Validating the high-precision measurement of Mo isotopes at the 5 ng level using double spike MC-ICP-MS

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With recent advancements in analytical methods of Mo isotopes, the $\delta^{98/95}$ Mo ratios of most geological and environmental samples can be determined. Still, it remains a challenge to obtain high-precision Mo isotope data for low-Mo samples with complex matrices such as igneous and plant samples. Here, we present an improved Mo purification and cleaning resin scheme for reducing the total procedure blank to \leq 0.16ng using common Muromac®1X8(AG1-X8) anion and AG50-X8 cation resins. By an improved Aridus II with ice chamber in sample introduction system (SIS) and adding nitrogen(N₂), high sensitivity measurement (⁹⁵Mo signal intensity: 200~330V ppm⁻¹) of Mo isotopes was achieved on Neptune Plus MC-ICP-MS. Thus, the sample size containing 30~60 ng Mo is sufficient to be purified for isotope measurement with high-precision ($\leq 0.06\%$, 2SD) can be determined at a concentration of $3 \sim 10$ ng level using a 97 Mo- 100 Mo double spike. The NIST 3134(0.00±0.05‰), SGR-1b(0.41±0.05‰), NOD-P-1(0.87±0.02‰) and other international reference materials (RMs) were analyzed at 3, 5, 10, and 20 ng mL $^{-1}$ levels to be in excellent agreement with the published $\delta^{98/95}$ Mo values, demonstrating that good accuracy and precision of Mo isotope analysis can be achieved with an injecting sample size as small as 5 ng Mo.

Our improved method can be applied to various geological and environmental samples. The $\delta^{98/95}$ Mo of CLB-1(1.25±0.03‰), JDO-1(0.50±0.02‰), GSV-2(0.47±0.02‰), and other 38 RMs with relatively higher and lower Mo concentrations are reported for the first time. The total average $\delta^{98/95}$ Mo ratio of 8 soils and 18 sediments is 0.003+0.277‰ (1SD, n=26), slightly lighter than that upper continent crust (0.05‰~0.15‰). The $\delta^{98/95}$ Mo ratios (0.23~0.79‰, n=8) of plant and animal organs from the land show they are enriched in heavy isotopes relative to the bulk silicate earth (BSE). The $\delta^{98/95}$ Mo ratios of carbonate are much lower than that in seawater.

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