

ISOTOPIC ANALYSIS OF NANO-GRAM AMOUNTS OF TUNGSTEN USING ELECTROTHERMAL VAPORIZATION (ETV)-MC-ICPMS TECHNIQUE. S. Okabayashi, S. Sakata and T. Hirata, Laboratory for Planetary Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan (okabayashi-s-aa@kueps.kyoto-u.ac.jp).

Introduction: Hf-W chronometer is based on the negative beta-decay of r-process nuclide ^{182}Hf to ^{182}W with a half-life of 8.9 ± 0.1 Myr[1]. Hafnium is strongly lithophile elements, whereas W is moderately siderophile elements, and therefore, it has been well recognized that the Hf-W age provided critical information about the timing of metal-silicate differentiation (core formation) processes at the early stage of the Earth formation. Moreover, both the Hf and W is strongly refractory elements, the Hf-W age can reflect the timing of condensation or segregation of the metallic nuggets from chondritic reservoir at the early sequence of the solar system. Despite the potential high versatility of this chronometer, the Hf-W age for the metallic nuggets in chondrite has not been widely used for the cosmochemical samples mainly due to analytical difficulty. Even with the thermal ionization mass spectrometry (TIMS), Hf-W chronological studies were based on the isotopic analysis from micro-gram amounts of W. For further applications using the Hf-W chronometer, enhancements in the analytical sensitivity for the W isotopic analysis is highly desired.

With the ICP-MS technique coupled with the conventional solution nebulization technique, total amount of W required for the isotopic ratio measurements could be 50 – 100 ng. Typical ion transmission efficiency from sample to ion collector would be <0.1% under the sample introduction using the nebulizer. It should be noted that more than 90% of sample solution was abandoned at the spray chamber, which acted as aerosol filter for the removal of large-sized solution mist. This suggests that the sample introduction efficiency (i.e., high transmission efficiency) can be dramatically improved when the loss of sample mist could be minimized. To achieve this, we have developed a sample introduction technique using the electrothermal vaporization (ETV) technique.

Experimental: With the ETV technique, W was introduced into the ICP as vapor, no filtration or size discrimination process is required, and therefore, magnitude of loss of sample could be remarkably reduced [2]. In this study, we have developed a micro-ETV device (Re filament) located in a small volume ETV chamber (approximately 25 mL) to achieve minimum loss of W vapor and also to reduce the memory of W within the chamber (Fig. 1). Tungsten in HNO_3 solution was loaded onto the Re filament, and the evaporated W was transferred into the ICP ion source with He carrier gas ($\sim 0.8 \text{ L min}^{-1}$). Temperature of the Re

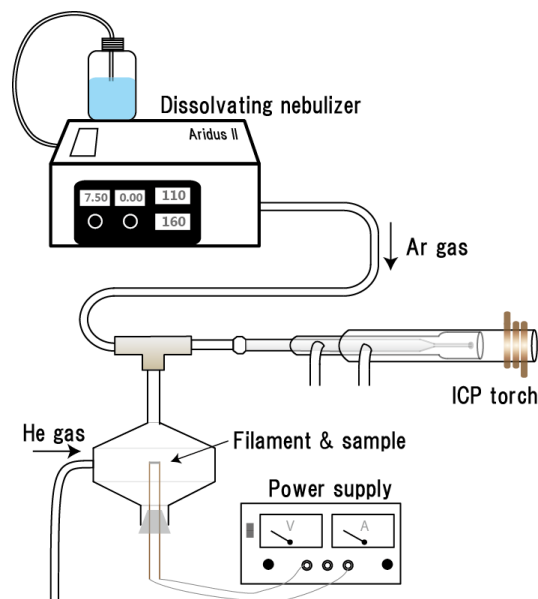


Fig 1. The schematic of ETV sample introduction system for MC-ICPMS used in this study. During the ETV analysis, deionized water was set for desolvating nebulizer system. The external power supply was controlled by PC and the impressed current can be changed smoothly.

filament is controlled by the incident current (0 – 4 A). It should be noted that the current for the W evaporation were largely different between the ambient gas. The current required for W evaporation was ~ 2 A for Ar ambient gas, and was ~ 3.5 A for He ambient gas. Difference in the current was mainly due to changes in thermal conductivity of these two gases ($\sim 150 \text{ mW m}^{-1} \text{ K}^{-1}$ for He and $\sim 18 \text{ mW m}^{-1} \text{ K}^{-1}$ for Ar). In this study, the He carrier gas with W vapor was merged with the dry aerosols produced by the Aridus desolvating nebulizer. Operational conditions of the ICP-MS (i.e., gas flow rates, torch positioning, lens settings or collector arrangements) can be optimized by monitoring the signal intensity of W obtained through nebulization of W solution. Tungsten free deionized water was introduced when the sample introduction through the ETV device, and this was very important to keep the optimum operational settings throughout the ETV analysis.

Results and Discussion: In this study, W evaporation was carried out under the two different ambient gasses (Ar and He). About 70 ng W (in 2wt% HNO_3) was loaded onto the Re filament, and the W was

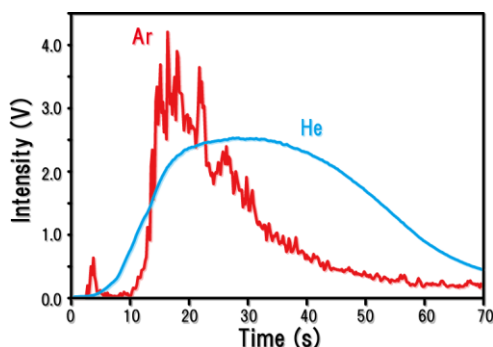


Fig 2. The signal profiles of ^{184}W evaporated in Ar environment (red line) and He environment (blue line). In both cases, 76 ng of W in 2wt% HNO_3 was loaded on a Re filament and evaporated at $\sim 1000^\circ\text{C}$.

evaporated at $\sim 1000\text{ K}$. The resulting signal intensity profiles obtained by Ar carrier gas and by He carrier gas were shown in Fig. 2. Signal intensity obtained under the Ar carrier gas (red line in Fig. 2) was spiky and unstable, and this was not suitable for the precise isotopic analysis. In strike contrast, the signal intensity profile obtained under the He carrier gas (blue line in Fig. 2) was very smooth and stable. The obvious difference in the stability of the signal intensities could be explained by the difference in the thermal conductivity of the ambient gas. The thermal conductivity for He was almost ten times higher than that for Ar. The higher thermal conductivity induces the expansion of the high temperature region above the filament, and this avoids growth of the solid W particles through the re-condensation from W vapor. This suggests that the size distribution of the W aerosols could be modified toward smaller when the He carrier gas was used. Moreover, with the He carrier gas, total number of W atoms was about 1.7 times higher than that achieved by the Ar carrier gas. This suggests that the some of the large-sized W particles could be lost through the transportation stages (ETV chamber, tubing or connectors). In this study, He carrier gas was used throughout the measurements. Based on the relationship between the amount of W loaded onto the filament and the resulting signal intensity profile, the sample transmission can be estimated. The calculated ion transmission for W was 0.91%, which was almost 10 times higher than that achieved by the conventional solution nebulization technique (0.10%) (Fig. 3).

For the isotope ratio measurements, ^{182}W , ^{183}W , ^{184}W and ^{186}W was monitored. The ^{188}Os was also monitored to evaluate the mass spectrometric interferences on ^{184}W and ^{186}W by ^{184}Os and ^{186}Os signals. Hence, no significant level of ^{188}Os was found throughout the measurement, and therefore, no correc-

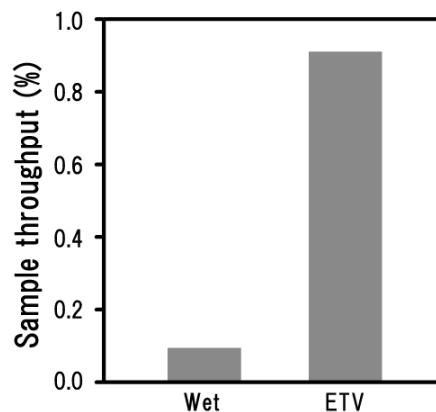


Fig 3. The sample throughput for W of the conventional wet plasma and the ETV sample introduction system.

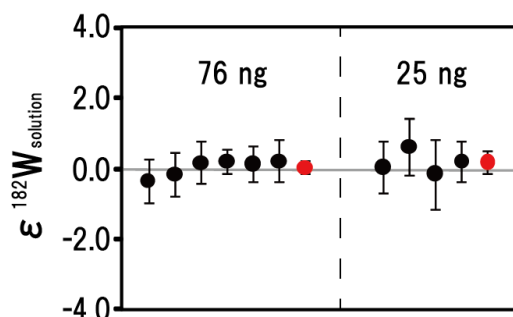


Fig 4. The figure of $\epsilon^{182}\text{W} (= (^{182}\text{W}/^{184}\text{W})_{\text{ETV}} / (^{182}\text{W}/^{184}\text{W})_{\text{solution}} - 1) \times 10000$ of JMC 22841. 76 ng (left) or 25 ng (right) of W was loaded on a filament.

tion for the mass spectrometric interferences by Os were made. The mass bias was internally corrected by normalizing $^{186}\text{W}/^{183}\text{W}$ being 1.9859 [3] using the exponential law. Isotopic analysis was carried out under the two different amounts of loading (76 ng and 25 ng), and the analysis was repeated several times to evaluate the repeatability of the isotope ratio measurements. The obtained W isotope ratios using ETV-MC-ICPMS technique agree well with the data obtained by the solution nebulization. In this study, the $^{182}\text{W}/^{184}\text{W}$ ratio for meteorite samples will be presented. The data obtained here demonstrate clearly that the ETV-MC-ICPMS technique has the potential to provide reliable W isotope ratio data from 25 ng amounts of W.

References: [1] Vockenhuber, C., Oberli, F., Bichler, M., Ahmad, I., Quitté, G., Meier, M., Halliday, A.N., Lee, D.C., Kutschera, W. and Steier, P. (2004) *Phys. Rev. Lett.*, 93, 172501. [2] Nixon, D.E., Fassel, V.A. and Kniseley, R.N. (1974) *Anal. Chem.*, 46, 210-213. [3] Kleine, T., Mezger, K., Münker, C., Palme, H. and Bischoff, A. (2004) *Geochim. Cosmochim. Acta*, 68, 2935-2946.