. Anderson, J. Morton and K. Mauersberger (1988). Geophys. Res. Lett. 14, 1258.