

**Oxygen and carbon isotope imaging of organics from Y793495 (CR2) and Murchison (CM2).** K. Hashizume<sup>1</sup>, N. Takahata<sup>2</sup>, H. Naraoka<sup>3</sup> and Y. Sano<sup>2</sup>, <sup>1</sup>Dept. Earth & Space Sciences, Grad. School of Science, Osaka Univ. (kohash@ess.sci.osaka-u.ac.jp); <sup>2</sup>Atmosphere & Ocean Research Institute, Univ. of Tokyo; <sup>3</sup>Dept. Earth & Planetary Sciences, Grad. School of Science, Kyushu Univ.

We report in this paper the detection of meteoritic organic grains from Y793495 (CR2) with the highest  $^{17,18}\text{O}/^{16}\text{O}$  ratios among all planetary materials besides the presolar grains.

Earlier studies [1-4] discovered that a tiny fraction of the meteoritic organic matter, opposed to the bulk of the organics which are likely homogenized by later planetary processes, may preserve primordial isotopic signatures acquired upon its birth in the space medium. The meteoritic organic matter can be a unique probe for searching isotope fractionations involved in the material-forming chemical reactions in the solar nebula or in the ancestral molecular clouds. Because oxygen has three stable isotopes, whereas other organic major elements previously studied [1-4], H, C and N, have only two, the O isotope anomaly, if detected, may tell us much more and clear-cut on the origin of the isotope fractionations, on the chemical reaction and on the place of the birth of the planetary materials.

The isotope imaging of acid-insoluble organic matters (IOM) extracted from two carbonaceous chondrites, Y793495 (CR2) and Murchison (CM2), was carried out in this study. CR chondrites are characterized by strong  $^{15}\text{N}$  and  $^2\text{H}$  enrichments in the IOM, interpreted as greater interstellar contribution and/or better preservation of its trace among the CR chondrites over other meteoritic groups, including the CM chondrites. Y793495 is suggested to have experienced a mild thermal metamorphism on the parent body [5,6]. We plan to make systematic search for the organic grains with peculiar isotopic signatures, particularly of O and C isotopes, among chondrites of different groups, and also among those with different degrees of metamorphisms/aqueous alteration. In this study, we compare the results between the first two chondrites examined.

We performed the isotope imaging of O, C, N and H isotopes using the Cameca NanoSIMS50 ion-microprobe equipped at the Atmosphere and Ocean Research Institute, University of Tokyo. Details on the methods are described in our recent publication [7]. The  $^{18}\text{O}/^{16}\text{O}$  image of the IOM sample extracted from Y793495 is shown in Fig. 1. Anomalous  $\delta^{17,18}\text{O}_{\text{SMOW}}$  values as high as +500‰ were observed among the organic phases. The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  showed paralleled values, plotted in the three isotope diagram slightly above the slope-1 line (Fig. 2), with an inclination of  $1.057 \pm 0.015$  ( $1\sigma$ ). Areas with prominent  $^{17,18}\text{O}$  enrichments coherently showed  $^{13}\text{C}$  enrichments, with  $\delta^{13}\text{C}_{\text{PDB}}$  as high as +290‰. The replicate analysis of a different  $50 \times 50$

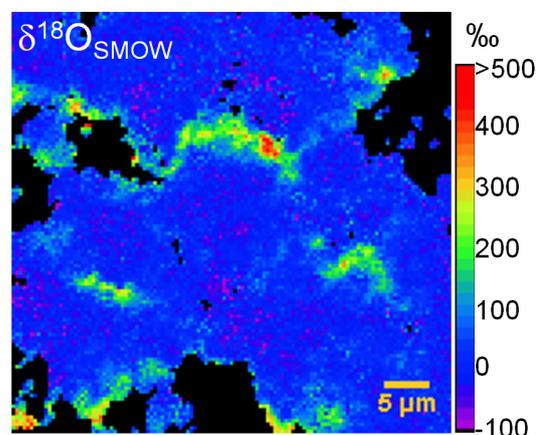


Fig. 1. The  $^{18}\text{O}/^{16}\text{O}$  isotope image of the IOM extracted from Yamato-793495 (CR2). An area of  $50 \times 50 \mu\text{m}^2$  was rastered by a 30 pA Cs primary ion beam for 40 hours [7]. Pixel size is  $390 \times 390 \text{nm}^2$ .

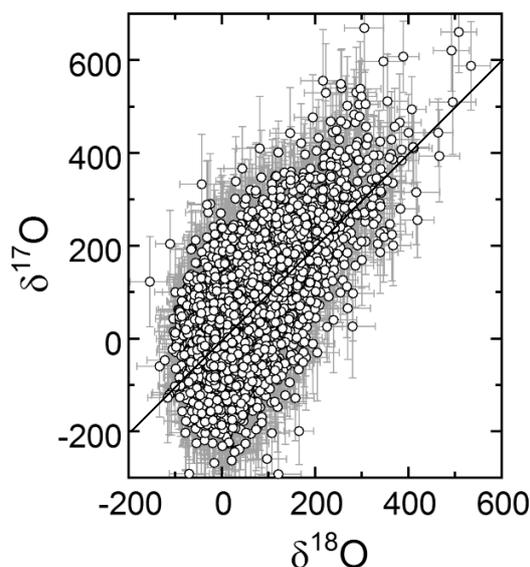


Fig. 2. The oxygen three-isotope diagram for the acid-insoluble organic matter extracted from Yamato-793495 (CR2), shown in Fig. 1.

$\mu\text{m}^2$  area of the organics from Y793495, reproducing the same isotope signatures of O and C as shown in Figs. 1 and 2 (Supplementary Materials in [7]), demonstrates the robustness of the observed results. Several spots with  $^{15}\text{N}$  and  $^2\text{H}$  enrichments were detected in the same area. However, there were no overlap between the  $^{17,18}\text{O}$ - $^{13}\text{C}$  enrichments and  $^{15}\text{N}$ - $^2\text{H}$  enrichments.

We explain the parallel enrichments of  $^{17}\text{O}$  and  $^{18}\text{O}$  in the organics from Y793495 by the self-shielding effect associated to the photodissociation of CO molecules that occurred at the onset of the organics-forming process. The  $^{13}\text{C}$  enrichments associated with the  $^{17,18}\text{O}$ -enrichments are naturally explained by the CO self-shielding. However, astrochemical theory [8] predicts that  $^{13}\text{C}$  enrichments produced by the CO photodissociation will be cancelled by the competing reaction, the ion molecule reaction (e.g.,  $^{12}\text{CO} + ^{13}\text{C}^+ = ^{12}\text{C}^+ + ^{13}\text{CO} + 35\text{K}$ ). The isotope effect of the ion-molecule reaction may grow stronger at lower temperature, and may overcome the  $^{13}\text{C}$ -enrichment effect by the CO self-shielding below  $\sim 60$  Kelvin. We therefore consider that the observed correlation in the organics of Y793495 between  $^{13}\text{C}$ - and  $^{17,18}\text{O}$ -enrichments indicates that the C and O isotope fractionation occurred at a relatively warm environment, at temperatures as high as 60 Kelvin. Such an environment may be compatible with the one expected, for instance, at the envelope of the solar nebula [9].

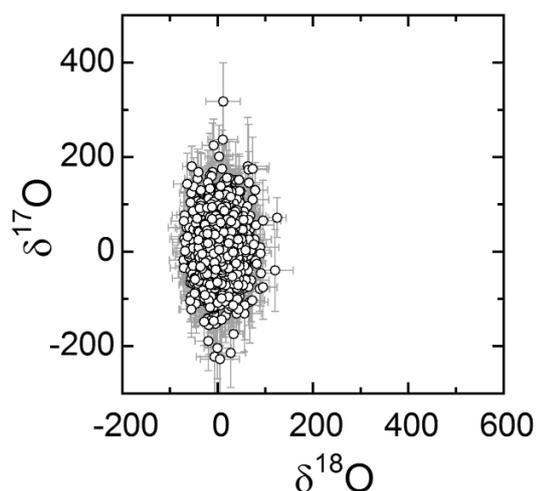


Fig. 3. The oxygen three-isotope diagram for the acid-insoluble organic matter extracted from Murchison (CM2). Four areas of  $20 \times 20 \mu\text{m}^2$  were rastered by a 30 pA Cs primary ion beam. Each data point represents secondary ion counts collected from a  $630 \times 630 \text{ nm}^2$  area. Distribution of the data points is compatible with the counting statistic theory assuming that all pixels have a normal isotope composition ( $\delta^{17,18}\text{O} \sim 0\%$ ).

Isotope imaging of organics from Murchison (CM2) was performed using the same methods. Four areas, respectively with  $20 \times 20 \mu\text{m}^2$  widths, were examined. However, no indication of a non-mass-dependent oxygen isotope fractionation was observed (Fig. 3), although numbers of spots with  $^{15}\text{N}$  enrichments were detected, confirming the previous study [1].

The difference in the appearance of the O-isotope anomaly between the two meteorites could be either due to (i) larger amounts of  $^{17,18}\text{O}$ -rich organics accreted to the CR parent body, or (ii) preferential elimination of the  $^{17,18}\text{O}$ -rich isotope signature in Murchison due to the chemical weathering associated to the aqueous alteration. The first option may indicate presence of a local/temporal process in the solar nebula that partially eliminated the organics that carried the non-mass-dependent O-isotope signatures. The second option may give us a fine view of the rock-water-organics interaction that occurred in the meteorite parent body.

#### References:

- [1] Busemann H. et al. (2006) *Science* **312**, 727-730.
- [2] Nakamura-Messenger K. (2006) *Science* **314**, 1439-1442.
- [3] Floss C. & Stadermann F. J. (2009) *Astrophys. J.* **697**, 1242-1255.
- [4] Remusat L. et al. (2009) *Astrophys. J.* **698**, 2087-2092.
- [5] Wang M.-S. & Lipschutz M. E. (1998) *Meteorit. & Planet. Sci.* **33**, 1297-1302.
- [6] Noguchi T. (1994) *Proc. NIPR Symp. Antarct. Meteorites* **8**, 33-62.
- [7] Hashizume K. et al. (2011) *Nature Geosci.* **4**, 165-168.
- [8] Visser R. et al. (2009) *Astron. Astrophys.*, 503, 323-343.
- [9] Lyons J. et al. (2009) *Geochim. Cosmochim. Acta* **73**, 4998-5017.