Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry. This journal is © The Royal Society of Chemistry 2024

Supporting Information



Proportion of DS (p) in DS-sample mixture

Figure S1. Comparison of theoretical errors in the natural fractionation factor (α) plotted against the proportion (p) of DS in a DS-sample mixture. The two curves denote the results of optimal ¹⁸⁰W-¹⁸⁴W and ¹⁸⁰W-¹⁸³W double spikes (both using ¹⁸⁰W-¹⁸³W-¹⁸⁴W-¹⁸⁶W inversion), respectively, both from Oak Ridge National Laboratory (ORNL). The ORNL single-spike compositions (¹⁸⁰W, ¹⁸²W, ¹⁸³W, ¹⁸⁴W, ¹⁸⁵W) are ¹⁸⁰W = (11.35%, 42.80%, 14.80%, 19.80%, 11.27%), ¹⁸³W = (<0.03\%, 5.51%, 79.03\%, 13.46\%, 2.00%), and ¹⁸⁴W = (<0.05\%, 1.79\%, 1.64\%, 94.64\%, 1.92\%).



Figure S2. (a) δ^{186} W and (b) δ^{98} Mo values of DS-NIST mixtures with variable DS proportions (*p*). Error bars represent 2 SD of individual measurements (n = 3). The shaded area shows the external reproducibility of ±0.03 (2 SD, n = 51) obtained for NIST 3163 solution (W) and ±0.04 (2 SD, n = 31) for NIST 3134 solution (Mo).



Figure S3. Elution profiles using anion exchange resin (AG1-X8) for the solutions of (A) AGV-2 (300 mg) with added interfering elements (1 μ g each of Ru and Ta) and (B) artificially mixed solution of single elements (1 μ g each of W, Mo, Ti, Mn, Fe, Zr, Nb, Ru, Hf, Ta): (a) the first-column and (b) the second-column procedures. The elution of Ru is not shown because it was removed during digestion and evaporation procedures.



Figure S4. (a) δ^{186} W and (b) δ^{98} Mo versus MgO for the geochemical reference materials of igneous rock series analyzed in this study. Error bars are the 2 SD obtained from replicate measurements of samples. MgO contents were obtained from online databases of the providers (USGS, GSJ, and CANMET-CCRMP). $\delta^{98/95}$ Mo are normalized relative to NIST 3134 (= 0‰) + 0.25‰.

	Average	$e \pm 2SD^{a}$ (ng	() Residual fraction ^b	X/W	X/Mo
Ti	3.00	± 2.58	3.3E-05	6.5E-03	8.3E-04
Mn	1.05	± 1.25	4.0E-07	2.7E-03	3.5E-04
Fe	336	\pm 703	3.3E-04	8.6E-01	1.1E-01
Zr	0.10	± 0.10	3.0E-05	3.3E-04	4.3E-05
Nb	0.03	$\pm \ 0.19$	9.0E-05	8.7E-05	1.1E-05
Ru	0.02	± 1.35	9.8E-03	4.0E-05	5.2E-06
Hf	0.003	± 0.030	4.5E-05	8.6E-06	1.1E-06
Та	0.050	± 0.049	6.7E-03	1.3E-04	1.7E-05

Table S1. Matrix elements in the JMn-1 solution (10 mg) obtained via the first column

Table S2. Matrix elements in the purified W and Mo solutions of the JMn-1 (10 mg) after the second column

	Purified solut	ion of W	Purified solution of Mo			
	Average $\pm 2SD^{a}$ (ng)	Residual fraction ^b	X/W	Average $\pm 2SD^{a}$ (ng)	Residual fraction ^b	X/Mo
Ti	$0.230 \ \pm \ 0.086$	3.0E-06	6.4E-04	$0.352 \ \pm \ 0.035$	4.6E-06	1.3E-04
Mn	Not Detected	_	<5.4E-4	Not Detected	_	<7.2E-5
Fe	$0.261 \ \pm \ 1.069$	2.5E-07	7.4E-04	$3.292 \ \pm \ 2.079$	3.1E-06	1.2E-03
Zr	$0.002 \ \pm \ 0.003$	4.0E-07	4.8E-06	$0.003\ \pm\ 0.009$	7.1E-07	1.1E-06
Nb	$0.002 \hspace{0.2cm} \pm \hspace{0.2cm} 0.001$	6.3E-06	6.6E-06	$0.011 \ \pm \ 0.004$	2.9E-05	3.9E-06
Ru	0.005 ± 0.341	2.7E-03	1.3E-05	$0.010 \ \pm \ 0.692$	6.0E-03	3.7E-06
Hf	Not Detected	_	<1.5E-6	Not Detected	_	<2.0E-7
Ta	Not Detected	—	<5.0E-6	Not Detected	—	<6.7E-7

^a 2SD was given by performing the separation procedures in triplicate.

^b Proportions were calculated using the recommended or preferable data for JMn-1 reported in Imai et al. (1999).

Reference list cited in Table 4

M. Tsujisaka, S. Takano, M. Murayama and Y. Sohrin, *Anal. Chim. Acta*, 2019, **1091**, 146-159.
D. Stubbs, R. Yang, C. D. Coath, T. John and T. Elliott, *Geochim. Cosmochim. Acta*, 2022, **334**, 135-154.

3. N. Krabbe, T. S. Kruijer and T. Kleine, Chem. Geol., 2017, 450, 135-144.

4. F. Kurzweil, C. Münker, J. Tusch and R. Schoenberg, Chem. Geol., 2018, 476, 407-417.

5. L. Roué, F. Kurzweil, M. Wille, A. Wegwerth, O. Dellwig, C. Münker and R. Schoenberg, *Geochim. Cosmochim. Acta*, 2021, **309**, 366-387.

- 6. T. Zhang, J. Liu, Q. Zhang, Y. Zhang and L. Qin, Geostand. Geoanal. Res., 2022, 47, 169-183.
- R. Yang, T. Li, D. Stubbs, T. Chen, S. Liu, D. B. Kemp, W. Li, S. Yang, J. Chen, T. Elliott, O. Dellwig, J. Chen and G. Li, *Geochim. Cosmochim. Acta*, 2022, 322, 227-243.
- 8. T. Breton and G. Quitt'e, J. Anal. At. Spectrom., 2014, 29, 2284-2293.
- 9. K. Abraham, J. Barling, C. Siebert, N. Belshaw, L. Gall and A. N. Halliday, *J. Anal. At. Spectrom.*, 2015, **30**, 2334–2342.

10. P. P. Zhao, J. Li, L. Zhang, Z. B. Wang, D. X. Kong, J. L. Ma, G. J. Wei and J. F. Xu, *Geostand*. *Geoanal. Res.*, 2016, **40**, 217-226.

11. M. Willbold, K. Hibbert, Y.-J. Lai, H. Freymuth, R. C. Hin, C. Coath, F. Vils and T. Elliott, *Geostand. Geoanal. Res.*, 2016, **40**, 389-403.

- 12. K. Irisawa and T. Hirata, J. Anal. At. Spectrom., 2006, 21, 1387.
- 13. N. Imai, S. Terashima, S. Itoh, and A. Ando, Geochem. J., 1995, 29, 91-95.
- S. E. Mazza, A. Stracke, J. B. Gill, J.-I. Kimura and T. Kleine, *Earth Planet. Sci. Lett.*, 2020, 530, 115942.
- D. Asael, F. L. Tissot, C. T. Reinhard, O. Rouxel, N. Dauphas, T. W. Lyons, E. Ponzevera, C. Liorzou and S. Chéron, *Chem. Geol.*, 2013, 362, 193-210.
- K. T. Goto, G. Shimoda, A. D. Anbar, G. W. Gordon, Y. Harigane, R. Senda and K. Suzuki, *Mar. Geol.*, 2015, **369**, 91-99.
- 17. J. Li, X. k. Zhu, S. h. Tang and K. Zhang, Geostand. Geoanal. Res., 2016, 40, 405-415.
- 18. N. Gaspers, T. Magna and L. Ackerman, Geostand. Geoanal. Res., 2020, 44, 363-374.
- T. Goldberg, G. Gordon, G. Izon, C. Archer, C. R. Pearce, J. McManus, A. D. Anbar and M. Rehkämper, JAAS, 2013, 28, 724-735.
- 20. J. S. Kane, B. Arbogast and J. Leventhal, Geostand. Newsl., 1990, 14, 169-196.
- 21. B. Kendall, S. Wang, P. Lillis, L. Xing, W. Zheng and C. Zhu, Chem. Geol., 2023, 617, 121244.
- 22. N. Imai, S. Terashima, S. Itoh and A. Ando, Geostand. Newsl., 1996, 20, 165-216.
- 23. G. P. Sindol, M. G. Babechuk, J. Conliffe, J. F. Slack, C. Rosca and R. Schoenberg, *Precambrian Res.*, 2022, **379**, 106750.
- 24. USGS Geochemical and Microanalytical Reference Materials Distribution:

https://www.usgs.gov/centers/gggsc/science/usgs-geochemical-and-microanalytical-reference-materials-distribution

- 25. NRC Digital Repository from National Research Council Canada: <u>https://nrc-digital-repository.canada.ca/eng/home/</u>
- 26. Canadian Certified Reference Materials Project: https://natural-resources.canada.ca/miningmaterials/resources/canadian-certified-reference-materials-project/price-certificates-list/8001