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Experimental constraints on the origin of analytical ^{183}W deficits

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Recent high-precision W isotope data revealed ^{182}W anomalies in many ancient rocks and modern OIBs, providing evidence for mantle heterogeneity that formed during the early Earth's history and its long-term preservation. The data also revealed ^{183}W deficits of analytical origin [1, 2], which are consistent with the effects of nuclear field shift (NFS). As ^{183}W can be used to detect nucleosynthetic anomalies [3], its accurate measurement is highly desired. Moreover, such ^{183}W deficits are typically accompanied by low W yields, decreasing the precision of both ^{182}W and ^{183}W measurements. Recently, it is shown that using a mixture of HNO_3 and H_2O_2 during sample dry-down steps can inhibit ^{183}W deficits [4], leading to the inference that the ^{183}W deficits result from the formation of insoluble W compounds during dry-down steps. Yet, its exact origin remains elusive.

To constrain the origin of the ^{183}W deficits, we analyzed variously processed NIST3163 W samples. We prepared three samples as follows: (1) a NIST3163 W in 4M HNO_3-0.5M HF was passed through an AG1-X8 resin column, and diluted to 0.5M HNO_3-trace HF without dry-down steps; (2) a NIST3163 in 4M HNO_3-0.5M HF was passed through the column and dried down with $HClO_4$, and re-dissolved in 0.5M HNO_3-trace HF; (3) a 4M HNO_3-0.5M HF solution without W was passed through the column and dried down with $HClO_4$, followed by heating in 0.5M HNO_3-trace HF and finally doping of NIST3163 at room temperature. The samples were introduced to a Neptune plus MC-ICPMS using an Aridus II desolvating nebulizer. All three samples showed ^{183}W deficits of up to 10 ppm, with ~30% decreases of signal intensity, relative to un-processed NIST3163. These results indicate that a material responsible for ^{183}W deficits forms even when no dry-down steps are included. We envisage that resin-derived organic matters are adsorbed by W in the sample solution, where the NFS effect is evident, and that the adsorbing W cannot be efficiently introduced to or ionized in the ICP.

[1] Kruijer et al. (2012) GCA
[2] Cook & Schonbachler (2016) JAAS
[3] Kruijer et al. (2012) PNAS
[4] Tusch et al. (2019) GCA