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An improved method for $^{182}W/^{184}W$ isotope measurements with high precision and accuracy using multiple collector inductively coupled plasma mass spectrometry and its application for terrestrial samples - *GSJ Medal Lecture*

ASAKO TAKAMASA[1,2], KATSUHIKO SUZUKI[1], YUSUKE FUKAMI[1,3], TSUYOSHI IIZUKA[4], MARIA LUISA GARCIA TEJADA[1], WATARU FUJISAKI[5], YUJI ORIHASHI[6] AND TAKUYA MATSUMOTO[7]

[1]JAMSTEC
[2]JANUS
[3]Gakushuin University
[4]The University of Tokyo
[5]University of Tsukuba
[6]Hirosaki University
[7]IAEA

Presenting Author: atakamasa@gmail.com

The relatively short-lived nuclide ^{182}Hf decays to ^{182}W. Before the ^{182}Hf extinction, Hf-W was fractionated in the early Earth, resulting in $^{182}W/^{184}W$ variation in terrestrial rocks. A very precise method is required to measure the subtle variation of $^{182}W/^{184}W$ in terrestrial rocks. In this study, an improved method to measure the $^{182}W/^{184}W$ ratio of terrestrial rocks with high precision and accuracy was achieved. Tungsten was extracted from the digested sample solution with 4-methyl-2-pentanone, purified by both cation and anion exchange chromatography, and W isotope ratios were subsequently measured using a desolvation nebulizer and a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Sample pretreatment removed matrix elements with masses close to the W isotopes (e.g., Hf, Ta, Os, Nb and Mo dimers), thereby removing the effect of these elements on the $^{182}W/^{184}W$ ratio measurements. The W standard solutions treated by ion-exchange chromatography and/or solvent extraction showed mass independent fractionation, with ^{183}W missing even after mass dependent fractionation correction of the measured isotope data. As previously reported, the corrected $^{182}W/^{184}W$ ratio increases when the $^{183}W/^{184}W$ ratio with ^{183}W defect is used for mass fractionation correction. However, for the basalt standard sample (JB-2), an accurate $^{182}W/^{184}W$ ratio was obtained by our standard-bracketing correction even when ^{183}W was used for mass fractionation correction. This result indicates that it is also possible to correct the effect of mass-independent fractionation on the $^{183}W/^{184}W$ ratio by performing sample standard bracketing using a W standard solution subjected to the same procedure used for the sample. The main advantage of the method developed here is the small sample volume required (0.2-0.3 g, 50-80 ng W for JB-2) compared to other reported methods (typically 0.7-15 g, 500-1000 ng W). This reduction in sample volume is made possible by the removal of matrix components from the sample solution. The cleaning of the desolvation nebulizer membrane between analyses also contributed to the higher W ion beam intensity stability and precision. Results from the analysis of different basalts from Loihi, Kilauea, and Ontong Java Plateau, with various W isotopic compositions that are consistent with previous studies, demonstrate the reliability of the method.