



Supporting Online Material for

Remnants of the Early Solar System Water Enriched in Heavy Oxygen Isotopes

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Published 14 June 2007 on *Science Express*
DOI: 10.1126/science.1142021

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Supporting Online Material

Materials and Methods

A polished thin section of a primitive carbonaceous chondrite Acfer 094 has been prepared for this study. The thin section was coated by a carbon evaporation film of about 30 nm in order to reduce electrostatic charging during high-energy electron and ion bombardments for chemical and isotopic analyses. A field-emission type scanning electron microscope (FE-SEM, JEOL JSM-7000F) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford INCAEnergy) has been used to analyze petrographical texture and chemical compositions.

A Hokudai isotope microscope system (*S1*) (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) (*S2*) in the chondrite matrices. 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 3×3 pixels was applied to Figures 1 and 2 to reduce the statistical error due to small ion integration of ^{17}O and ^{18}O . As a result, a spatial resolution of Figures 1 and 2 is 0.6 μm , and the oxygen isotopic precision per the spatial resolution is $\pm 25\%$ (σ) for $\delta^{17}\text{O}_{\text{SMOW}}$ and $\pm 10\%$ (σ) for $\delta^{18}\text{O}_{\text{SMOW}}$. On the other hand, the standard deviations of Table S1 were calculated from original image without the image processing. Other analytical methods for isotopography were described in detail elsewhere (*S1*, *S2*).

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 micro-probe ($2.0 \times 1.3 \mu\text{m}^2$) 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 $\delta^{17,18}\text{O}_{\text{SMOW}}$ -values for new-PCP and silicates, respectively. Other analytical procedures were described in detail elsewhere (*S3*).

Dead time correction of the electron multiplier would introduce an analytical artifact of systematic shift of oxygen isotopic compositions along the slope-1 line of Fig. 3. The dead time is estimated to be 16.0 ± 0.5 ns by measurements of Ti isotopes. Because the

dead time correction mainly modifies secondary ion intensities of the most dominant oxygen isotope, the count rates and the counting losses estimated by the dead time are shown in Table S2 for each measurement point. All measurements have been carried out similar conditions of secondary ion emission. Estimated counting losses of secondary ion intensities are smaller than oxygen isotopic variations between new-PCP and other phases. Such dead time corrections are not necessary to consider for the isotopography because the SCAPS is an integral type detector.

An analytical transmission electron microscope (ATEM, JEOL JEM-2010) equipped with EDS (Thermo Electron Noran system SIX) has been used to analyze crystal structure, crystal size, texture and compositions. A sample for ATEM study was directly cut out from the thin section by focused ion beam (FIB) method using SII NanoTechnology SMI3050TB instrument. A film of $\sim 8\mu\text{m} \times 8\mu\text{m} \times 50\text{ nm}$ was prepared and a 200 keV electron beam was used for the observation.

References

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Fig. S1(A) Transmission electron micrograph showing the texture of new-PCP. (B) a diffraction pattern and (C) an X-ray elemental spectrum from a single new-PCP grain. The main spots in the diffraction pattern are similar to those of magnetite (space group $Fd3m$); the weak extra spots indicate a 3-fold superstructure. This pattern is viewed along $[111]$ of the $Fd3m$ cell of the main spots.

Table S1

Table S1. Oxygen isotopic compositions (‰) of new-PCPs, tochilinite, matrix and AOA of meteorites. Averaging areas: # of analysis areas (μm^2) used for averaging.

$$\Delta^{17}\text{O}_{\text{SMOW}} = \delta^{17}\text{O}_{\text{SMOW}} - 0.52\delta^{18}\text{O}_{\text{SMOW}}$$

Object name	Analysis area	Averaging areas	$\delta^{17}\text{O}_{\text{SMOW}}$	σ_{mean}	$\delta^{18}\text{O}_{\text{SMOW}}$	σ_{mean}	$\Delta^{17}\text{O}$
Isotopography							
new-PCP of Acfer 094							
#14	0.8 x 0.8	5	167	12	161	4	83
#15	0.8 x 0.8	5	162	13	159	2	80
#17	2.0 x 2.0	5	176	4	178	3	83
#19	0.6 x 0.4	5	148	10	152	1	69
#20	0.6 x 0.6	5	153	18	159	6	70
#21	0.4 x 0.6	3	171	9	179	4	78
Tochilinite of Murchison							
#38	2.0 x 2.0	5	-5	2	-2	3	-4
AOA of Acfer 094							
#18	3.2 x 3.2	5	-45	4	-37	2	-26
#23	4.0 x 4.0	5	-38	2	-38	1	-18
Point SIMS							
new-PCP of Acfer 094							
#17-s29	2.0 x 1.3	1	183	3	191	2	84
#17-s47	2.0 x 1.3	1	173	4	176	3	82
Matrix of Acfer 094							
#s39	2.0 x 1.3	1	2	2	1	2	1
#s40	2.0 x 1.3	1	3	2	10	2	-2
#s41	2.0 x 1.3	1	18	3	18	2	8
#s43	2.0 x 1.3	1	9	2	15	1	1
#s44	2.0 x 1.3	1	13	3	21	2	2
#s45	2.0 x 1.3	1	-7	3	0	2	-6
#s46	2.0 x 1.3	1	11	2	16	2	3
#s49	2.0 x 1.3	1	6	2	16	2	-2
mean		8	7	3	12	3	1
AOA of Acfer 094							
#s50	2.0 x 1.3	1	-44	3	-43	2	-21

Isotopography: extracted from an isotope image by SCAPS using imaging SIMS.

Point SIMS: measured by an electron multiplier using an oval-shaped ion micro-probe. AOA: amoeboid olivine aggregate.

Table S2

Table S2. Secondary ion count rate (cps) and calculated counting loss (%) of $^{16}\text{O}^-$ secondary ion for each measurement point.

Object name	Count rate	Counting loss
new-PCP of Acfer 094		
#17-s29	5.3E+05	0.9
#17-s47	3.4E+05	0.5
Matrix of Acfer 094		
#s39	4.1E+05	0.6
#s40	3.6E+05	0.6
#s41	3.6E+05	0.6
#s43	4.0E+05	0.6
#s44	3.6E+05	0.6
#s45	3.2E+05	0.5
#s46	4.1E+05	0.7
#s49	4.4E+05	0.7
AOA of Acfer 094		
#s50	3.8E+05	0.6
Standard		
Olivine	4.1E+05	0.6
Magnetite	4.5E+05	0.7

Fig. S1.

