HOKKAIDO UNIVERSITY

Title	Discovery of 17,18 O-rich material from meteorite by direct-imaging method using stigmatic-SIMS and 2D ion detector
Author(s)	Sakamoto, Naoya; Itoh, Shoichi; Yurimoto, Hisayoshi
Citation	Applied Surface Science, 255(4), 1458-1460 https://doi.org/10.1016/j.apsusc.2008.05.052
Issue Date	2008-12-15
Doc URL	https://hdl.handle.net/2115/38751
Type	journal article
File Information	255-4_p1458-1460.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Discovery of ^{17,18}O-rich material from meteorite by direct-imaging method using stigmatic-SIMS and 2D ion detector

Naoya Sakamoto*, Shoichi Itoh, Hisayoshi Yurimoto

Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, JAPAN

Abstract

We report a discovery of a chemically and isotopically unique material distributed ubiquitously in fine-grained matrix of a primitive carbonaceous chondrite Acfer 094. The observations were made *in situ* using a novel high precision imaging technique adopted direct-imaging method. The material is extremely enriched in heavy oxygen isotopes of ^{17}O and ^{18}O of +18% relative to the Earth's ocean while previously reported variation of oxygen isotopes is as large as a range from –8% to 0%. Based on the unique chemical composition of the material, the abundance of the material in the meteorite matrix is calculated to be 94±20 (σ) ppm by volume using elemental mapping with a 7 μm^2 spatial resolution by FE-SEM-EDS on the meteorite thin section. The average size of identified materials is 5x5x5 μm^3. Therefore, isotope imaging capability over 500 x 500μm^2 area with micron resolution and an isotopic ratio precision of 1 percent is required to investigate about the presence of such material.

Keywords: Direct-imaging; Stigmatic-SIMS; Ion detector; Oxygen isotope; Meteorite; Solar System

1. Introduction

Isotopes are useful tracer to determine origin and circulation of elements in nature. In order to distinguish material with different origin, isotope ratio imaging has become increasingly critical in cosmo- and geo-chemistry.

Isotope imaging is achieved by raster-scanning and direct-imaging methods. The direct-imaging method uses stigmatic ion optics to transfer the sputtered ions from sample surface to two-dimensional ion-detector installed at the image plane of the optics with positional relationship. The spatial resolution of direct-imaging method is determined by the ion optics, whereas the raster-scanning method is limited by probe size. Therefore, direct-imaging method can increase probe intensity to increase the precision and shorten the measurement time without degradation of spatial resolution if the 2D detector has sufficient capability. Abundances of isotopes in natural materials are distributed over ranges of 6 orders of magnitude and their isotopic ratios are usually fluctuating less than percent order. In order to satisfy these conditions, a Stacked CMOS-type Active Pixel Sensor (SCAPS) has been proposed [1]. The SCAPS has high advantages over conventional systems including two-dimensional detection, wide dynamic range, no insensitive period, direct detection of charged particles, a high degree of robustness, and high fill factor [2]. High precision isotope ratio imaging of micro-scale under high mass resolution (isotopography) has been realized by the combination of a stigmatic secondary ion

* Corresponding author. Tel.: +81-011-706-2725; fax: +81-011-706-2725;
E-mail address: naoya@ep.sci.hokudai.ac.jp

mass spectrometry (SIMS) instruments (e.g., Cameca ims-1270) and SCAPS [1]. Here we demonstrate the ability of isotopography with chemically and isotopically unique material discovered in meteorite [3].

2. Experimental

Acfer 094 chondrite is the most primitive carbonaceous chondrite that shows no evidence of thermal alteration and minimal evidence of aqueous alteration [4]. The matrix of Acfer 094 contains the highest content of presolar silicate grains among meteorites [5,6]. Therefore, a polished thin section with carbon coating (30 nm depth) of an Acfer 094 chondrite was prepared for this study.

Oxygen isotopic ratios in meteorites follow not only by mass-dependent isotope fractionation law, but also by large mass-independent isotope fractionation (MIF) keeping nearly constant $^{17}O/^{18}O$ ratio. The observed MIF for oxygen is as large as a range of -80‰ < $\delta^{17,18}O_{SMOW}$ < 0‰ where $\delta^{i}O_{SMOW}$ (‰) ≡$[(^{i}O/^{16}O)_{sample}/(^{i}O/^{16}O)_{SMOW}$ - 1]×1000, i =17 or 18 and SMOW is the standard mean ocean water [7,8].

A Hokudai isotope microscope system [1] (Cameca ims-1270 + SCAPS) has been used for isotopography in the Acfer 094 matrix. A static Cs^+ primary beam of 20 keV has homogeneously irradiated the sample surface over ~80 μm in diameter with a beam current of ~0.3 nA (Fig. 1). 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 $^{12}C^-$, $^{13}C^-$, $^{12}C^-$, $^{27}Al^-$, $^{28}Si^-$, $^{16}O^-$, $^{18}O^-$, $^{16}O^-$, $^{17}O^-$, and $^{16}O^-$ in this order for one analytical sequence. The exposure time was 20s for $^{12}C^-$, 1000s for $^{13}C^-$, 100s for $^{27}Al^-$, 200s for $^{28}Si^-$, 20s for $^{16}O^-$, 3200s for $^{17}O^-$ and 1600s for $^{18}O^-$. Beam irradiation time for the sequence was ~2 hours. The sputtering depth was less than 200 nm for the sequence. A 50 μm contrast aperture was used and the mass interference contributions were cut by the exit slit to separate the $^{16}OH^-$ from $^{17}O^-$ sufficiently [1]. Typical spatial resolution under the condition of isotopography was ~0.3 μm estimated with the way of [9]. The width of a pixel of SCAPS corresponds to 0.2 μm on the sample surface and the typical count rate in a pixel was ~140 count/second for $^{16}O^-$. An image processing method of moving average with 3 x 3 pixels was applied to Fig. 1 to reduce the statistical error due to small ion integration of ^{17}O and ^{18}O. As a result, the spatial resolution is 0.6 μm, and the statistical error on the 0.6 x 0.6 μm^2 pixel is ±25‰ (σ) for $\delta^{17}O$ and ±10‰ (σ) for $\delta^{18}O$. Other analytical procedures were described in detail elsewhere [1,9].

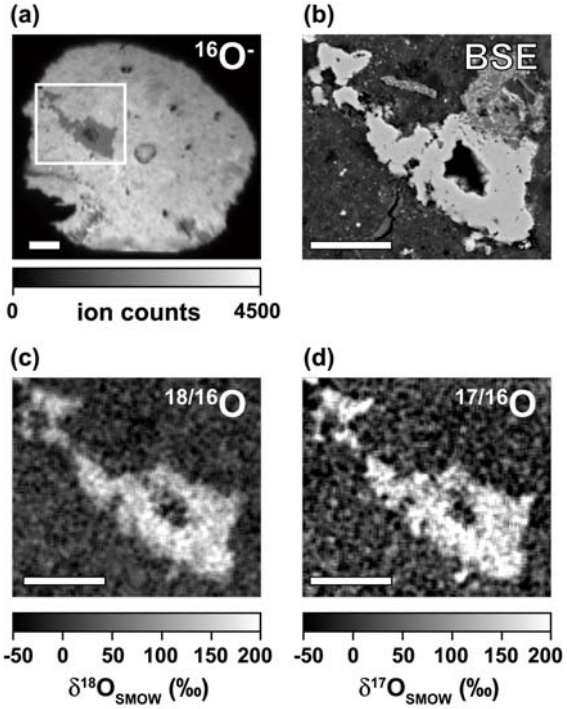


Fig. 1. One of analyzed area in Acfer 04 matrix. (a) $^{16}O^-$ image obtained by isotopography. Bright area corresponds to the size of primary ion beam. (b) Backscattered electron image of square region in (a). (c) (d) Isotope ratio images for $^{18}O/^{16}O$ and $^{17}O/^{16}O$. Scale bars are 10 μm.

A conventional point SIMS analysis has been also applied to determine oxygen isotopic compositions using the Cameca ims-1270. An oval-shaped Cs^+ ion micro-probe (2.0 x 1.3 μm^2) with 20 keV impact energy was used. Secondary ions of $^{16}O^-$-tail, $^{16}O^-$, $^{17}O^-$, $^{16}OH^-$, and $^{18}O^-$ were measured by an electron multiplier. Terrestrial magnetite and olivine standards were used to normalize secondary ion-ratios to the δO-values. Other analytical procedures were described in detail elsewhere [10].

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).

3. **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 [11,12] but O/S atom ratios are about 4 times larger in new-PCP than in tochilinite.

Ten new-PCP grains from Acfer 094 were analyzed by isotopography and one of them was analyzed by point SIMS. Amoeboid olivine aggregates (AOA) which reported as ^{16}O-rich material [13] and matrix

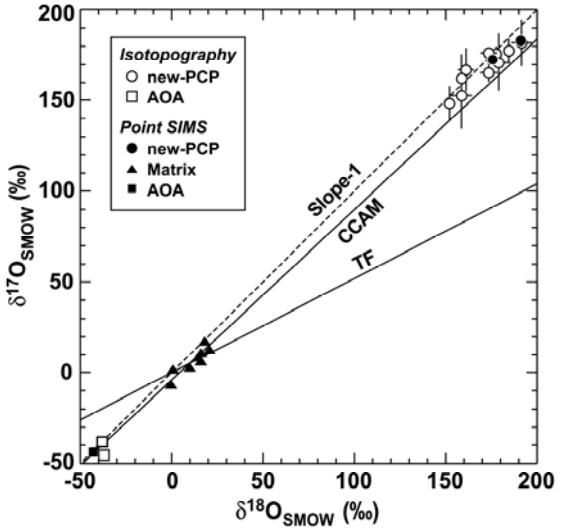


Fig. 2. Oxygen isotopic characteristics of new-PCP. Isotopography: analyzed by precise isotopic imaging using isotope microscope, Point SIMS: analyzed by conventional point analysis by SIMS, AOA: amoeboid olivine aggregate.

were also analyzed for reference. Isotopographs show that the new-PCP is significantly enriched in ^{17}O and ^{18}O relative to the matrix (Fig. 1). The matrix and AOAs are plotted in the range of the conventional variations (Fig. 2). On the other hand, the new-PCP is extremely enriched in ^{17}O and ^{18}O up to +180‰ and plotted on an extrapolation of the well-known carbonaceous chondrite anhydrous mineral (CCAM) [14] or slope-1 line [15] established by meteorite constituents (Fig. 2).

Based on the unique chemical composition of new-PCP, we have counted the new-PCP grains in a total 11mm^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 average size of identified new-PCP is 5x5x5 μm^3. The abundance of new-PCP in the matrix is calculated to be 94±20 (σ) ppm by volume and 3.3±0.7(σ) mm^{-2} for grain density in the matrix. Because the numbers of the new-PCP grains increase exponentially with

decreasing size toward the resolution-limit, this estimate must represent the lower limit of its abundance. Therefore, isotope imaging totally 500μm x 500μm area with micron resolution and an isotopic ratio precision of 1 percent would have been needed to discover a new-PCP grain when we do not know the existence of such material.

The mass-independent fractionation of oxygen isotopes in our Solar System is generally considered to have resulted from mixing of two isotopically distinct nebular reservoirs – ^{16}O-rich and ^{17,18}O-rich [6]. The material shows extremely large MIF enriched in ^{17}O and ^{18}O of +180‰ relative to SMOW. This extreme MIF shows that the oxygen isotopic heterogeneity in our solar system has extended more than three times larger ever believed. Because our Solar System has been believed resulting from mixing of ^{16}O-rich and ^{17,18}O-rich components, oxygen isotopic ratios of new-PCP are originated from an end member of primordial building blocks and provide new information for the formation history of early Solar System.

Recent theoretical studies suggest that O isotopic composition of water ice in the solar nebula was extremely enriched in ^{17}O and ^{18}O [16]. The enrichment factor of the water estimated to be 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.

4. Summary

A chemically and isotopically anomalous material was discovered from meteorite using a novel *in situ* high precision isotope imaging method. The abundance and the degree of isotopic anomaly show that the discovery of this new material required an isotope imaging instrument of percent order precision and micron resolution as we applied. The discovery of new-PCP is one of the successful applications that demonstrate the capabilities of isotopography.

Acknowledgement

We thank Y. Matsuhisa for providing a magnetite standard, and Y. Seto, K. Kuramoto, K. Fujino, K. Nagashima, A. N. Krot for discussion. This work was partly supported by Monkasho (H.Y.).

References

[1] H. Yurimoto, K. Nagashima and T. Kunihiro, Appl. Surf. Sci. 203/204 (2003) 793.

[2] I. Takayanagi, J. Nakamura, H. Yurimoto, E. R. Fossum, T. Kunihiro and K. Nagashima, IEEE Trans. Electron Devices 50 (2003) 1.

[3] N. Sakamoto, Y. Seto, S Itoh, K. Kuramoto, K. Fujino, K. Nagashima, A. N. Krot and H. Yurimoto, Science 317 (2007) 231.

[4] A. Greshake, Geochim. Cosmochim. Acta. 61 (1997) 437.

[5] K. Nagashima, A. N. Krot and H. Yurimoto, Nature 428 (2004) 921.

[6] A. N. Nguyen and E. Zinner, Science 303 (2004) 1496.

[7] R. N. Clayton, Science 313 (2006) 1743.

[8] S. Kobayashi, H. Imai and H. Yurimoto, Geochim. J. 37 (2003) 663.

[9] T. Kunihiro, K. Nagashima, H. Yurimoto, Geochim. Cosmochim. Acta. 69 (2005) 763.

[10] S. Itoh and H. Yurimoto, Nature 423 (2003) 728.

[11] L. H. Fuchs, E. Olsen and K. J. Jensen, Smithsonian Contrib. Earth Sci. 10 (1973) 1.

[12] K. Tomeoka and P. R. Buseck, Geochim. Cosmochim. Acta. 49 (1985) 2149.

[13] A. N. Krot, M. I. Petaev, S. S. Russell, S. Itoh, T. J. Fagan, H. Yurimoto, L. J. Chizmadia, M. K. Weisberg, M. Komatsu, A. A. Ulyanov, and K. Keil, Chem. Erde 64 (2004) 185.

[14] R. N. Clayton, Annu. Rev. Earth Planet. Sci. 21 (1993) 115.

[15] E. D. Young and S. S. Russell, Science, 282 (1998) 452.

[16] H. Yurimoto, K. Kuramoto, A. N. Krot, E. R. D. Scott, J. N. Cuzzi, M. H. Thiemens and J. R. Lyons, in Protostars and Planets V, (Ed.) B. Reipurth, D. Jewitt, K. Keil, Univ. Arizona Press, Tucson, AZ, 2007 p849.