

LETTER

New extreme ^{16}O -rich reservoir in the early solar system

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An enrichment of oxygen-16 of about 8% relative to the Earth has been found in a chondrule from the Acfer 214 carbonaceous chondrite. In contrast, isotopic abundances of major cations, Mg and Si, are similar to those of the Earth. These suggest that oxygen isotopic heterogeneity in the early solar system was much larger ever thought and assist mass-independent-isotopic fractionation for the origin. Because the chondrule has solar abundance for refractory and normal lithophile elements, we propose that silicate dusts in the early solar system were initially enriched in ^{16}O corresponding to the ^{16}O -rich reservoir.

INTRODUCTION

Primitive meteorites, i.e., chondrites, are kinds of cosmic sediments, agglomerations of solar nebular materials (McSween, 1999). Chondrites contain numerous sub-millimeter to millimeter size rounded objects called chondrules, which formed from molten droplets of ferromagnesian silicate precursors in the solar nebula (Grossman *et al.*, 1988). Refractory inclusions are tens of micrometer- to centimeter-sized objects known as the oldest solar material composed of refractory minerals having high vaporization temperatures ($>1300\text{K}$) in the solar nebula (MacPherson *et al.*, 1988). Refractory inclusions are classified into Ca-Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs) and are commonly present in chondrites as minor constituents (<10 volume %).

Oxygen isotopic variations have been observed in refractory inclusions and chondrules, but the reported variations are small in chondrules compared to refractory inclusions (Clayton, 1993). Oxygen isotopic compositions among chondrules from all chondrite groups are close to the terres-

trial value, typically within $+5/-10\%$ deviation in δ -notation ($\delta^i\text{O}_{\text{SMOW}} = \{({}^iR_{\text{sample}}/{}^iR_{\text{SMOW}}) - 1\} \times 1000$, ${}^iR = {}^i\text{O}/^{16}\text{O}$, $i = 17$ or 18 , SMOW: standard mean ocean water) (Fig. 1). In contrast, O isotopic compositions among refractory inclusions are enriched in ^{16}O relative to the terrestrial value typically up to $\delta^{17,18}\text{O}_{\text{SMOW}} \cong -40\%$. Thus, it is widely believed that ^{16}O -poor and -rich reservoirs of oxygen existed in the solar nebula.

Meteoritic records of oxygen isotope systematics between ^{16}O -rich and -poor reservoirs (Clayton, 1993) are an important tracer for origin and global evolution of early solar system because O accounts for over 50 atomic % of the terrestrial planets and is third in abundance, after H and He, in the solar nebular gas (Anders and Grevasse, 1989). The ^{16}O -rich reservoir has been recorded in minor meteoritic constituents having Ca-Al-rich composition with about 4% ^{16}O -enrichment relative to the earth (Clayton, 1993; MacPherson *et al.*, 1988). Other portions of meteorites are composed mostly of Mg-Si-rich materials having a ^{16}O -depleted composition similar to that of the earth (Clayton, 1993; McSween, 1999). Therefore,

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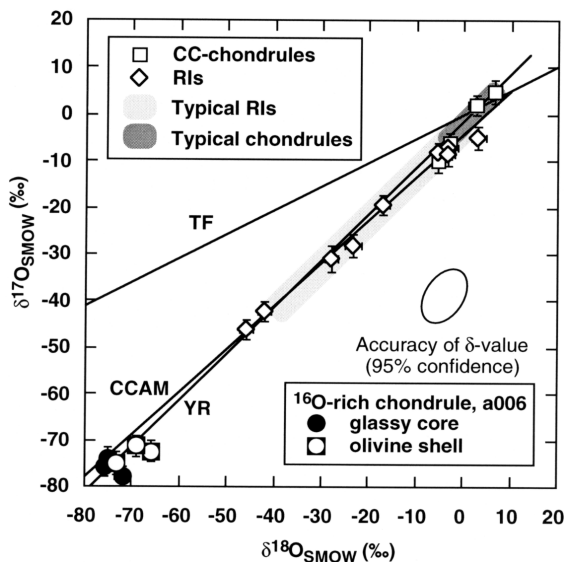


Fig. 1. Variation of oxygen isotopic compositions in typical chondrite constituents and the Acfer 214 CH chondrite. All measurements are plotted along carbonaceous chondrite anhydrous minerals (CCAM) line (Clayton, 1993) or slope-1 (YR) line (Young and Russell, 1998). O isotopic compositions of refractory inclusions (RIs) in this study are distributed over the range of typical RIs (Clayton, 1993; Itoh *et al.*, 2000) and overlap with reported RI values from CH chondrites (McKeegan *et al.*, 2002). O isotopic compositions of cryptocrystalline chondrules (CC-chondrules) are plotted over the range of typical chondrules (Clayton, 1993) except for a ^{16}O -rich chondrule, a006. All plots of RIs and chondrules can be explained by O isotope mixing between the ^{16}O -richest and ^{16}O -poorest CC-chondrules. TF: terrestrial fractionation line. Accuracy of δ -value for each plot is shown in an error ellipse of 95% confidence calculated by repeated analyses of the standard. Each value is shown in Table 1.

most solids in the solar nebula including chondrules were formed in the ^{16}O -poor reservoir, whereas refractory inclusions were formed in the ^{16}O -rich reservoir.

Here we report a chondrule with an ^{16}O -enrichment of about 8% relative to the earth. This value is twice the ^{16}O -enrichment of the conventional limit. Existence of such ^{16}O -rich chondrule has been predicted by the contemporaneous chondrule-CAI-formation model (Itoh and Yurimoto, 2003). This finding demonstrates that

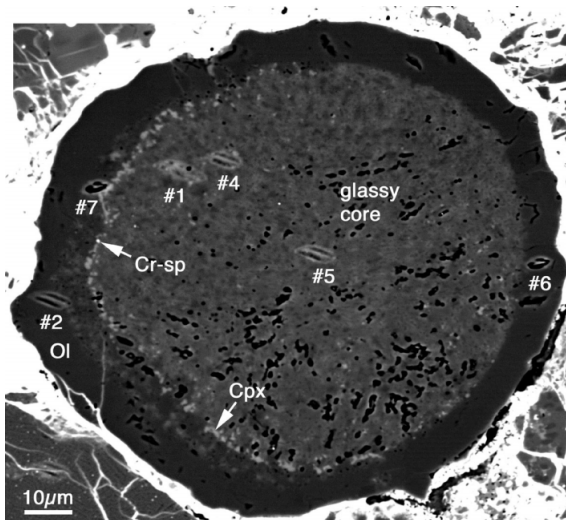


Fig. 2. Back-scattered electron image of an extremely ^{16}O -rich chondrule a006. Sputtered craters of O isotopic measurements (5 to 7 μm across) are shown by numbers. The numbers are shown in Table 1. Ol: olivine, Cpx: Ca-rich pyroxene, Cr-Sp: Chromium spinel.

dusts in the early solar system were originally enriched in ^{16}O corresponding to the ^{16}O -rich reservoir because it is believed that chondrules were formed from melting of precursor dusts that were abundant in the early solar system.

SAMPLE DESCRIPTIONS

An extreme ^{16}O -rich chondrule of $\delta^{17,18}\text{O}_{\text{SMOW}} \cong -75\text{‰}$ (Table 1), which we have designated a006, was found in a thin section of the Acfer 214 CH carbonaceous chondrite. In contrast, we have detected no difference for isotopic abundances for major cations, Mg and Si, in the chondrule from the terrestrial values (Table 2).

The a006 chondrule has spherical core-shell structure $\sim 130 \mu\text{m}$ across. The core is $\sim 100 \mu\text{m}$ across and shows multiple extinction under polarized optical microscope, indicating a nonporphyritic cryptocrystalline texture (Fig. 2). The core is composed of submicrometer-size crystalline minerals (probably olivine and enstatite) and Ca-Al-containing glass enclosing small vesi-

Table 1. Oxygen isotopic composition (‰) of Acfer 214

	$\delta^{17}\text{O}_{\text{SMOW}}$	σ_m	$\delta^{18}\text{O}_{\text{SMOW}}$	σ_m
chondrule; a006*				
glassy core				
#1	-78.0	2.1	-72.0	1.5
#4	-73.9	2.4	-75.2	1.3
#5	-75.7	2.2	-75.8	1.5
surrounding olivine shell				
#2	-75.0	2.5	-73.4	1.3
#6	-72.5	2.2	-65.9	1.6
#7	-71.3	2.3	-69.2	1.7
cryptocrystalline-chondrules				
a000	2.1	2.0	2.6	1.5
a005	4.8	2.4	6.8	1.4
a013	-6.0	2.0	-2.9	1.5
a014	-9.8	2.7	-5.3	1.4
refractory inclusions				
spinel-melilite-fassaite; a008				
spinel	-46.1	2.1	-45.9	1.4
spinel	-42.3	2.2	-41.8	1.4
grossite-melilite-fassaite; a009				
grossite	-28.2	2.6	-23.4	1.8
melilite	-30.9	2.8	-27.9	1.4
grossite-hibonite-spinel-melilite-fassaite; a011				
grossite	-7.1	2.5	-3.1	1.9
spinel	-8.1	2.1	-5.3	1.2
melilite	-4.9	2.4	3.2	1.6
fassaite	-8.5	2.3	-3.1	1.4
hibonite-spinel-melilite-fassaite; a001				
hibonite	-19.5	2.2	-17.0	1.5

*Numbers correspond to the analytical points in Fig. 2. In situ oxygen isotope analyses were collected with a TiTech Cameca 1270 SIMS instrument under analytical conditions previously described (Yurimoto *et al.*, 1998). σ_m : standard error.

cles. Chromian spinel of $<0.3 \mu\text{m}$ across appears on the surface as a minor phase. In contrast to typical cryptocrystalline chondrules, the core is surrounded by an olivine shell of $\sim 10 \mu\text{m}$ thick. Ca-rich pyroxene grains of $<1 \mu\text{m}$ across are concentrated at the boundary between the glassy core and olivine shell.

Chemical compositions of each layer are shown in Table 3. The olivine shell is composed of homogeneous forsterite (Fo_{99}). Assuming a spherical shell structure and a cross section along a great circle, the bulk composition of the chondrule has been calculated (Table 3). The Cr_2O_3 content may be underestimated because it is highly concentrated into small chromian spinel grains and is probably distributed heterogeneously in the core. The MgO content may be slightly over-

estimated because of possible oblique slicing of olivine shell on the surface. The bulk compositions are depleted in iron and moderately volatile elements such as Mn and Na. These characteristics are similar to other nonporphyritic chondrules in CH chondrites (Krot *et al.*, 2001). On the other hand, refractory and normal lithophile elements in the chondrule show close to solar abundance ratios. Major element compositions of this chondrule are similar to CR or O chondrites and plotted in chondrule compositional range of FeO-poor magnesian chondrules that are commonly observed in chondrites (Fig. 3). Chemically similar chondrules with cryptocrystalline and skeletal olivine textures have been observed in CH chondrites (Krot *et al.*, 2001).

DISCUSSION

Table 2. Mg and Si isotopic composition (‰) of glassy core in a006 chondrule

$\delta^{25}\text{Mg}_{\text{JB2}}$	$2\sigma_m$	$\delta^{26}\text{Mg}_{\text{JB2}}$	$2\sigma_m$	$\delta^{30}\text{Si}_{\text{JB2}}$	$2\sigma_m$	$\delta^{30}\text{Si}_{\text{JB2}}$	$2\sigma_m$
0.4	0.9	0.2	0.8	-3.6	0.9	-5.2	1.1

In situ isotope analyses were collected with a TiTech Cameca 1270 SIMS instrument under analytical conditions previously described (Yurimoto and Wasson, 2002). Definition of δ -values is the same manner as the case of oxygen isotopes. Terrestrial basalt standard, JB-2 issued by Geological Survey of Japan, was used for the normalization. Small mass-dependent fractionation relative to the terrestrial value is detected for Si isotope ratios.

Table 3. Representative chemical compositions (wt%) of a006 chondrule

	Ol	Cpx	Glassy core	Bulk*
SiO ₂	43.55	54.30	55.53	49.42
TiO ₂	0.07	0.38	0.13	0.11
Al ₂ O ₃	0.08	6.76	4.73	2.69
Cr ₂ O ₃	0.05	0.00	0.03	0.04
FeO	0.72	0.46	0.42	0.55
MnO	0.07	0.03	0.07	0.07
MgO	57.13	24.40	36.71	44.71
CaO	0.18	16.38	3.48	2.40
Na ₂ O	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00 </td <td>0.00</td> <td>0.00</td>	0.00	0.00
Total	101.86	102.70	101.11	100.00

*Calculated bulk composition normalized to 100%. An electron microprobe, JEOL JXA-8800, was used for measurements. Spot sizes of 1 μm for olivine in olivine shell (Ol) and for Ca-rich pyroxene (Cpx), and of 20 μm for glassy core were used. Compositions of the olivine shell and glassy core were averaged by ten and fifteen analyses, respectively. Only one analysis is available for the Ca-rich pyroxene composition because of the small size.

The cryptocrystalline texture with surrounding olivine shell and the spherical shape indicate that the a006 chondrule crystallized from a totally molten liquid droplet. The bulk chemical composition indicates that olivine is the first liquidus mineral. This crystallization sequence is consistent with the texture.

Oxygen isotopic compositions of cryptocrystalline chondrules in Acfer 214 are commonly ¹⁶O-poor (Fig. 1) and are distributed within the range of chondrules of other carbonaceous chondrites (Clayton, 1993). Refractory inclusions in Acfer 214 exhibit a range in $\delta^{17,18}\text{O}_{\text{SMOW}}$ from about -5 to -45‰ (Fig. 1), similar to refractory inclusions

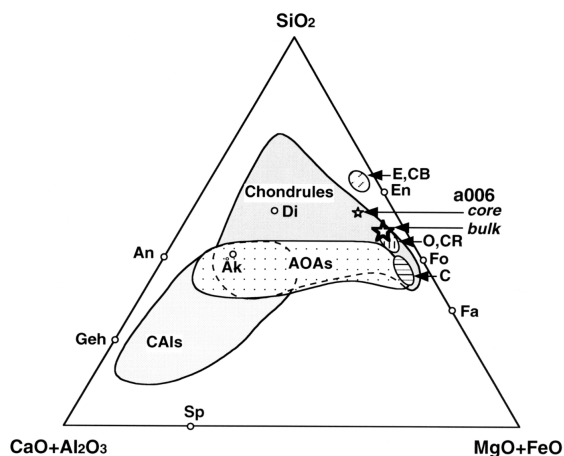


Fig. 3. Bulk compositions of an extremely ¹⁶O-rich chondrule a006 and various chondrite constituents. Refractory inclusions are basically classified into Ca-Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs). The compositions of minerals that are common in chondrules and refractory inclusions are also plotted for reference. Whole-rock compositions of carbonaceous chondrites are plotted in three separate regions indicating that iron is reduced in the CR clan (CR, CB) compared to other carbonaceous chondrite groups (C). An extremely ¹⁶O-rich chondrule a006 is plotted in the chondrule region and the major compositions are similar to whole-rock composition of CR or O chondrites. Sources of data are: CAIs from (Mason and Martin, 1977; McSween, 1977); AOAs from (McSween, 1977); chondrules from (Bischoff and Keil, 1984; McSween, 1977; Sheng *et al.*, 1991); Enstatite (E), Ordinary (O), Carbonaceous chondrites from (Haramura *et al.*, 1983; Jarosewich, 1990). Sp: spinel, Fo: forsterite, Fa: fayalite, Di: diopside, En: enstatite, An: anorthite, Geh: gehlenite, Ak: åkermanite.

in other CH-chondrites (McKeegan *et al.*, 2002). In contrast, the chondrule a006 is extremely enriched in ^{16}O with $\delta^{17,18}\text{O}_{\text{SMOW}} \cong -75\%$ and plotted on the carbonaceous chondrite anhydrous minerals (CCAM) line (Clayton, 1993) or slope-1 line (Young and Russell, 1998) extrapolated towards pure ^{16}O composition (Fig. 1). This is the lightest atomic weight of O in solids formed in the solar system ever found. The lightest O composition is homogeneously distributed in the whole chondrule.

The homogeneous distribution of O isotopic composition is consistent with complete melting origin of the chondrule indicating the liquid droplet of $\delta^{17,18}\text{O}_{\text{SMOW}} \cong -75\%$. Although large ^{16}O -enrichments had been only observed in refractory inclusions, oxygen isotopic compositions of refractory inclusions (Clayton, 1993; Itoh *et al.*, 2000, 2003) including Acfer 214 and other CH chondrites (McKeegan *et al.*, 2002) are distributed in $\delta^{17,18}\text{O}_{\text{SMOW}} > -50\%$ (Fig. 1). Therefore, refractory inclusions or refractory inclusion bearing chondrules (Krot *et al.*, 1999; Yurimoto and Wasson, 2002) are not appropriate candidates as a006 precursor.

Discovery of this chondrule demonstrates that the ^{16}O -rich reservoir in the solar system must have had an O isotopic composition of $\delta^{17,18}\text{O}_{\text{SMOW}} \leq -75\%$, which clearly exceeds the conventional ^{16}O -rich limit. The O isotopic heterogeneity observed in solar system is apparently explained by O isotope mixing between the cryptocrystalline chondrule of a006 and other cryptocrystalline chondrules having typical O isotopic values (Fig. 1). These results indicate that chondrule precursors had very wide variations of ^{16}O -enrichment. We emphasize that the maximum ^{16}O -enrichment is observed in a chondrule but not in refractory inclusions. Therefore refractory inclusions previously reported are not a proxy for a pristine signature of ^{16}O -rich reservoir in the early solar system. Refractory inclusions have experienced some modification to change not only chemical composition but also O isotopic composition.

As discussed previously, chondrule a006 is

depleted in moderately volatile elements, similar to other cryptocrystalline chondrules from CH chondrites that may have formed from direct liquid condensation from a hot nebular gas with complete dust evaporation (Krot *et al.*, 2001). Another possibility is the conventional chondrule forming model (i.e., chondrules were formed by flash melting of precursor dusts (Grossman *et al.*, 1988)). In either case, existence of the ^{16}O -rich chondrule suggests that an ^{16}O -rich reservoir was present during chondrule formation. The degree of ^{16}O -enrichment was much larger than that of refractory inclusion formation.

IMPLICATIONS FOR OXYGEN ISOTOPIC HETEROGENEITY IN THE SOLAR NEBULA

Since the extreme ^{16}O -rich chondrule has the major element composition of a representative solid expected in the solar nebula, it is plausible that the ^{16}O -rich reservoir was globally distributed in the early solar system. Although temporally and/or spatially heterogeneous O-isotopic reservoirs existed in the early solar system, if we can apply Ockham's razor, origin of the ^{16}O -rich chondrule can be explained by a simple nebular setting for two O isotopic reservoirs, i.e., the ^{16}O -rich reservoir is common nebular dust and the ^{16}O -poor reservoir is the solar nebular gas, and contemporaneous chondrule-CAI-formation process (Itoh and Yurimoto, 2003). The extreme ^{16}O -rich composition of $\delta^{17,18}\text{O}_{\text{SMOW}} \cong -75\%$ suggests that the chondrule a006 was formed by flash heating in an area having the largest dust enrichment or largest gas depletion ever found, i.e., dust heating in very low pressure (Itoh and Yurimoto, 2003; Yurimoto *et al.*, 2001). A ^{16}O -rich gaseous reservoir in the solar nebula (Krot *et al.*, 2002) would have temporarily existed during dust evaporation in such high dust/gas region. Subsequent thermal nebular events gradually erased the extreme ^{16}O -enrichment of dusts through isotopic dilution with surrounding abundant ^{16}O -poor nebular gas. The ^{16}O -rich chondrules certainly more primitive than others found, and so it could be older.

Although the extreme ^{16}O -enrichment in the

chondrule may have a nuclear origin, a model of injection of ^{16}O -enriched nucleosynthetic materials into the solar nebula (Clayton *et al.*, 1973) is implausible for the origin because no clear nucleosynthetic evidence has been observed in Mg and Si isotopes in a006 (Table 2). This interpretation is consistent with the lack of a correlation between ^{16}O -rich compositions and anomalies in stable isotopic systems (e.g., in Ti, Ca, Cr) attributed to nucleosynthetic sources (Clayton, 1993). Therefore we infer that the ^{16}O variations in the solar system have resulted from mass-independent-isotopic fractionation in the solar nebula (Clayton, 2002; Kitamura and Shimizu, 1983; Thiemens and Heidenreich, 1983) or in the parent molecular cloud (Yurimoto and Kuramoto, 2002) and the magnitude of initial ^{16}O variations among O isotopic reservoirs was larger than 10% in the early solar system. The ^{16}O -rich value of ~10% may represent bulk O isotopic composition of our solar system if O isotopic fractionation processes by Yurimoto and Kuramoto (2002) occurred.

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