

Mass Independent Isotopic Fractionation of Oxygen in Earth Wind (EW) with Relevance to Exotic Oxygen in Lunar Metals. A. Yamada¹, S. Nanbu², Y. Hiraki³, T. Seta⁴, Y. Kasai⁴, and M. Ozima¹, ¹Department of Earth and Planetary Science, Graduate school of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, yamada@eps.s.u-tokyo.ac.jp, ²Research Institute for Information Technology, Kyushu University, Hakozaki, Fukuoka, Japan, ³Solar-Terrestrial Environment Lab, Nagoya University, Nagoya, Aichi, Japan, National Institute of Information and Communications Technology (NICT), Tokyo, Japan.

Introduction: 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 $\Delta^{17}\text{O}$ ranging from $\sim -20\%$ [1] to $\sim +25\%$ [2]. Since a substantial amount of Earth escaping O^+ flux from the upper atmosphere (Geotail Mission [3]) is likely to reach the lunar surface [4], Ozima et al. [5] 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 in the upper atmosphere (above 100 km), from where O^+ ions most likely to be picked up by SW.

There are isotope exchange reactions and photolyses (photo-ionization and photo-dissociation due to UV solar radiation), which may yield mass independent isotopic fractionation (MIF) of oxygen in the Earth's upper atmosphere. We reported [6], [7] that photochemical reactions would produce large MIF provided that reaction rates for different isotopes differ substantially (a few ten percents), but such significant difference in reaction rates were yet to be confirmed if not totally impossible. Here, we report the case for photo-dissociations.

Methods: Navon and Wasserburg [8] 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 (^{i}O ; $i = 17, 18$). However, this assumption needs to be exam-

ined. 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 [9], which was developed to calculate isotopic fractionation of stratospheric N_2O .

We first calculated a potential energy curve for an excited state of O_2 with the MRCI method (MOLPRO 2006.1 program package [10]). Here, as a preliminary test we examined a case for a potential curve of an excited state, for which experimental information are available [11]. 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, in the cases of $^{16}\text{O}^{17}\text{O}$ and $^{16}\text{O}^{18}\text{O}$, absorption lines shift from that of $^{16}\text{O}^{16}\text{O}$ at 176-201 nm by 0.05-0.1 nm and 0.1-0.2 nm, respectively. Following Yung and Miller, we calculated cross sections on mirror image method using the potential energy curve of an excited state as a mirror. For example, we obtained that while an absorption line of $^{16}\text{O}^{16}\text{O}$ at 185.21 nm gave a cross section $0.16000 \times 10^{-18} \text{ cm}^2$, the calculated values for $^{16}\text{O}^{17}\text{O}$ at 185.16 nm were $0.15993 \times 10^{-18} \text{ cm}^2$ and $0.15987 \times 10^{-18} \text{ cm}^2$ for $^{16}\text{O}^{18}\text{O}$ at 185.11 nm, respectively. Basic absorption lines and corresponding cross sections (for $^{16}\text{O}^{16}\text{O}$) were taken from Ackerman et al. [11]. We then interpolated the data with a cubic non-periodic spline to obtain absorption lines for isotopomers, and estimated cross sections of respective isotopomers relative to the observed cross section.

Results and discussions: To assess the isotopic effects on photo-dissociation of O_2 , we used 1-D photochemical model developed by Hiraki et al. [6], in which we used the above calculated cross sections for respective isotopomers. In contrary to the Navon and Wasserburg method, the Hiraki model considered both production and loss of isotopomers (including ion exchange reactions,

which was pointed out to erase isotopic fractionation effects by Navon and Wasserburg) as well as vertical diffusion of atoms and molecules (see [5] for details). Solving the equations with the above calculated cross sections of photo-dissociation, we estimated total isotopic effect in oxygen in final stationary states.

The results are shown in Table 1 for the altitude range of 300-400 km, where ion-picking by SW are most likely to occur. The calculated $\Delta^{17}\text{O}^+$ values are relatively too small to account for the observed large values in lunar metals. However, it should be noted 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, it is essential to extend the calculation for wider UV ranges to conclude isotopic fractionation in EW. Since the Yung-Miller method 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.

References: [1] Hashizume and Chaussidon (2005) *Nature*, 434, 619-622. [2] Ireland et al. (2006) *Nature*, 440, 776-778. [3] Yau and Andre (1997) *Space Sci. Rev.*, 80, 1-25 [4] Seki et al. *Science*, 291, 1939-1941. [5] Ozima et al. (2008) *PNAS*, 105, 17654-17658. [6] Hiraki et al. (2008) *LPS XXXIX*, Abstract #1175. [7] Yamada et al. (2008) *71st Annual Meeting of the Meteoritical Society*, Abstract #5205. [8] Navon and Wasserburg (1985) *Earth Planet. Sci. Lett.*, 73, 1-16. [9] Yung and Miller (1997) *Science*, 278, 1778-1780. [10] MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles. Version 2006.1. See the MOLPRO homepage, <http://www.molpro.net>. [11] Ackerman et al. (1970) *Planet. Space Sci.*, 18, 1639-1651.

Table 1.

Height (km)	$\delta^{17}\text{O}^+$ (‰)	$\delta^{18}\text{O}^+$ (‰)	$\Delta^{17}\text{O}^+$ (‰)
300.0	-0.27	1.99	-1.30
320.0	-0.26	1.92	-1.26
340.0	-0.25	1.85	-1.21
360.0	-0.24	1.79	-1.17
380.0	-0.23	1.72	-1.13
400.0	-0.22	1.66	-1.08

Oxygen isotopic ratios at the altitude of 300-400 km. Isotopic ratios are calculated by following equations.

$$\delta^i\text{O}^+ = \left(\frac{(i\text{O}^+/^{16}\text{O}^+)}{(i\text{O}^+/^{16}\text{O})_{\text{SMOW}}} - 1 \right) \times 1000 \quad (i=17\text{or}18)$$

$$\Delta^{17}\text{O}^+ = \delta^{17}\text{O}^+ - 0.52 \times \delta^{18}\text{O}^+$$

$^{17}\text{O}^+/^{16}\text{O}^+$ ratios are nearly equal to SMOW. On the other hand, $^{18}\text{O}^+/^{16}\text{O}^+$ are 1.6-2 permils larger than SMOW. Then, $\Delta^{17}\text{O}^+$ are negative.