

THE EFFECT OF VARIABLE WAVELENGTH ULTRAVIOLET LIGHT ON THE PRODUCTION OF OXYGEN ISOTOPIIC ANOMALIES; Mark H. Thiemens and Teresa Jackson, Chem. Dept., B-017, Univ. of Calif., San Diego, La Jolla, California 92093.

It was first shown by Hulston and Thode (1) that isotopic ratio measurements of meteoritic materials may be used to distinguish nuclear and non-nuclear processes for elements possessing three or more stable isotopes. The fundamental premise is based on the theory of equilibrium and kinetic isotope effects (2). It is now known (3) that it is possible to chemically produce isotopic fractionations which do not obey the mass rule. Therefore, measurement of meteoritic multi-isotopic compositions alone is insufficient to distinguish between nuclear and non-nuclear components. Careful analysis of the potentially relevant astrophysical and chemical processes must also be made before it may be determined which process(es) a specific isotopic composition represents. A crucial requirement for the analysis is a thorough knowledge of the nature of chemically produced isotope effects, particularly processes which resemble nuclear fractionations. In addition to the necessity for mechanism determination of these processes, the effect of varying excitation should be known, since there are a wide variety of energy sources available in the astrophysical environment. These ultraviolet light experiments further extend our knowledge of both the mechanism for chemical production of mass independent isotopic fractionations and the effect of differing energy dissociation sources.

We have recently demonstrated that ozone production from O_2 photolysis by UV light (127-160 nm) at liquid nitrogen temperatures produces isotopic fractionations with $\delta^{18}O \approx \delta^{17}O$ (4), as in the original RF plasma experiments at both 0.5 and 13.6 MHz (3,5). We have constructed a set of electrodeless microwave powered rare gas continuum lamps (Ar, Kr, Xe) which emit $\sim 10^{14}$ photons sec^{-1} in the regions 110-140, 127-160 and 155-210 nm respectively. All lamps emit directly into a 40 cm pathlength reaction vessel which is maintained at liquid nitrogen temperatures during O_2 photolysis to immediately remove O_3 . Ozone separation and isotopic analysis is performed as discussed in (3). The extended spectral range permits investigation of possible dissociation quantum state specificity, since O_2 dissociation at $\lambda \leq 175$ nm is a continuum process from the transition $3\Sigma_g^- \longrightarrow 3\Pi_u$ and the 175-200 nm region corresponds to the Schumann Runge band system and the transition $3\Sigma_g^- \longrightarrow 3\Sigma_u^-$ (6).

Ozone produced from UV radiation by the Kr, Xe and Ar lamps is enriched in ^{17}O , ^{18}O with $\delta^{17}O \approx \delta^{18}O$, though subtle, but significant, differences in the magnitude of isotopic fractionation and $\delta^{17}O/\delta^{18}O$ ratio for O_3 produced by different lamps may exist, which requires more extensive investigation. The largest extent of fractionation is 101.7%. There is no clear pressure dependency over an O_2 pressure range 2.3 to 150 torr, although it may not be ruled out yet since the 40 cm pathlength does not provide suitable optical depth for the very lowest pressures or actinic regions where $\sigma_{O_2} \approx 10^{-21} cm^2$. A 1½ meter pathlength reaction system and dewar is presently under construction. The extended reaction cell and cryogenic system will also permit us to clearly document whether minor, though important, isotopic differences exist between the different energy light sources. In addition, the light intensity needs to be more precisely known for each of the lamps. Unfortunately, there are no reliable chemical or electronic actinometers available for this portion of the UV.

The present results are consistent with the proposed mechanism for mass independent isotopic fractionation based on O_3 isotopic symmetry (4,7). Metastable O_3 of Cs ($^{17}O^{16}O^{16}O$, $^{18}O^{16}O^{16}O$) symmetry has twice the number of rotational lines in the diffuse bands as C_{2v} ($^{16}O^{16}O^{16}O$) symmetry O_3 . This results in an extended lifetime (τ) for the excited Cs species, which ultimately leads to their preferential stabilization. Thus, stable O_3 is enriched in ^{17}O and ^{18}O on a symmetry dependent basis ($\delta^{17}O = \delta^{18}O$) as observed. The demonstration that mass independently fractionated ozone is produced from O_2 photolysis in both continuum and vibrationally structured absorption regions is further evidence that the effect is rather general. The present results are also evidence against self-shielding, since that process cannot occur in a continuum but rather requires absorption of radiation at discrete wavelengths for the isotopically substituted species.

If the proposed mechanism is correct, there are several significant aspects for meteoritic oxygen. The general nature of the effect may allow the production of mass independent fractionation in reactions such as $O + TiO$, $O + MgO$ and $O + CaO$. Since the mechanism is a gas phase reaction feature, there are, in general, no dissociation restrictions and appears to be temperature and pressure independent. Finally, there are no limitations on the number of atoms in the product molecule provided it exceeds two. In fact, it is known that the recombination yields increase as the level density in the diffuse bands increases (6). Since the level density is a direct function of the number of atoms, the effect should be enhanced for larger molecules due to the increased vibrational degrees of freedom (and provided the symmetry restrictions are met).

The proposed mechanism for chemical mass independent fractionations is consistent with the recent experimental results, though further verification and study of the functional dependency is needed. Other molecules also need to be investigated, since differing nuclear and electronic configurations influence the lifetime of the metastable species and may produce additional isotopic fractionations.

References:

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