Development of precise isotopic analysis of small-size W using negative thermal ionization mass spectrometry

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Tracking the thermal evolution of planetes and small bodies is key to understanding Solar System history. Determining when and how metal separated from silicates constrains thermal evolution models. The short-lived ^{182}Hf–^{182}W system (half-life 9 Ma) dates differentiation: during silicate–metal separation, Hf partitions into silicate and W into metal, so the metal' s $^{182}W/^{184}W$ records the timing of separation. Analytical precision of $^{182}W/^{184}W$ directly controls the accuracy of the inferred age. Conventional W isotope measurements with negative thermal ionization mass spectrometry (N-TIMS) have achieved $^{182}W/^{184}W$ ratio analysis with approximately ±2 ppm precision (2 SD) using 300–1250 ng of W [1]. Using smaller W quantities is expected to reduce beam intensity of WO_3^-, potentially degrading measurement repeatability [2]. However, few studies have quantitatively evaluated the relationship between W quantity and isotope ratio analytical precision. For achieving high-precision W isotope measurements using even smaller quantities in the future, this study attempted to optimize isotope analysis conditions using W standard samples ranging from 150 ng to 1000 ng. Furthermore, the optimized condition was applied to meteorite samples to measure their W isotopic composition.
In N-TIMS measurements, increasing the amount of W on the filament from 150 ng to 300 ng and then to 500 ng did not change the WO_3^- beam intensity. Increasing the loaded amount to 1000 ng increased the WO_3^- beam intensity, but the resulting beam intensity was only 1.5 times that obtained with 150 ng. This is most likely due to the saturation of electron emission from the activator loaded on the filament, inhibiting effective WO_3^- ionization for larger quantity of W. In the W isotope measurements using 150 ng of W, we found that the reproducibility of the $^{182}W/^{184}W$ ratio deteriorated with increasing ReO_3^-/WO_3^- beam intensity ratio. This was attributed to differences in the acid concentration of the W standard sample solution (mixed acid of HCl and HF) applied to the filament. When the acid concentration was adjusted to suppress ReO_3^- generation, the repeatability of the $^{182}W/^{184}W$ ratio was ±8.2 ppm (2SD, n = 4). As an application of the optimized analytical condition, we measured the W isotopic compositions of an iron meteorite Chinga (CC group) and a mesosiderite NWA 8741 (NC group). The $\mu^{183}W$ values for Chinga and NWA 8741 (13.8 ±2.7 ppm and -12.7 ±1.6 ppm, respectively) fall within the typical ranges for CC and NC iron meteorites, consistent with results from Mo isotopes and other studies. Converting the $\mu^{182}W$ value of Chinga (-307 ±2.6 ppm) to age yields 3.9 ±0.3 Ma after CAI formation. This value supports the model [3] proposing that remelting occurred in the Chinga parent body following core separation due to an asteroid impact. In contrast, the $\mu^{182}W$ value for NWA 8741 (-262.4 ±3.6 ppm) was significantly higher than that typical for NC iron meteorites (-340 ±10 ppm). One proposed origin for mesosiderite meteorites involves a large-scale collision between asteroid Vesta and another body, during which ejected core and crustal material from Vesta mixed [4]. Based on this model, the high $\mu^{182}W$ value in NWA 8741 is thought to result from isotopic exchange between Vesta's core and crustal materials during metal–silicate mixing accompanying partial melting, reflecting the high $\mu^{182}W$ value inherent in silicate phases.
References: [1] Mundl-Petermeier et al. (2022), Thermo Fisher Application Note, 000969, 1-3. [2] Trinquier et al. (2016), Analytical chemistry, 88(3), 1542-1546. [3] Worsham et al. (2017), Earth and Planetary Science Letters, 467, 157-166. [4] Haba et al. (2019), Nature Geoscience, 12(7), 510-515.

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