Mass Independent Isotopic Fractionation of Oxygen; Calculations in relevance to the O isotopic abundances in Earth Wind (EW)

\# Akinori Yamada[1]; Shinkoh Nanbu[2]; Yasutaka Hiraki[3]; Takamasa Seta[4]; YASUKO KASAI[4]; Minoru Ozima[5]

[1] Earth and Planetary Sci., Univ. of Tokyo; [2] RIIT, Kyushu Univ.; [3] Nagoya Univ.; [4] NICT; [5] NONE

It is well established that the Earth and the Moon (Apollo samples and lunar meteorites) have almost identical oxygen isotopic ratios. However, oxygens implanted within a few hundred nanometers below the surface of metal particles separated from lunar soils show large mass-independently fractionated isotopic ratios with $D^{17}O$ ranging from -20 permils [1] to +25 permils [2]. Ozima et al. [3] suggested that the extraordinary oxygen implanted on lunar metals could be attributed to terrestrial oxygen picked up from the upper atmosphere by the Solar Wind, which we call the Earth Wind (hereafter EW). To test this hypothesis, we have been investigating isotopic fractionation of O^+ ions at the altitude of 300-400 km, from where O^+ ions most likely to be picked up by SW.

Navon and Wasserburg [4] examined isotopic fractionation in photo-dissociation of O_2 due to UV for various gas compositions and temperatures. They concluded that a considerable mass independent isotopic fractionation could occur, but subsequent much faster ion exchange reactions may destroy the isotopic effects. In their calculation, they assumed a same photo-dissociation rate for all isotopomers (^iO; i = 17, 18). However, this assumption needs to be examined. Therefore, we calculated photo-dissociation cross section for O_2 and its isotopomers on the basis of a zero point energy (ZPE) model proposed by Yung and Miller [5].

We first calculated a potential energy curve for an excited state of O_2 with the MRCI method (MOLPRO 2006.1 program package [6]). Difference in ZPE for isotopomers results in different absorption bands, which in turn gives rise to different cross sections of photo-dissociation of isotopomers. For example, we obtained that while an absorption line of $^{16}O^{16}O$ at 185.21 nm gave a cross section 0.16000 x 10^{-18} cm^2, the calculated values for $^{16}O^{17}O$ at 185.16 nm were 0.15993 x 10^{-18} cm^2 and 0.15987 x 10^{-18} cm^2 for $^{16}O^{18}O$ at 185.11 nm, respectively. Basic absorption lines and corresponding cross sections at 176-201 nm (for $^{16}O^{16}O$) were taken from Ackerman et al. [7].

To assess the isotopic effects on photo-dissociation of O_2, we used 1-D photochemical model developed by Hiraki et al. [8], in which we used the above calculated cross sections for respective isotopomers. The results are $D^{17}O^+$ = -1.30 permils at 300 km, $D^{17}O^+$ = -1.08 permils at 400 km. The calculated $D^{17}O^+$ values are relatively too small to account for the observed large values in lunar metals. However, we note that our calculation was carried out only for UV ranges from 7.5 nm to 100 nm which was assumed by Hiraki et al. to be an effective UV for photochemical reactions and for 176 nm to 201 nm for which some experimental data are available. Since photo-dissociation reactions are subject to much wider ranges of UV radiation than those assumed bands in the present calculation and the ZPE model on which our calculation is based is a semi-empirical theory, we are undertaking to calculate photo-dissociation rates more rigorously on the basis of a first principle of wave packet dynamics (quantum mechanics) theory.

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