

MASS INDEPENDENT ISOTOPE FRACTIONATION OF MOLECULAR OXYGEN DURING ELECTRON IONIZATION. O. Abe¹, M. Ozima, A. Yamada². ¹Nagoya University. E-mail: osamu.abe@nagoya-u.jp. ²University of Tokyo.

Introduction: It is theoretically demonstrated that almost all of isotope fractionations, which occur during both chemical reactions in thermodynamically equilibrium systems and kinetic processes (e.g., evaporation, condensation, adsorption and so on), can be described as simple equations in connection with mass differences between isotopes (mass dependent isotope fractionation, MDF). On the other hand, evidences of mass independent isotope fractionation (MIF) have been found in oxygen three-isotopic composition of CAI chondrites and/or photochemical ozone formation and dissociation processes at the Earth's stratosphere. In MIFs, reaction rates should be equal among isotopologues (e.g., among $^{16}\text{O}^{16}\text{O}$, $^{17}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{16}\text{O}$), so changes in isotopic composition will be plotted along 1:1 line on the δ - δ diagram. MIF processes are one of the most active research topics both in theoretical and experimental earth-planetary sciences.

Anomalous isotope shifts observed in mass spectrometry: Recently, Abe and Yoshida [1] reported anomalous results during "normal" oxygen gas sample analyses. They measured three-isotope composition of oxygen gas mixed with nitrogen or argon gases. They found that 1) oxygen isotopic composition ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) increased with increasing N_2 or Ar mixing rates although identical O_2 gas was used, 2) Ar-mixed O_2 showed more isotopic enrichments than N_2 -mixed one, and 3) $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ variations did not obey MDF relation [$d(\delta^{17}\text{O})/d(\delta^{18}\text{O}) \neq 0.5$]. Almost simultaneously, Barkan and Luz [2] also showed similar results using O_2 -Ar mixture.

Main purposes of both studies were to suggest the necessity of correcting raw isotope data in connection with their mixing rates when one measured oxygen three-isotopic composition as a mixture form, so they did not argue the possibility of MIF processes in the mass spectrometer.

Purpose of this study: To discuss the possibility of MIF processes during the electron ionization in the mass spectrometer [3] with following experimental procedures; 1) to determine the abundance and isotope ratios of fragment ions of oxygen, 2) to determine the influence of doubly-charged ions of oxygen molecule to the fragment ion analysis, and 3) to use other interfering gases (He and Ne) in addition to N_2 and Ar and determine their apparent effects on oxygen isotope ratios.

References: [1] Abe O. and Yoshida N. 2003. *Rapid Commun. Mass Spectrom.* 17: 395-400. [2] Barkan E. and Luz B. 2003. *ibid.*: 2809-2814. [3] Griffith K. S. and Gellene G. I. 1992. *J. Chem. Phys.* 96: 4403-4411.