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## **Supporting Information**

## A simple single-stage extraction method for Mo separation from geological samples for isotopic analysis by MC-ICP-MS

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## Double spike design and preparation

A double-spike (DS) technique was used to correct for isotope fractionation that could occur during ion-exchange chromatography and in combination standard-sample bracketing for mass bias correction to improve the measurement precision and accuracy. This DS technique encompasses mixing the sample with a high purity double-spike solution enriched in two isotopes of the target element. With seven naturally occurring stable isotopes of Mo, there are numerous possible combinations for the Mo double-spike and for the double-spike inversion. Due to the isobaric interferences from Zr ( ${}^{92}\text{Zr}^+$ ,  ${}^{94}\text{Zr}^+$ ,  ${}^{96}\text{Zr}^+$ ), the Mo isotope of 92, 94 and 96 were exclude from the choice of double spike combinations. Although  ${}^{100}\text{Mo}^+$  suffers from the isobaric interference of  ${}^{100}\text{Ru}^+$ ,  ${}^{97}\text{Mo}^{-100}\text{Mo}$  double spike is still the optimal choice, considering the relative high ratio of Mo/Ru in terrestrial samples. Furthermore, this double spike is able to provide relatively small theoretical measurement uncertainties as calculated by the Monte Carlo simulations<sup>1,2</sup> (Figure S1). Therefore, the  ${}^{97}\text{Mo}^{-100}\text{Mo}$  double spike for the mass fractionation correction of  ${}^{98}\text{Mo}/{}^{95}\text{Mo}$  ratios was chosen.



**Figure S1**. Contour plot of error for the  ${}^{97}Mo{-}^{100}Mo$  double-spike with a  ${}^{95}Mo{-}^{97}Mo{-}^{98}Mo{-}^{100}Mo$  inversion, as a function of double-spike composition and double spike in sample mixture proportions, estimated by the Monte Carlo simulations<sup>1,2</sup>. Contours are at intervals of 1 % of the optimal error on  $\delta^{98}Mo$ . The blank cross marks the actual

 $^{97}$ Mo $^{-100}$ Mo double spike composition used in this study ( $^{97}$ Mo =51.6%, double spike = 45%).

<sup>97</sup>Mo-<sup>100</sup>Mo double spike was prepared as a mixture of single enriched spikes of <sup>97</sup>Mo and <sup>100</sup>Mo, which were purchased from Oak Ridge National Laboratory (Oak Ridge, TN, USA). The enriched spikes were digested by 2 ml concentrated HNO<sub>3</sub> in 15 ml PFA vails and then diluted with DIW in 60 ml FEP bottles, separately. Optimal double spike composition and the proportion of the double spike in the mixture were calculated by Monte Carlo simulations<sup>1,2</sup>, as shown in Figure S1. The <sup>97</sup>Mo-<sup>100</sup>Mo double spike solution was subsequently produced by mixing the two single spike solutions with about 40 % <sup>97</sup>Mo and 60 % <sup>100</sup>Mo and then diluted to a concentration of about 16 ppm by 5 % HNO<sub>3</sub>. The isotopic composition of <sup>97</sup>Mo-<sup>100</sup>Mo double spike was calibrated relative to NIST Mo SRM 3134. First, we separately measured pure solutions of NIST SRM 3134 and double spike. The unspiked SRM 3134 and pure double spike solutions were analyzed in SRM 3134 - double spike - SRM 3134 sequence. The instrumental mass bias was corrected with the assumption of a "true" value of <sup>98</sup>Mo/<sup>95</sup>Mo=1.5321 of SRM 3134<sup>3</sup>. The mass bias factor of each SRM 3134 was calculated by the comparison of the measured and the "true" <sup>98</sup>Mo/<sup>95</sup>Mo, and then used for correcting other isotopic ratios of measured SRM 3134 and the bracketing double spikes. Second, we measured the mixture of double spike and SRM 3134. Then the double spike was calibrated against SRM 3134 using a reverse process that calculates sample compositions by assuming the corrected value of SRM 3134 was the true value (Table S1). Note that the double spike composition calibrated in this study was just a relative value to obtain delta zero of <sup>98</sup>Mo/<sup>95</sup>Mo (relative to SRM 3134) but not the actual or absolute value.

**Table S1**. Compositions of the <sup>97</sup>Mo-<sup>100</sup>Mo double spike and NIST SRM 3134 Mo reference material.<sup>a</sup>

<sup>94</sup>Mo/<sup>95</sup>Mo <sup>96</sup>Mo/<sup>95</sup>Mo <sup>97</sup>Mo/<sup>95</sup>Mo <sup>98</sup>Mo/<sup>95</sup>Mo <sup>100</sup>Mo/<sup>95</sup>Mo

NIST SRM 3134 <sup>b</sup>	0.578733	1.050936	0.604371	1.532100	0.615313
2RSD (n = 7)	0.000019	0.000013	0.000109	0.000000	0.000064
<sup>97</sup> Mo- <sup>100</sup> Mo double					
spike	0.538081	1.545435	58.574229	3.556414	54.975086
2RSD(n = 6)	0.000629	0.000116	0.000245	0.000161	0.000249

<sup>a</sup> <sup>92</sup>Mo/<sup>95</sup>Mo ratio was not listed because of <sup>92</sup>Mo was not collected during measurement.
 <sup>b</sup> Ratios normalized to <sup>98</sup>Mo/<sup>95</sup>Mo = 1.5321, reported by Song et al.<sup>3</sup>



**Figure S2**. Elution profiles of BCR-2 (50 mg) under different concentrations of nitric acid. Sample was loaded in 2 mL and eluted by another  $14 \times 1$  mL selected eluent.

Mass	<sup>92</sup> Mo	<sup>94</sup> Mo	<sup>95</sup> Mo	<sup>96</sup> Mo	<sup>97</sup> Mo	<sup>98</sup> Mo	<sup>100</sup> Mo
Isobars	$^{92}Zr^{+}$	$^{94}Zr^{+}$		<sup>96</sup> Zr <sup>+</sup> , <sup>96</sup> Ru <sup>+</sup>		$^{98}\mathrm{Ru}^{+}$	$^{100}Ru^{+}$
Argides ions	<sup>54</sup> Cr <sup>38</sup> Ar <sup>+</sup> ,	<sup>56</sup> Fe <sup>38</sup> Ar <sup>+</sup> ,	<sup>55</sup> Mn <sup>40</sup> Ar <sup>+</sup> ,	<sup>56</sup> Fe <sup>40</sup> Ar <sup>+</sup> ,	<sup>57</sup> Fe <sup>40</sup> Ar <sup>+</sup> ,	<sup>58</sup> Fe <sup>40</sup> Ar <sup>+</sup> ,	60Ni40Ar+,
	<sup>54</sup> Fe <sup>38</sup> Ar <sup>+</sup> ,	<sup>54</sup> Cr <sup>40</sup> Ar <sup>+</sup> ,	<sup>57</sup> Fe <sup>38</sup> Ar <sup>+</sup> ,	58Ni38Ar+	<sup>61</sup> Ni <sup>36</sup> Ar <sup>+</sup> ,	58Ni40Ar+	<sup>68</sup> Zn <sup>36</sup> Ar <sup>+</sup> ,
	<sup>56</sup> Fe <sup>36</sup> Ar <sup>+</sup> ,	<sup>54</sup> Fe <sup>40</sup> Ar <sup>+</sup> ,	59Co36Ar+		59Co38Ar		
	$^{52}Cr^{40}Ar^+$	<sup>58</sup> Ni <sup>36</sup> Ar <sup>+</sup> ,					
Doubly	<sup>184</sup> W <sup>++</sup> ,	<sup>188</sup> Os <sup>++</sup>	<sup>190</sup> Os <sup>++</sup>	<sup>192</sup> Pt <sup>++</sup> ,	$^{194}Pt^{++}$	<sup>196</sup> Pt <sup>++</sup>	$^{200}{\rm Hg^{++}}$
charged species	<sup>184</sup> Os <sup>++</sup>			<sup>192</sup> Os <sup>++</sup>			

 Table S2 List of major potential interferences on Mo isotopes.

Reference material	Lithology	δ <sup>98</sup> Mo (‰)	2SD <sup>a</sup>	n	Notes
BHVO-2	Basalt	-0.01	0.02	3	Spiked after separation
		-0.06	0.04	3	
		-0.04	0.05	3	
		-0.02	0.05	3	
		-0.01	0.08	3	
		-0.07	0.04	3	
		-0.07	0.09	3	
		-0.04	0.03	3	
		-0.01	0.07	3	
		-0.02	0.04	3	
		-0.05	0.06	3	
		-0.02	0.07	3	Spiked after separation
Average		-0.03	0.05	12	
AGV-2	Andesite	-0.13	0.09	3	Spiked after separation
		-0.07	0.09	3	
		-0.06	0.05	3	
		-0.16	0.03	3	
		-0.15	0.03	3	
		-0.14	0.03	3	

**Table S3**. The molybdenum isotopic compositions (relative to SRM 3134) of sevengeological reference materials determined by MC-ICP-MS in this study.

Average	-0.12	0.08	7	
	-0.14	0.00	3	

Average		-0.86	0.03	5	
		-0.85	0.06	3	
		-0.87	0.05	3	
		-0.87	0.06	3	
		-0.84	0.09	3	
NOD-P-1	Nodule	-0.87	0.05	3	Spiked after separation
	Manganese				

	Manganese				
NODA-1	Nodule	-0.67	0.04	3	Spiked after separation
		-0.71	0.06	3	
		-0.73	0.00	3	
		-0.68	0.04	3	
		-0.70	0.06	3	
Average		-0.70	0.05	5	

W-2a	Diabase	-0.03	0.02	3	Spiked after separation
		-0.08	0.06	3	
		-0.02	0.02	3	
		-0.04	0.04	3	
		-0.04	0.07	3	
		0.01	0.01	3	

Average		-0.03	0.06	6	
SGR-1	Oil shale	0.46	0.10	3	Spiked after separation
		0.43	0.05	3	
		0.47	0.06	3	
		0.46	0.04	3	
		0.45	0.06	3	
		0.46	0.04	3	
Average		0.45	0.03	6	
Seawater	Seawater	2.06	0.01	3	Spiked after separation
		2.06	0.07	3	
		2.06	0.02	3	
		2.03	0.04	3	
		2.04	0.09	3	
		2.03	0.17	3	
		2.01	0.05	3	
		2.04	0.06	3	
		2.04	0.04	3	
Average		2.04	0.03	9	

<sup>a</sup> The repeatability of each sample solution was estimated by doubling the standard deviation (2SD) of the mean value of three replicate measurements; Bold 2SD is the two standard deviation of mean value of different sample solutions of each geological RM.

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