

MASS INDEPENDENT OXYGEN ISOTOPIC FRACTIONATION IN THE MICROWAVE REGION; Swroop K. Bains and Mark H. Thiemens, Chemistry Department, B-017, University of California, San Diego, La Jolla, California 92093.

Now that it has successfully been demonstrated that it is possible to chemically produce mass independent isotopic fractionations similar to those observed in chondritic meteorites (1), it is important to develop a thorough understanding of these processes. The effect of dissociation energy, frequency and gas pressure (mean free path) are relevant parameters, and their involvement in the mass independent fractionation process requires characterization for assessment of its role in early solar system chemistry. The effect of varying excitation/dissociation sources is of particular interest, since there are many potentially relevant astrophysical energy sources. The present experiments extend our studies into the microwave region.

A flow discharge system has been constructed which permits maintenance of constant gas pressure and isotopic composition plus permits low pressure O_3 production (<1 torr). The excitation source is a 2450 MHz, 0-120 watt microwave generator which is coupled to the flowing O_2 gas with an Evenson cavity. The discharge cavity is positioned upstream of a glass U-trap which may be chilled with liquid nitrogen to collect ozone produced in the discharge. Forward and reflected power meters are used for cavity resonance for optimal power transfer to the discharge.

The experiments are performed as follows. Ultra high purity tank oxygen flows (30 liters min^{-1}) through the glass line while being pumped with an oil diffusion pump. The U-trap is immersed in liquid nitrogen and the O_2 pressure monitored. The microwave power is set and the discharge ignited. The reaction is terminated by interrupting the power. Although precise reaction time determination is desirable for kinetic information, it is unobtainable since reaction times are short (<30s), and precise ignition times are poorly defined ($\pm 10s$). Following reaction termination, the flow is stopped and ozone separated and isotopically analyzed, as previously described (1,2).

The results are shown in Figure 1 where the flow gas has isotopic composition $\delta^{18}O = \delta^{17}O = 0$. The best fit line has a slope of 0.71, $\hat{y} = 8.9$ and $r = 0.99$. The pressure dependence for the isotopic fractionation is shown in Figure 2.

Based on the data expressed in both figures, it is clear that there are at least 3 processes operative and which differentially contribute as a function of pressure. At pressures above 25 torr, a mass independent process is operative ($\delta^{18}O = \delta^{17}O$ fractionation) but with some contribution of a process (es) unique to the flow, since substitution of a Tesla discharge for the microwave produces similar isotopic results. It is known that flow systems may introduce catalytic wall effects (3). A possible explanation for the mass dependent process is heterogeneous wall formation of O_3 , enriching ozone in ^{18}O , since, at liquid nitrogen temperatures, heavy O_2 is concentrated on the cold walls due to its lower vapor pressure. This may become more pronounced at higher pressures. As the pressure decreases (<25 torr), light O_3 is formed by some, presently undefined, mass dependent process. At pressures <3 torr, ozone again becomes enriched in ^{18}O (Figure 2) in a mass dependent fashion. This may result from partial loss of ^{16}O from the condensation region, due to insufficient mean free path for three body O_3 formation or $O + O$ wall recombination. Both processes are known to occur at these pressures (3). Either process would produce heavy, mass fractionated ozone. It is also observed that variation of power at constant pressure (15,30,60 watts) has no effect

on the isotopic fractionation, although the rate is altered considerably. This is further evidence that the effect is not in the dissociation process.

Microwave induced dissociation produces isotopic fractionations similar to those observed in static hf discharges and UV photolysis. The flow system superimposes additional processes which require further investigation but have allowed observation of the pressure and excitation source dependencies. The experiments show that there are no apparent restrictions on the nature of the dissociation process. Further work utilizing other excitation sources should be pursued to determine possible limitations on the fractionation process.

References:

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