Discovery of non-radiogenic tungsten isotopic anomalies in the Allende CV3 chondrite

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We have measured high-precision W isotope ratios for series of carbonaceous and ordinary chondrites. The resulting $^{184}W/^{183}W$ ratios for three carbonaceous chondrites (Murchison CM2, Y-793321 CM2, and Y-86751 CV3) did not vary significantly from that of the W isotopic standard (NIST SRM 3163) and various terrestrial rocks, whereas the $^{184}W/^{183}W$ ratios for Allende CV3 showed ~0.4ε lower value than the other chondrites and terrestrial samples. This deficiency in the measured $^{184}W/^{183}W$ ratio for the Allende CV3 could not be attributed to the incomplete digestion of acid-resistive presolar components such as SiC grains with abundant s-process nuclides, because the SiC contents in the Allende was significantly lower than those for other carbonaceous chondrites. Several possible explanations for the deficiency in the ^{184}W found in the Allende CV3 were explored. We conclude the results could be best explained by the isotopic heterogeneity of W by contribution of r-process enriched components to the source material of the Allende CAIs. The finding is consistent with the recent observation of some CAIs in Allende was enriched in the r-process nuclide of W (Burkhardt et al., 2008) and supported by the fact that the CAI contents in the Allende chondrite are significantly higher than that in other carbonaceous chondrites.

Keywords: W isotopes, isotope heterogeneity, chondrites, nucleosynthesis, GCR exposure age

INTRODUCTION

The β-decay of short-lived nuclide ^{182}Hf with the half-life of 8.90 ± 0.09 Myr (Vockenhuber et al., 2004) can produce the variation in the isotopic composition of ^{182}W in the geochemical samples, provided the samples were coming from a reservoir formed sufficiently early (i.e., during the life time of ^{182}Hf, circa 60 Ma from the beginning of the Solar System). In the past decade, precise W isotope measurement enabled us to discuss the timing of the core-mantle differentiation during the planetary accretion in the early Solar System (Lee and Halliday, 1995, 1996; Harper and Jacobsen, 1996; Kleine et al., 2002, 2005; Yin et al., 2002a; Schoenberg et al., 2002; Schérsten et al., 2004; Quitté et al., 2000, 2005; Quitté and Birck,

2004; Markowski et al., 2006). All the chronological discussions for the timing of planetary accretion or core formation are based on an assumption that the isotopic composition of Hf and W in the early solar nebula was homogenous. However, whether this assumption was satisfied in general or only in some special cases were not closely examined until recently.

All the W stable isotopes are produced through various stellar nucleosynthesis processes. The solar W isotopic abundances should have received contributions from all of these various nucleosynthetic sources. Therefore, it is natural to expect that the isotopic compositions of W in meteorites can vary with the different mixing ratios of materials from different stellar sources. Different stellar processes producing W isotopes could be r-, s-, and p-processes. At very high-neutron flux environment such as supernova explosion, ^{182}W, ^{183}W, ^{184}W, and ^{186}W isotopes are produced through the rapid-neutron capture reaction (r-process). Moreover, ^{182}W, ^{183}W, ^{184}W, and ^{186}W isotopes can also be produced through slow neutron addition known as s-process, in which radionuclides have time to decay before acquiring another neutron in a stellar environment where a neutron flux was not quite high enough such as an asymptotic giant branch (AGB) star (Burbidge et al., 1957; Arlandini et al., 1999). The minor

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W isotope (^{180}W) could be produced through the so-called *p*-process, which included the photodisintegration reactions associated with the supernova.

Although isotopes for various elements would have come from different stellar sources and nucleosynthetic processes, it has been suggested that the isotopic systems in the solar system were homogenized in the very early stage of the solar system formation and that contributions of different stellar nucleosynthetic processes were diminished by homogenization. However, a series of recent studies using high precision multiple collector-inductively-coupled-plasma-mass spectrometry (MC-ICP-MS) and thermal ionization mass spectrometry (TIMS) have revealed that the isotopic homogeneity for many elements in meteoritic materials are not warranted (e.g., Mo, Yin *et al.*, 2002b; Dauphas *et al.*, 2002; Becker and Walker, 2003; Ba, Hidaka *et al.*, 2003; Ranen and Jacobsen, 2006; Carlson *et al.*, 2007; Nd, Sm, Andreasen and Sharma, 2006; Carlson *et al.*, 2007; Cr, Trinquier *et al.*, 2007; Ni, Regelous *et al.*, 2008; W, Qin *et al.*, 2008; Os, Brandon *et al.*, 2005; Yokoyama *et al.*, 2007). Qin *et al.* (2008) first reported the significant level of ^{184}W deficiencies in ~0.1ε units from the IVB iron meteorites. The resulting variations in the isotopic composition of ^{184}W found in the IVB iron meteorites was attributed to reflect the heterogeneous distribution of *s*- and *r*-process nuclides at the nebula scale for the source materials of parent body of the IVB irons accreted (an asteroid of ~2–4 km radius; Haack *et al.*, 1990). If in the case that the W isotopes were heterogeneously distributed in the early solar nebula, the resulting Hf–W age data would require scrutiny.

Some of the mineral grains in chondrites retain a memory of presolar conditions. The refractory inclusions in chondrites tell us of the earliest recoded events in the solar system. Much chemical processing occurred very early, which resulted in the formation of CAIs, chondrules, separation of metal, sulfide, and silicate phases, and depletion of volatile elements in the inner parts of the solar nebula. At an early stage, the nebula refers to a fragment that separated from a molecular cloud. At a slightly later stage, the solar nebula refers to the disk of dust and gas remaining during and after the formation of the Sun, and from which the planets, satellites, and asteroids were formed. There has been a general consensus that the composition of the original nebula, assuming solar photospheric spectra estimates the composition of the solar nebula, is given by that of carbonaceous chondrites. Thus, the homogeneity/heterogeneity of the elemental and isotopic compositions for chondrites can provide us insights on processes occurred within the solar nebula. To investigate the further possible heterogeneity of the W isotopic composition in the solar nebula, we have measured the W isotopic ratios (^{182}W/^{183}W and ^{184}W/^{183}W) from series of carbonaceous and ordinary chondrites.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The carbonaceous and ordinary chondrites subjected to the isotopic analysis of W were two CV3 chondrites (Allende and Y-86751), two CM2 chondrites (Murchison and Y-793321), and four ordinary chondrites (Gruver H4; Salaices H4; Landry West L4; NWA869 L5) in order to evaluate the potential W isotopic heterogeneities among the parental planetesimals. Meteorite samples were cut into the small pieces of 1~3 g. These fragments were washed by deionized water (purified by Milli-Q, Millipore LTD, Massachusetts, USA) with an ultrasonic bath for ten minutes. This was followed by crushing and grinding with an agate mortar. All stony meteorites were dissolved in a mixture of HF–HNO$_3$–HClO$_4$ (5:3:2) in precleaned Savillex vials at ~180°C on a hotplate. After the digestion, the samples were dried and re-dissolved in 6 M HCl. The resulting sample solution for stony meteorites was then heated up to dryness, and was redissolved in 30 mL of 0.5 M HF-2 M HCl. The sample solution was then passed through the chemical separation procedure.

The chemical separation of W from the matrix was carried out using two-stage anion exchange columns modified after the procedure described in Quitté *et al.* (2002) and Irisawa and Hirata (2006). An anion exchange resin (BIORAD AG 1X8, 200–400 mesh, chloride form) was used for both the first (10 mL) and the second (1 mL) separation techniques. The column for the first chemistry step were cleaned successively with 30 mL of 0.5 M HF-4 M HCl, 30 mL of deionized water, 30 mL of 5 M HNO$_3$, and 30 mL of deionized water. This cleaning procedure was repeated twice to minimize possible cross contamination of W. This was followed by the conditioning procedure by loading 15 mL of 2 M HF, and then, about 30 mL of sample solution was loaded onto the column. Matrix elements and possible mass spectrometry interfering elements were eluted and removed by loading 10 mL of 0.5 M HF-2 M HCl, 10 mL of 1 M HF, and 5 mL of 0.5 M HF-4 M HCl, and W was collected by adding 35 mL of 0.5 M HF-4 M HCl mixture. The recovered W-fraction was heated to dryness at 120°C for overnight, and the resulting residue was then redissolved in 5 mL of 0.6 M HF-0.6% H$_2$O$_2$. The dissolved sample solution was subjected to the chemical separation procedure using the second column.

The second column (1 mL) was preconditioned by 5 mL of 2 M HF before the sample solution was loaded. After washing with 10 mL of 1 M HCl-0.9% H$_2$O$_2$ and 1 mL of 0.5 M HF-4 M HCl, W was eluted with 10 mL of 0.5 M HF-4 M HCl. The main purpose of this clean-up step is to remove other high-field strength (HFS) elements, such as Hf or Nb. Prior to the W isotopic analysis, W separated by the second column was re-dissolved in a mixture of HNO$_3$–H$_2$O$_2$ to remove residual Os, and then

Table 1. Summary of the present $\varepsilon^{182}W$ and $\varepsilon^{184}W$ values for carbonaceous and ordinary chondrites

Sample		Instruments	n	$\varepsilon^{182}W$		2S.E.	$\varepsilon^{184}W$		2S.E.	
Carbonaceous chondrite										
Allende #1	CV3	Nu Plasma 500		−1.75	±	0.48	−0.35	±	0.39	
Allende #2	CV3	Nu Plasma 500		−1.91	±	0.45	−0.39	±	0.31	
Allende #3	CV3	Nu Plasma 500		−2.48	±	0.56	−0.70	±	0.37	
Allende #4	CV3	Nu Plasma 500		−2.14	±	0.56	−0.50	±	0.33	
Allende #5	CV3	Nu Plasma 500		−1.95	±	0.40	−0.56	±	0.26	
Allende #6	CV3	Nu Plasma 500		−1.74	±	0.42	−0.29	±	0.31	
Allende #7	CV3	Nu Plasma HR		−2.51	±	0.56	−0.12	±	0.39	
Allende #8	CV3	Nu Plasma HR		−1.48	±	0.39	−0.51	±	0.22	
Allende #9	CV3	Nu Plasma HR		−1.56	±	0.34	−0.08	±	0.21	
average	CV3	Nu Plasma	9	−1.95	±	0.25	−0.39	±	0.14	
Allende	CV3	IsoProbe	1	−1.90	±	0.40	0.00	±	0.50	Kleine *et al.*, 2002
(recalculated)	CV3	IsoProbe	5	−1.96	±	0.30	−0.02	±	0.27	Kleine *et al.*, 2004
(recalculated)	CV3	Neptune	1	−1.99	±	0.29	−0.09	±	0.20	Schérsten *et al.*, 2004
(recalculated)	CV3	Neptune	1	−2.16	±	0.23	−0.26	±	0.26	Schérsten *et al.*, 2004
Y-86751	CV3	Neptune	1	−2.06	±	0.29	0.08	±	0.24	
Murchison #1	CM2	Neptune		−2.03	±	0.03	−0.26	±	0.11	
Murchison #2	CM2	Neptune		−1.66	±	0.51	0.37	±	0.30	
Murchison #3	CM2	Neptune		−1.99	±	0.36	0.29	±	0.31	
average	CM2	Neptune	3	−1.89	±	0.24	0.13	±	0.39	
(recalculated)	CM2	IsoProbe	1	−1.40	±	0.40	0.04	±	0.35	Kleine *et al.*, 2002
Y-793321	CM2	Neptune	1	−1.74	±	0.25	0.14	±	0.23	
CC average			4	−1.91	±	0.13	−0.01	±	0.26	
Ordinary chondrite										
Gruver	H4	Nu Plasma	1	−2.34	±	0.39	0.02	±	0.33	
Salaices	H4	Nu Plasma	1	−1.63	±	0.42	0.22	±	0.28	
Landry west	L4	Nu Plasma	1	−1.86	±	0.36	0.08	±	0.31	
NWA869	L5	Nu Plasma	1	−1.60	±	0.43	0.01	±	0.45	
OC average			4	−1.85	±	0.34	0.08	±	0.10	

heated up to dryness at 120°C. To achieve the quantitative removal of Os from the analyte, this procedure was repeated 3-5 times. This was followed by the re-dissolution of W with 0.05% TMAH (Tetra Methyl Ammonium Hydroxide, prepared by Tama Chemicals, Kawasaki, Japan) or 0.01 M HF-0.5 M HNO_3 in order to introduce W solution into a MC-ICP-MS. Total procedural blanks were <900 pg for the W isotope composition measurements.

In this study, isotopic analysis of W was made by a multicollector-ICP-mass spectrometer (MC-ICP-MS). The MC-ICP-MS instruments used in this study were a Nu Plasma 500 (Nu Instruments, Wrexham, Wales, UK) at Tokyo Institute of Technology, a Nu Plasma HR at UC Davis, and a Neptune (Thermo Fisher Scientific Inc., Waltham, MA, USA) at Kochi Institute for Core Sample Research. Tungsten isotope ratios for Allende CV3 and ordinary chondrites were determined by the Nu Plasma 500, and W isotope ratios for Allende CV3 have been measured by the Nu Plasma HR at Davis. The other three carbonaceous chondrites have been analyzed by the Neptune at Kochi. Operating conditions have been described in our previous study (Irisawa and Hirata, 2006). Tungsten isotope compositions were typically measured with a signal intensity of ~1.4 V on ^{183}W, which was obtained for 500 ppb of W solution at Tokyo Tech and for ~100 ppb of W solution at UC Davis. For these samples, 40 ratios (1 blocks of 40 ratios, 5 s integrations) were measured. The analytical uncertainties are two standard errors for 40 ratios on one sample for independent chemical separation procedure, and average W isotope data for Allende CV3, Murchison CM2, CC, and OC are 2 standard errors.

RESULTS

The results of W isotopic compositions are summarized in Table 1 and Fig. 1. The normalization value of $^{186}W/^{183}W$ = 1.985935 (Völkening *et al.*, 1991) was adopted in all the $^{182}W/^{183}W$ and $^{184}W/^{183}W$ isotope ratio measurements. The data are expressed as parts per 10,000 deviation from the terrestrial standard NIST SRM 3163,

$$\varepsilon^{x}W = [(^{x}W/^{183}W)_{Sample}/(^{x}W/^{183}W)_{NIST\text{-}3163} - 1] \times 10,000$$
$$(x = 182 \text{ or } 184). \quad (1)$$

The resulting $\varepsilon^{182}W$ value were $-1.95 \pm 0.25\varepsilon$ for Allende (CV3), $-2.06 \pm 0.29\varepsilon$ for Y-86751 (CV3), $-1.89 \pm 0.24\varepsilon$ for Murchison (CM2) and $-1.74 \pm 0.25\varepsilon$ for Y-793321 (CM2). The overall average of $\varepsilon^{182}W$ value for the carbonaceous and ordinary chondrites (Gruver H4, Salaices H4, Landry West L4, and NWA869 L5) were $-1.91 \pm 0.13\varepsilon$ and $-1.85 \pm 0.34\varepsilon$, respectively. The present $\varepsilon^{182}W$ values for carbonaceous and ordinary chondrites did not vary significantly within and among the chondrite groups. The results are consistent with the previously reported data (Kleine *et al.*, 2002, 2004; Yin *et al.*, 2002a).

For other W isotopes, the resulting $\varepsilon^{184}W$ values show $-0.39 \pm 0.14\varepsilon$ for Allende (CV3), $-0.08 \pm 0.24\varepsilon$ for Y-86751 (CV3), $0.04 \pm 0.35\varepsilon$ for Murchison (CM2), $0.14 \pm 0.23\varepsilon$ for Y-793321 (CM2), demonstrating that the $\varepsilon^{184}W$ value for Allende CV3 was significantly lower than that for terrestrial standard NIST SRM 3163. The $\varepsilon^{184}W$ values calculated by the average of carbonaceous and ordinary chondrites were $-0.01 \pm 0.26\varepsilon$ and $0.08 \pm 0.10\varepsilon$, respectively. This indicates the good agreement with the $\varepsilon^{184}W$ data for the most other carbonaceous chondrites except for the Allende CV3. There is a clear deficit of $\varepsilon^{184}W$ for Allende CV3 relative to the terrestrial standard materials (NIST SRM 3163, igneous and sediment rocks) and other chondrites.

Our $\varepsilon^{184}W$ data for Allende CV3 are consistent with the previously reported values, but all the previous results show significantly larger analytical uncertainties. Our precise $^{184}W/^{183}W$ isotope data, however, revealed the difference in the $\varepsilon^{184}W$ between the Allende CV3 and other carbonaceous chondrites. As indicated in the Table 1 and Fig. 1, the resulting $\varepsilon^{184}W$ data for Allende CV3 was based on nine repeated analyses of separate sample pieces, independent chemical separation procedure of W and different analysis date on different instruments. To test the possible artifact in the $\varepsilon^{184}W$ values for the Allende, we have measured the $\varepsilon^{184}W$ data from same type of carbonaceous chondrite (Y-86751) as an analogous chemical composition to the Allende. Despite the similar petrologic type of chondrite group, the $\varepsilon^{184}W$ values for the Y-86751 CV3 showed good agreement with other carbonaceous chondrites, and no significant deficiency in the $\varepsilon^{184}W$ was found for Y-86751 CV3. Although the
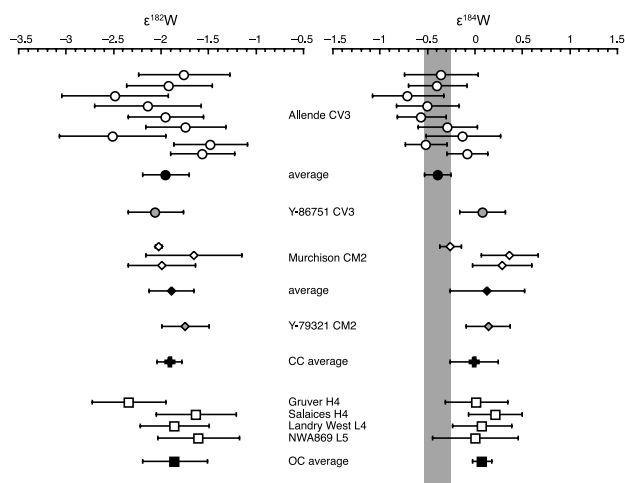

Fig. 1. The $\varepsilon^{182}W$ and $\varepsilon^{184}W$ values for carbonaceous and ordinary chondrites obtained in this study. Solid symbols show average of W isotope data for the chondrites. Gray and open symbols indicate W isotope data through individual chemical separation procedure. The gray bar shows the average of $\varepsilon^{184}W$ for Allende CV3 chondrite.

number of W isotopic data for the CV3 chondrites was very limited in the present study, the deficiency in the $\varepsilon^{184}W$ was a unique feature only found in the Allende so far.

DISCUSSION

There are several possible explanations for the deficit in the $\varepsilon^{184}W$ for the Allende, including (a) the nuclear reaction induced by the galactic cosmic-ray (GCR), (b) nucleosynthesis effects (incomplete digestion of insoluble presolar components, contribution of isotopically heterogeneous presolar-W carrier phases, or heterogeneous distribution of W isotopes in the early solar nebula).

Cosmogenic effects by galactic cosmic-ray

Concerning the nuclear effect induced by the GCR, several explanations for the changes in the W isotope compositions for meteorites have been offered, such as nuclear spallation, neutron capture or ^{182}W-burnout reactions induced by the GCR (Masarik, 1997; Leya *et al.*, 2003; Markowski *et al.*, 2006). Masarik (1997), Leya *et al.* (2003), and Markowski *et al.* (2006) demonstrated that the $^{182}W/^{184}W$ ratio for iron meteorites could change by about 0.6ε, after the irradiation by GCR for 1 Gyr. W isotopic composition changes as a function of GCR exposure duration and the meteorite radius (or meteoroid size) as the effect depends on the exact location (depth) of the sample within the meteorite. It should be noted that the cosmic-ray exposure age for iron meteorites is generally longer than that for other meteorites, including

Table 2. *The calculated atomic percentage of s- and r-processes for each isotope listed are based on the stellar model from Arlandini et al. (1999)*

	^{182}W	^{183}W	^{184}W	^{186}W
s-process (%)	46	54	71	50
r-process (%)	54	46	29	50

chondrites. In fact, the GCR exposure age for the Allende chondrites estimated from the $^3He/^{21}Ne–^{22}Ne/^{21}Ne$ isotopes is only ~5 million years (Scherer and Schultz, 2000), while the exposure age for iron meteorites is typically between 200 and 1000 Ma (e.g., Herzog 2006). This indicate that the possible changes in the $\varepsilon^{184}W$ value for the Allende CV3 could be much smaller than ~0.1ε. Consequently, the contribution of the GCR-induced nuclear effects must be negligible.

Nucleosynthesis effects

The variations of the W isotopes due to different contribution of two or more nucleosynthetic processes can be evaluated by their isotopic composition of W in the corresponding stellar environment (Arlandini *et al.*, 1999). In their model, the s-process yields are 46%, 54%, 71% and 50% for ^{182}W, ^{183}W, ^{184}W and ^{186}W, respectively (Table 2). It should be noted that the ^{184}W was preferentially produced through the s-process. In this study, we have used $^{186}W/^{183}W$ ratio for the correction of the mass discrimination effects in instruments. The difference in the s- and r-process components on ^{184}W would be most readily identifiable (Table 2). We therefore suggest the observed deficit in the $^{184}W/^{183}W$ ratio for Allende CV3 is due to the heterogeneous distribution of s- and r-processes in the solar nebula, or source material of the Allende and other chondrites. A caveat must be noted to Arlandini *et al.* (1999) distribution. After the Arlandini *et al.* (1999) paper was published, the neutron capture cross section of ^{182}Ta was revised downward by 50%, which increased the production of ^{182}W by 40%. This has been discussed in (Qin *et al.*, 2008). We discuss the issue further below (Fig. 2) and conclude such an effects is not resolvable with the current precision on $\varepsilon^{182}W$.

(1) Influence of s-process enriched components Present W isotopic compositions for the Allende chondrites exhibited the clear difference from that for the Bulk Silicate Earth and the other chondrites. One possibility is that s-process components such as presolar SiC grains were not digested completely, because presolar SiC grains are extremely acid resistant and strongly enriched in s-process nuclides (Nittler, 2003; Zinner *et al.*, 2003).

Tungsten, as well as metallic Os, is one of the most refractory elements. Recently, Os isotopic composition
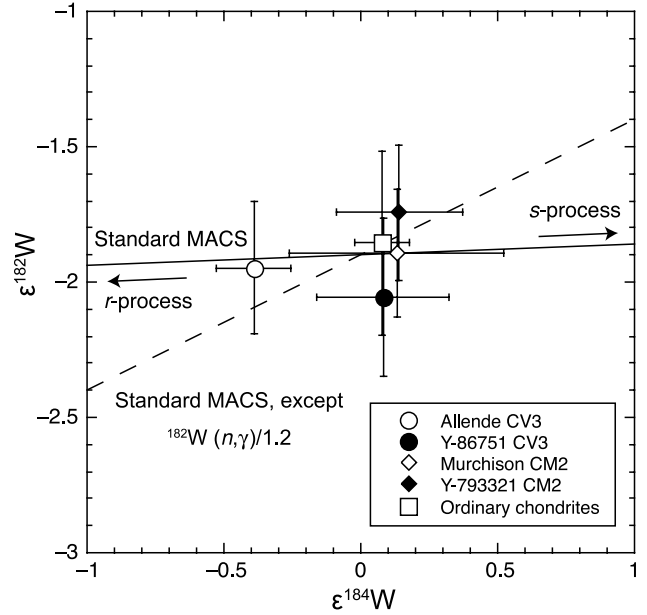

Fig. 2. *Correlation between $\varepsilon^{184}W$ and $\varepsilon^{182}W$ (both normalized to $^{186}W/^{183}W$) for various proportions of s- and r-process W in chondrites. The $\varepsilon^{184}W$ and $\varepsilon^{182}W$ correlation lines were calculated by Qin et al. (2008) using recommended values of Maxwellian-averaged (n, γ) cross sections (MACS, Bao et al., 2000). The dashed line is obtained by using a ~20% reduction in the ^{182}W production from that of Arlandini et al. (1999) due to ~50% increase in ^{182}Ta cross-section, which would yield more realistic results for the ^{182}W r-process component (see Qin et al., 2008). As shown in Fig. 2, the effect on ^{182}W is small, and not resolvable with the current analytical precision. Therefore, the impact on $^{182}Hf–^{182}W$ chronology is expected to be minimal.*

in various bulk chondrites were precisely measured and significant deficit in isotopes with large contribution from s-process nucleosynthesis (^{186}Os, ^{188}Os, and ^{190}Os) were found in some carbonaceous and possibly enstatite chondrites (Brandon *et al.*, 2005). Brandon *et al.* (2005) concluded that the deficiency in the s-process nuclides may reflect the incomplete acid dissolution of the chondrites, with acid insoluble SiC hosting the complementary enriched Os. In fact, Os isotopic data obtained from total decomposition using an alkaline fusion demonstrated that the $^{186}Os/^{189}Os$, $^{188}Os/^{189}Os$, and $^{190}Os/^{189}Os$ ratios did not vary measurably (Yokoyama *et al.*, 2007). The SiC contents in Murchison CM2 and Allende CV3 meteorite were 13.5 ppm and 0.0062 ppm, respectively (Huss *et al.*, 2003). A factor of 2000 difference in SiC content in the two meteorites suggests that the present deficiency in ^{184}W isotope found in the Allende cannot be attributed to the presence or absence of the acid insoluble components including presolar SiC grains. The point was highlighted in Yin *et al.* (2002b) with Mo iso-

tope anomalies.

For individual isotope data in Murchison CM2, the ε^{184}W value for Murchison #1 is significantly lower than that for Murchison #2 and #3 (Table 1 and Fig. 1). This variation could not be due to cosmogenic effects induced by the galactic cosmic-ray, because the exposure age of Murchison CM2 is 1.8 ± 0.3 Ma (Herzog *et al.*, 1997). It is likely that the variation was due to *s*-process deficit caused by incomplete digestion of heterogeneously distributed, insoluble presolar components given that Murchison has abundant presolar grains such as SiC and much less CAIs compared to Allende. Further investigations of SiC and CAIs in Murchison are needed to evaluate this discrepancy.

For ordinary chondrites, the resulting ^{184}W/^{183}W ratio did not vary significantly from that of the terrestrial materials. It is well known that all class 4 and 5 ordinary chondrites have experienced thermal metamorphism in the meteorite parent bodies, which may have homogenized *s*- and *r*-process nuclides, consistent with the observed W isotopes for ordinary chondrites.

(2) Influence of r-process enriched components Ruling out *s*-process deficit from SiC effects for Allende leaves the possibility that the ^{184}W deficits for Allende reflect enhancement of *r*-process enriched component. In the case of Mo, *r*- and *p*-process nuclides were decoupled in carbonaceous chondrites, revealing both *r*- and *p*-process were enriched, rather than the *s*-process nuclide was depleted in Allende (Yin *et al.*, 2002b). Moreover, Mo isotopic composition demonstrated that the CAI from Allende had *r*-process enhanced-pattern. Our new W isotopic data is consistent with the Mo isotopic data suggesting that the Allende was enriched in the *r*-process components.

Quantifying the effects that a heterogeneous distribution of these two components would have on the W isotope composition requires knowledge of the *s*- and *r*-process yields for each of the W isotopes. These have recently been estimated by Qin *et al.* (2008) and these authors show that the *s*-process produces significantly more ^{184}W than the *r*-process and that different proportions of *s*- and *r*-process components should result in a correlation between ε^{184}W and ε^{182}W anomalies (normalized to a given ^{186}W/^{183}W) (Qin *et al.*, 2008). The slope of this correlation line depends on the calculated *s*-process composition of W isotopes, which in turn depend on the neutron-capture cross sections of the stable W isotopes and the cross sections and β^--decay rates at the relevant branching points.

We have estimated the W isotopic composition for *s*- and *r*-process nuclides using the AGB stellar model by Bao *et al.* (2000). Figure 2 shows the changes in the W isotope ratios due to various level of contribution of the *s*- and *r*-process components (solid black line). Negative deviation in the ε^{184}W can be explained by small contri-

bution of the *r*-process components. Similar to the calculation reported by Dauphas *et al.* (2004) for Mo, the slope of the regression line is given by

$$\varepsilon^{182}W = (\rho^{182} - \rho^{186}\mu^{182})/(\rho^{184} - \rho^{186}\mu^{184}) \times \varepsilon^{184}W \quad (2)$$

where ρ^i is the *s*-process composition normalized to the solar composition,

$$\rho^i = (^iW/^{183}W)_{s\text{-process}}/(^iW/^{183}W)_{terrestrial} - 1 \quad (3)$$

and μ^i is the mass difference relative to the normalizing pair (183 and 186),

$$\mu^i = (i - 183)/(186 - 183) \quad (i = 182, 184). \quad (4)$$

The resulting W isotope ratios for Allende CV3 show *r*-process enrichment (Fig. 2). Using recommended values of Maxwellian-averaged cross sections (MACS) (Bao *et al.*, 2000), Qin *et al.* (2008) obtained a slope for the ε^{182}W–ε^{184}W correlation line of ~0.04 ± 0.20 (i.e., ^{184}W anomalies should be ~25 times larger than ^{182}W anomalies). However, these authors also note that the cross section of ^{182}W might be ~20% lower, in which case the slope of the ε^{182}W-ε^{184}W correction line would be ~0.5 (dashed line).

In Fig. 2, which is adapted from Qin *et al.* (2008), the expected ε^{182}W and ^{184}W variations that are due to the presence of different proportions of *s*- and *r*-process W isotopes are shown together with W isotope data for four carbonaceous and average of ordinary chondrite investigated here. Figure 2 illustrates that three of four carbonaceous chondrites (Murchison, Y-793321, and Y-86751) and average of ordinary chondrites studied here have ^{184}W/^{183}W ratios identical within analytical uncertainty to those of the terrestrial standard, indicating that these chondrites have a W isotope composition indistinguishable from that of the average solar system.

Allende exhibits a ~0.4ε unit deficit in ^{184}W, whereas its ^{182}W/^{183}W ratio (normalized to ^{186}W/^{183}W) is indistinguishable from those of the other chondrites. This is consistent with predictions from the standard MACS model shown in Fig. 2 and suggests that Allende is enriched in *r*-process relative to *s*-process isotopes.

We note, however, that our ^{184}W/^{183}W ratios for Allende are not consistent with the previous reported data by Kleine *et al.* (2004). All individual measurements for Allende are in a range from −0.7 to 0ε (Table 1 and Fig. 1). This variation of ^{184}W/^{183}W ratio for Allende chondrites could be attributed to the variable abundances of CAIs in Allende pieces, since some Allende CAIs exhibit ^{184}W deficit by *r*-process enrichment in Allende CAIs (Burkhardt *et al.*, 2008). Thus, it is possible that W isotope data for the Allende sample pieces analyzed here

could reflect different abundance of *r*-process enriched component in Allende CAIs. This result might imply that the [184]W anomalies obtained here are not representative for the entire Allende chondrite but for the Allende piece analyzed, because the observed [184]W deficit in Allende may reflect an overabundance of CAIs in the analyzed piece.

CONCLUSIONS

We have measured high-precision W isotope ratios for series of carbonaceous chondrites and ordinary chondrites using MC-ICP-MS. The resulting [182]W/[183]W isotope ratios are consistent with the previous reported data (Yin *et al.*, 2002a; Kleine *et al.*, 2002, 2004). No difference in [184]W/[183]W isotope ratios among three carbonaceous chondrites (Murchison CM2, Y-793321 CM2, and Y-86751 CV3) could be discerned from that for the W isotopic standard (NIST SRM 3163) and various terrestrial rocks, whereas the [184]W/[183]W ratios for Allende CV3 showed significantly lower value than the other carbonaceous chondrites and terrestrial samples. This present W isotope data for each Allende piece is due to overabundance of an *r*-process enriched CAIs in Allende.

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