Molybdenum stable isotope analysis of geological samples by double-spike MC-ICPMS using enriched ⁹⁷Mo and ¹⁰⁰Mo isotopic reference materials

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Molybdenum is one of the transition metals, and essential trace elements in human, animals and plants. A better understanding of the natural distribution and mass-fractionation mechanisms of molybdenum isotopic compositions contributed many areas of science, including geochemistry, cosmochemistry, mineral resources, biological and medical sciences. For instance, the isotopic compositions of molybdenum in ocean sediments could be used as a paleoredox proxy owing to its redox-sensitive feature; besides, studies on molybdenum isotopes applied information to identify the formation process of meteorites in palladium correlation with ruthenium or isotopic analysis; furthermore, the use of stable isotope techniques for the studying of human molybdenum metabolism provided recommendations on nutrition intake and associated disease diagnosis.

The double-spike method is a well-established approach for the precise determination of isotope ratios, and has been applied to a broad range of isotope systems using both TIMS and MC-ICPMS. This approach has a number of advantages over other methods, such as the possibility to determine mass-dependent isotopic fractionation from a single isotope measurement, and correct for any mass-dependent isotope fractionation induced during chemical purification as well as mass spectrometry. The double-spike method is also less susceptible to potential analytical artefacts induced by trace amounts of sample matrix that may remain and incomplete yields of the analyte following chemical purification.

In this study, we present the high-precision method to analysis the stable isotopic composition of molybdenum in geological materials using double-spike MC-ICPMS. The enriched ⁹⁷Mo and ¹⁰⁰Mo isotopic reference materials (GBW04511 and GBW04512) were developed and used for preparing the doublespike calibration solution. The property values of these iCRMs were displayed in Table 1. The proportions of ⁹⁷Mo-¹⁰⁰Mo double -spike and the double-spike-sample mixtures were optimized by the contour plot of error in *a* using the MC-ICPMS measurement data. Then, we apply this method to analyse the molybdenum stable isotopic compositions in five geological reference materials and one terrestrial sample. The measurement results of this study (Solid dots) and that in literature reports (Hollow dots) were summarized in Figure 1, demonstrated the effectiveness of the proposed double-spike approach. Table 1

Name of CRM	Amount content (µg . g ⁻¹)		$U \; (\mu g \cdot g^{-1})$
	8.43		0.04
	Isotope ratio		U
Isotopically	⁹² Mo/ ⁹⁷ Mo	0.002212	0.000009
Enriched ⁹⁷ Mo Spike	⁹⁴ Mo/ ⁹⁷ Mo	0.002013	0.000007
Solution	⁹⁵ Mo/ ⁹⁷ Mo	0.004936	0.000007
(GBW04511)	⁹⁶ Mo/ ⁹⁷ Mo	0.013118	0.000014
	⁹⁸ Mo/ ⁹⁷ Mo	0.03589	0.00003
	100 _{Mo} /97 _{Mo}	0.003249	0.000003
Name of CRM	Amount content (µg , g ⁽¹⁾)		U (μg . g ⁻¹)
	8.10		0.04
	Isotope ratio		U
Isotopically	⁹² Mo/ ¹⁰⁰ Mo	0.0003220	0.0000027
Enriched 100Mo	⁹⁴ Mo/ ¹⁰⁰ Mo	0.0002175	0.0000016
Spike Solution	⁹⁵ Mo/ ¹⁰⁰ Mo	0.0003906	0.0000011
(GBW04512)	⁹⁶ Mo/ ¹⁰⁰ Mo	0.0004801	0.0000017
	⁹⁷ Mo/ ¹⁰⁰ Mo	0.0004020	0.0000019
	⁹⁸ Mo/ ¹⁰⁰ Mo	0.004586	0.000013

Figure 1

