

AN EXTREME ^{17}O - ^{18}O -RICH MATERIAL FROM ACFER 094. N. Sakamoto¹, S. Itoh¹, K. Kuramoto², K. Nagashima³, A. N. Krot³ and H. Yurimoto¹, ¹Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, JAPAN (naoya@ep.sci.hokudai.ac.jp), ²Department of Cosmochemistry, Hokkaido University, Sapporo 060-0810, JAPAN, ³Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu, HI 96822, USA.

Introduction: Oxygen isotopes of meteorites are a key tracer to solve issues for origin and early evolution of the solar system [1]. Oxygen in meteorites changes their isotopes not only by mass-dependent isotope fractionation law, but also by large mass-independent isotope fractionation (MIF) keeping nearly constant $^{17}\text{O}/^{18}\text{O}$ ratio. The observed MIF for oxygen is as large as a range from -80‰ to 0‰ relative to the standard mean ocean water (SMOW) [2]. In this study, we report new end member of oxygen MIF. The carbonaceous chondrite Acfer 094 contains a chemically unique material. The material shows extremely large MIF enriched in ^{17}O and ^{18}O of +180‰ relative to SMOW.

Experimental: Polished thin sections of Acfer 094 C3-ungrouped chondrite and Murchison CM2 chondrite were used in this study.

The chemical compositions have been determined by electron probe microanalysis using an energy dispersive X-ray spectrometer (EDS, Oxford INCA Energy) attached on a field-emission type scanning electron microscope (FE-SEM, JEOL JSM-7000F).

A Hokudai isotope microscope system [3] (Cameca ims-1270 + SCAPS; originally installed in Tokyo Institute of Technology and now in Hokkaido Univ. (Hokudai)) has been used to image precise isotope distribution (isotopography) [3] in the meteorite matrix. A Cs^+ primary beam of 20 keV was homogeneously irradiated on the sample surface of approximately 80 μm in diameter with a beam current of ~ 0.3 nA. A normal incident electron gun was used to compensate positive charging of the sputtered region due to the primary beam. We obtained secondary ion images of $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{12}\text{C}^-$, $^{27}\text{Al}^-$, $^{28}\text{Si}^-$, $^{16}\text{O}^-$, $^{18}\text{O}^-$, $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{16}\text{O}^-$ sequentially for one analytical sequence. The exposure time was 20 seconds for $^{12}\text{C}^-$, 1000 seconds for $^{13}\text{C}^-$, 100 seconds for $^{27}\text{Al}^-$, 200 seconds for $^{28}\text{Si}^-$, 20 seconds for $^{16}\text{O}^-$, 3200 seconds for $^{17}\text{O}^-$ and 1600 seconds for $^{18}\text{O}^-$ isotopography. A 50 μm contrast aperture was used and the secondary ion contributions except for objective isotopes were cut by the exit slit. Beam irradiation time for the sequence was ~ 2 hour. The sputtering depth was less than 200 nm for the sequence. Typical spatial resolution under the condition of isotopography was ~ 0.3 μm . The width of a pixel of SCAPS corresponds to 0.2 μm on the

sample surface. An image processing method of moving average with 3 x 3 pixels was applied Fig. 1 to reduce the statistical error due to small ion integration of ^{17}O and ^{18}O . As a result, a spatial resolution is 0.6 μm , and the oxygen isotopic precision per the spatial resolution is $\pm 25\%$ (σ) for $\delta^{17}\text{O}$ and $\pm 10\%$ (σ) for $\delta^{18}\text{O}$. Other analytical methods for isotopography were described elsewhere in detail [3].

A conventional point analysis of secondary ion mass spectrometry (SIMS) has been also applied to determine oxygen isotopic compositions using the Cameca ims-1270. An oval-shaped Cs^+ ion microprobe (2.0 x 1.3 μm^2) with 20 keV was used. Secondary ions of $^{16}\text{O}^-$ -tail, $^{16}\text{O}^-$, $^{17}\text{O}^-$, $^{16}\text{OH}^-$, and $^{18}\text{O}^-$ were measured by an electron multiplier. Terrestrial magnetite and olivine standards were used to normalize secondary ion-ratios to the δO -values. The other analytical procedures were described elsewhere in detail [4].

Results and discussion: The typical composition of the chemically unique material may be represented as Fe: 61.6 wt%, Ni: 5.4, O: 19.3, S: 9.6, Mg: 0.1, and Si: 0.2. Other elements detected are below 0.1 wt%. These elements distribute homogeneously within a grain as well as among different grains. Because a mineral having this composition seems to have never been reported, more detail characterization is necessary to identify the phase. Following traditional nomenclature for unidentified phases of cosmochemistry, we label these materials as new poorly characterized phase (new-PCP) because conventional PCPs or tochilinite observed in aqueously altered carbonaceous chondrites consist of those elements [5-7] but O/S atom ratios are about 4 times larger in new-PCP than in tochilinite.

Based on the unique chemical composition of new-PCP, we have counted the new-PCP grains in totally 11 mm^2 area of an Acfer 094 thin section under 7 μm^2 -resolution. We found 22 new-PCP grains in the area. The grains scattered randomly in matrix in the area. The new-PCP is shaped by irregular outline and the largest grain we found is 160 μm^2 . Numbers of the grains increase exponentially with decreasing size toward the resolution-limit. The abundance of new-PCP in the matrix is calculated to be 94 ± 20 (σ)

ppm by volume and $3.3 \pm 0.7(\sigma)$ mm⁻² for grain density in the matrix.

Six new-PCP grains from Acfer 094 were analyzed by isotopography and one of them was analyzed by point SIMS. One PCP grain from Murchison was also analyzed by isotopography.

Isotopographs show the new-PCP is significantly enriched in ¹⁷O and ¹⁸O relative to the matrix, while the PCP is slightly poor in the isotopes (Fig. 1). The PCP is plotted in the range of the conventional variations of meteorite constituents and on an aqueous alteration line (“CM waters”) [8] supporting the aqueous alteration formation on the parent body [6] (Fig. 2). On the other hand, the new-PCPs are plotted on an extrapolation of the well-known carbonaceous chondrite anhydrous mineral (CCAM) [9] or slope-1 line [10] established by meteorite constituents.

The new-PCP is extremely enriched in ¹⁷O and ¹⁸O of +180%. This extreme MIF shows that the MIF of oxygen in our solar system have extended more than double ever believed. The oxygen isotope ratios between new-PCP and conventional PCP suggest that the formation environment was different each other.

Recent theoretical studies suggest that O isotopic composition of water ice in the solar nebula was extremely enriched in ¹⁷O and ¹⁸O [11]. The enrichment factor of the water estimated is comparable to that of the new-PCP. Therefore, new-PCP would be formed in the water ice enriched environment in the early solar system. The oxygen isotopic composition of new-PCP would be a proxy of nebular water ice.

References: [1] Clayton R. N. (2006) *Science*, 313, 1743-1744. [2] Kobayashi S. et al. (2003) *Geochim. J.*, 37, 663-669. [3] Yurimoto H. et al. (2003) *Appl. Surf. Sci.*, 203-204, 793-797. [4] Itoh S. & Yurimoto H., (2003) *Nature*, 423, 728-731. [5] Fuchs L. H. et al., (1973) *Smithsonian Contrib. Earth Sci.*, 10, 1-39. [6] Tomeoka K. & Buseck P. R., (1985) *Geochim. Cosmochim. Acta*, 49, 2149-2163. [7] Zolensky M. E. & Mackinnon I. D. R. (1986) *Am. Mineral.*, 59, 4029-4056. [8] Young E. D. (2001) *Phil. Tran. R. Soc. Lond., A* 359, 2095-2110. [9] Clayton R. N. (1993) *Annu. Rev. Earth Planet. Sci.*, 21, 115-149. [10] Young E. D. & Russell S. S. (1998) *Science*, 282, 452-455. [11] Yurimoto H. et al. (The University of Arizona Press, Tuson, in press) in *Protostars and Planets V*.

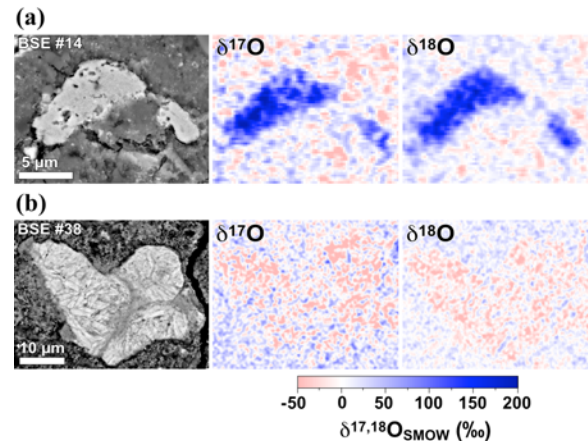


Fig. 1. Corresponding images of back scattered electrons and O-isotope ratios ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) in matrix. (a) new-PCP in Acfer 094, (b) PCP in Murchison.

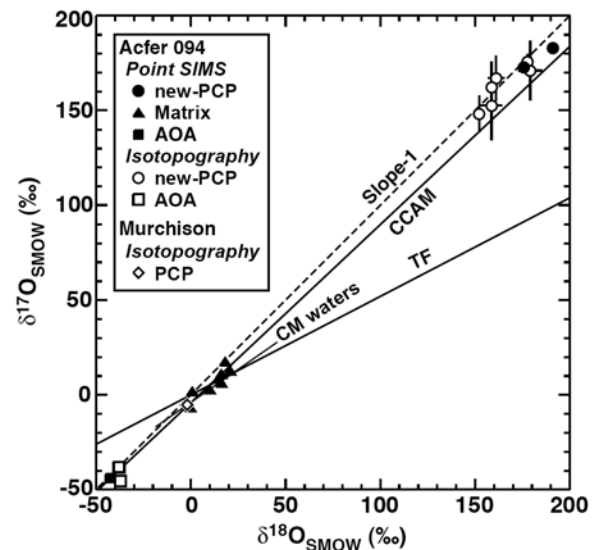


Fig. 2. Oxygen isotopic characteristics of new-PCP. Isotopography: analyzed by precise isotopic imaging using isotope microscope, Point SIMS: analyzed by conventional point analysis by SIMS, AOA: amoeboid olivine aggregate.