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High Precision Tungsten Isotope Measurements by MC-ICPMS

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1 Introduction

The short-lived ^{182}Hf-^{182}W system is generally acknowledged as the best chronometer of metal-silicate segregation that occurred during the early evolution of asteroids and terrestrial planets due to its following properties: (1) Hf-W fractionation commonly occurs during metal-silicate differentiation; (2) Both Hf and W are highly refractory elements, therefore most bulk planetary objects are considered to have a consistent chondritic Hf/W ratio; (3) The half-life of 8.9 ± 0.1 Myr (Vockenhuber et al., 2004) for ^{182}Hf-^{182}W system can be used to reveal the information of the first ~ 60 Myr of the Solar System, and this timescale is exactly appropriate for examining the formation and early differentiation of asteroids and terrestrial planets.

It is worth noting that the W isotope compositions of some meteorites and lunar samples exposed in space are likely to be affected by the galactic cosmic rays (GCR) (Lee et al., 2002; Leya et al., 2000; Masarik, 1997). Correcting for the cosmogenic effect accurately is crucial for acquiring the correct knowledge of these GCR-effected samples. In addition, nucleosynthetic W isotope anomalies were observed among the chondrites (Burkhardt et al., 2012). To correct the nucleosynthetic W isotope anomalies is the key to establishing the initial ^{182}W/^{184}W of Ca-Al-rich inclusions (CAIs) which is an essential parameter for the ^{182}Hf-^{182}W chronometry.

Recently, well-resolved ^{182}W excesses relative to modern terrestrial mantle have been observed in terrestrial rocks (Liu et al., 2016; Rizo et al., 2016; Touboul et al., 2012; Willbold et al., 2011; Willbold et al., 2015). Combined with the ^{146}Sm-^{142}Nd short-lived system and the highly siderophile elements, W isotopic data provide significant constraints on the early Earth's mantle differentiation.

High precision and accurate W isotope measurement is the basic guarantee of breaking down the limitations of ^{182}Hf-^{182}W chronometry mentioned above (i.e., cosmogenic and nucleosynthetic effects), and makes it possible to reveal the tungsten isotopic variations among terrestrial rocks.

2 Method

A mixture of concentrated HF-HNO_3 was used for the primary sample decomposition. Repeated dissolutions with mixtures of HCl-HF in ultrasonic baths were adopted to extract the fraction of W which was trapped in the lattice of the insoluble fluorides.

After the examination of the previously published W-isotope analytical method by Touboul and Walker (2012) in our laboratory, we found that it is inefficient to elute Ti with large amount of 3.6 M HAc-8 mM HNO_3-1% H_2O_2 for the high-Ti silicate rocks. Using A mixture of HCl with trace HF to elute Ti, Zr, and Hf would be preferable (Qin et al., 2007). If separation of Hf from Ti is needed, chromatography based on Ln-Spec resin could be an effective method (Münker et al., 2001). In addition, eluting Hf with 6 M HCl-0.01 M HF would lead to a nonnegligible W losing. Increasing the concentration of HCl in the elution acid (using 8 M HCl-0.01 M HF or 9 M HCl-0.01 M HF) could solve the problem. After a three-step ion exchange chromatography procedure modified after that of Touboul and Walker (2012), pure W was obtained for mass spectrometry.

The final W was analyzed using *Thermo Scientific Neptune Plus* multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). The measurements were normalized to ^{186}W/^{184}W=0.92767 or ^{186}W/^{183}W=1.98594 using the exponential law. These two different normalization schemes are denoted (6/4) and

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(6/3), respectively.

3 Results

Results of the measurements of Alfa Aesar W and basalt standard JB-3 are shown in Fig. 1. The measured $^{182}W/^{184}W$ ratio of the standard JB-3 is identical to that of the Alfa Aesar W standard solution. We achieve an external reproducibility of the $\varepsilon^{182}W$ of 13 ppm (2SD) for natural samples. The terrestrial $^{182}W/^{184}W$ (6/4) and $^{182}W/^{183}W$ (6/3) ratios averaged over a period of two years are 0.864893±0.000018 (2SD) and 1.851504±0.000034 (2SD). These values are in good agreement with previously reported results (i.e., Markowski et al., 2006; Trinquier et al., 2016).

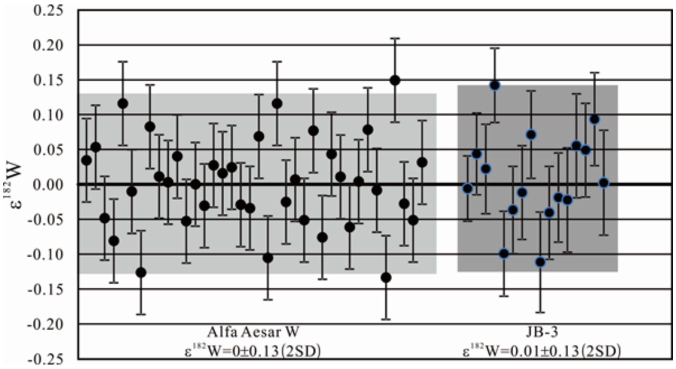

Fig. 1. Results of the repeated measurements of Alfa Aesar W and JB-3 using MC-ICPMS .
($\varepsilon^{182}W=\{[(^{182}W/^{183}W)_{sample}/(^{182}W/^{183}W)_{BSE}]-1\}\times10^4$, all W isotopic ratios were normalized to $^{186}W/^{183}W$=1.98594).

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