

**Low Temperature Mass-Independent Ozone Formation on Cold Surfaces.** Gerardo Dominguez<sup>1,2</sup>, Terri Jackson, Morgan Nunn<sup>2</sup>, Dimitri Basov<sup>2</sup>, Mark Thiemens<sup>2</sup>

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**Introduction:** Even since the discovery of mass-independently fractionated oxygen reservoirs in the solar system in the 1970s [1], the origin of these remains unclear. The earliest explanations of the anomalous distribution of oxygen isotopes favored exotic nucleosynthetic mechanisms as quantum symmetry driven isotopic fractionation was not discovered until the early 1980s for the gas-phase production of O<sub>3</sub> [2]. Since then, self-shielding of CO has been adopted by various authors and appears to be the favored explanation.

Recent experiments and their interpretation have challenged self-shielding of CO on the grounds that the photolysis of CO introduces additional mass independent fractionations that are inconsistent with the CCAM line[3]. Alternatives to self-shielding exist including the possibility that the oxygen reservoir carried by interstellar dust grains were isotopically (and mass-independently) distinct from the gas-phase oxygen reservoirs [4].

Non-equilibrium radical chemistry on interstellar dust grain surfaces was recently been proposed as a potential mechanism to explain some or all of the anomalous distribution of oxygen isotopes in the solar system [5]. Ozone is believed to be a major oxidant and precursor to H<sub>2</sub>O in cold (T~10K), dense (n<sub>H</sub>~10<sup>5</sup>) molecular clouds [6] where new stars are observed to form in the interstellar medium[7]. Ozone formation in H<sub>2</sub>-rich environments is not precluded on the surfaces of interstellar dust grains where oxygen (and other elements) is preferentially concentrated compared to hydrogen[5]. Therefore, understanding the isotopic fractionation associated with O<sub>3</sub> formation may pro-

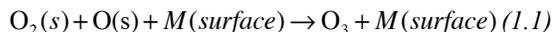
vide new constraints on the formation of our Solar System.

We have performed experiments involving the UV irradiation of O<sub>2</sub>-ice in the laboratory. Our preliminary results on the isotopic characterization of O<sub>3</sub> formed via the photolysis of cold (T~30 K) O<sub>2</sub>-ice strongly suggests that heterogeneous surface processes in the parent molecular cloud need to be considered before a complete picture of the formation of the solar system can be compiled.

Below we describe our experiments, isotopic characterization, and present the first evidence that the formation of O<sub>3</sub> on cold surfaces (T~30 K) is a mass-independent process. This finding has potentially significant consequences for our understanding of the formation and evolution of our Solar System.

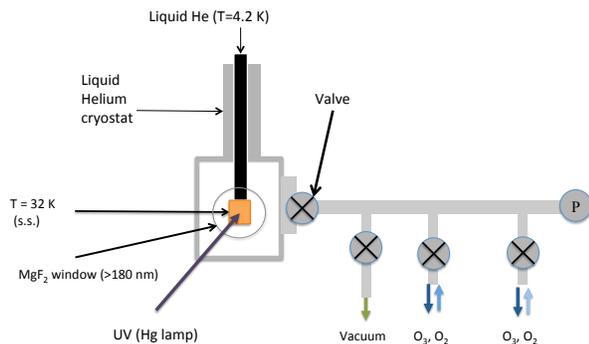
**Experimental Setup.** Our experiments consist of a modified R. Hansen He Cryostat system with optical shroud, a MgF<sub>2</sub> (3 mm thick) UV transparent window, and diffusion pump/turbo pump for vacuum system (P<= 10<sup>-5</sup>). A Hg lamp powered by a microwave generator (Ophos) was used to provide a flux (~10<sup>16</sup> cm<sup>-2</sup>) of UV photons (λ=184.5 nm). A schematic of our experimental set-up is shown in Figure 1. To produce O<sub>3</sub>, we first introduced molecular O<sub>2</sub> into a stainless steel optical shroud with a cold (T~30 K) metallic (stainless-steel) surface using a specially designed stainless steel capillary (~ 0.5 mm). At these low-temperatures, O<sub>2</sub> is efficiently absorbed onto cold surfaces as an O<sub>2</sub>-ice.

**Photolysis and Surface Chemistry.** The absorption of 184.5 nm (6.72 eV) photons by O<sub>2</sub> (ice) is expected to lead to the production of atomic O. This atomic O is then believed to form O<sub>3</sub> on the cold stainless steel surface as follows:



**Ozone Isolation.** After photolyzing the O<sub>2</sub> ice for periods ranging from 1 to 5 hours, we attempted to separate the large O<sub>2</sub> (~200 μmol) reservoir from the much smaller O<sub>3</sub> (<1 μmol) cryogenically by exploiting differences in their vapor pressures at 50-70 K. We also attempted cryogenic trapping of O<sub>3</sub> at liquid nitrogen to increase the separation efficiency (T=77K).

**Isotopic Analysis:** O<sub>3</sub> samples were cryogenically transferred to molecular sieve sample tubes (where O<sub>3</sub> decomposes into O<sub>2</sub>) and sealed. These samples were



**Figure 1.** Setup for low temperature surface photolysis experiments and sample collection.

measured on a MAT 253 IRMS (UCSD) in dual inlet mode to determine their  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  isotopic compositions.

**Results:** Measurements of the isotopic composition of the  $\text{O}_3$  fraction for several experiments are shown in Table 1. Isotopic anomalies for these experiments are found to range between 0. Isotopic analysis clearly shows that the collected samples are mass-independently fractionated, strongly suggesting that the photolysis of  $\text{O}_2$  ices and subsequent surface chemical processes result in the formation of a mass-independently fractionated  $\text{O}_3$ .

**Table 1.** Isotopic composition\* of  $\text{O}_3$  fraction with respect to the initial isotopic composition of the  $\text{O}_2$  ice reservoir. Results clearly indicate the presence of mass-independent isotopic fractionation processes on cold ( $T \sim 32\text{ K}$ ) surfaces. #  $\Delta^{17}\text{O}$  was calculated using  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$ .

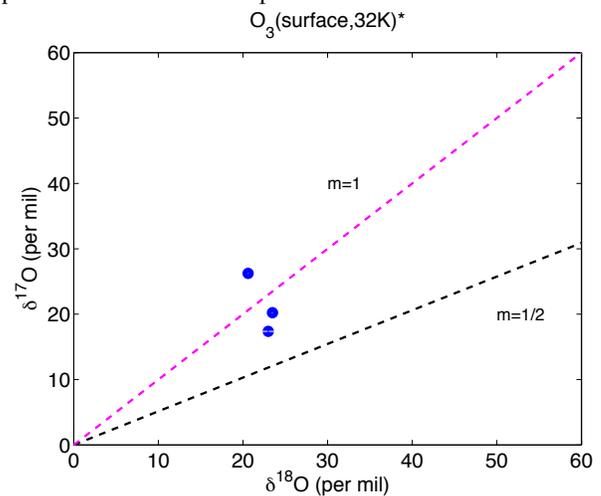
Exp #	$\delta^{18}\text{O}^*(\text{‰})$	$\delta^{17}\text{O}^*(\text{‰})$	$\Delta^{17}\text{O}^{\#}$ (‰)	Slope ( $\delta^{17}\text{O}/\delta^{18}\text{O}$ )
1	23.48 +/- 0.086	20.213 +/- 0.208	8.00	0.86
2	22.99 +/- 0.060	17.377 +/- 0.067	5.42	0.76
3	20.603 +/- 0.066	26.247 +/- 0.058	15.53	1.27

**Discussion and Conclusions:** We report the first evidence that radical chemistry in molecular cloud conditions or cold solar nebular conditions can lead to mass-independently fractionated oxygen reservoirs. These results confirm the suggestion by [5] that heterogeneous processes on cold dust grain surfaces may explain the anomalous distribution of oxygen isotopes observed in the solar system. It should be noted that previous work has inferred that  $\text{O}_3$  formation on surfaces *at room temperature* is a mass-dependent process [8]. Our observation that  $\text{O}_3$  formation on cold surfaces is mass-independent should not be surprising as the  $\text{O}_3$  isotope effect in the gas-phase is well known to be modulated by temperature and pressure. We note that a factor of 10 difference in temperature result in much bigger differences in the chemical kinetics for chemical processes, which are generally Arrhenian ( $k = A \exp(-E_A/T)$ ).

The magnitudes of the  $\Delta^{17}\text{O}$  anomalies observed to date from these experiments do not by themselves explain the range of oxygen isotopic anomalies observed in the solar system ( $\Delta^{17}\text{O} \sim [-26, -3 \text{‰}]$  [9], from isotopic differences between the most anomalous CAIs

and inferred isotopic composition of the solar wind as reported recently by GENESIS [10]. However, it should be noted that the cryogenic separation of  $\text{O}_3$  from  $\text{O}_2$  is not 100% since the vapor pressure differences between these compounds, while significant, do not differ by more than a factor of 2-3. Thus, there is potential dilution of the  $\Delta^{17}\text{O}$  anomaly by un-reacted  $\text{O}_2$ . Current experiments are focused on improving the separation efficiency of this process and investigating the effect that different surfaces and temperatures may have on the isotopic composition of  $\text{O}_3$ .

Additional experiments focusing on the isotopic fractionation factors associated with  $\text{O}_3$  photolysis on surfaces are required to better understand the range of slopes observed in these experiments.



**Figure 2.** Isotopic composition of  $\text{O}_3$  formed in  $\text{O}_2$  ice deposited on cold stainless steel surface. Terrestrial Fractionation ( $m=1/2$ ) Line (TFL) and isotopic composition of  $\text{O}_3$  fraction are shown in figure above.

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