

Electronic Supporting Information

Efficient preconcentration of ultra-trace rhenium in geological materials by induced adsorption for accurate isotope analysis

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Table S1. Column chemistry procedure

step	reagents and dosage	
	this study	reference ¹
Resin filling	0.2ml AG1-X8 resin	1ml AG1-X8 resin
Precleaning	3ml 8N HNO ₃ + 2ml MQ	30ml 8N HNO ₃ + 5 ml MQ
Conditioning	3ml 0.5N HCl	5ml 1N HCl
Loading	2ml 0.5N HCl	2-50ml 1N HCl
Rinse	16ml 0.5N HCl	10ml 1N HCl + 15ml 0.5N HNO ₃ + 1.5ml 4N HNO ₃
Collection	2ml 8N HNO ₃	12.5ml 4N HNO ₃

Table S2. Rhenium removal rates from aqueous solutions under different conditions.

SW/MQ ^a	medium	Na ₂ S (M)	AC ^b (g/L)	reaction time (hours)	initial Re concentration (ppb)	Re removal (%)
MQ	0.3M HNO ₃	0.004	0.5	18	94.32	58.8
MQ	0.3M HNO ₃	0.01	0.5	1	93.76	52.6
MQ	0.3M HNO ₃	0.02	0.5	18	92.86	98.4
MQ	0.3M HNO ₃	0.04	0.5	18	91.29	99.8
MQ	0.3M HNO ₃	0.01	1.5	18	93.92	99.4
MQ	0.3M HNO ₃	0.01	0.5	18	94.11	93.0
MQ	0.3M HNO ₃	0.01	0.25	18	93.78	91.4
MQ	0.6M HNO ₃	0.01	0.5	18	91.71	95.7
MQ	0.6M HNO ₃	0.02	0.5	18	90.42	99.7
MQ	0.5M HCl	0.01	0.5	18	90.15	98.9
MQ	0.5M HCl	0.02	0.5	18	89.69	99.9
SW	0.3M HNO ₃	0.004	0.5	18	444.96	83.2
SW	0.3M HNO ₃	0.01	0.5	18	429.34	96.0
SW	0.3M HNO ₃	0.02	0.5	18	459.79	99.8
SW	0.3M HNO ₃	0.04	0.5	18	435.32	100.0
SW	0.3M HNO ₃	0.01	1	18	468.46	97.4

^a SW = seawater, MQ = Milli-Q water.

^b AC = activated carbon.

Table S3. Rhenium recoveries by CuS coprecipitation working on 50 ml seawater.

number	reagents and dosage	recovery (%)
1	0.075mM CuSO ₄ + 0.05mM Na ₂ S	0.5
2	0.05mM FeSO ₄ + 0.1mM CuSO ₄ + 0.1mM Na ₂ S	1.0
3	0.4mM cysteine + 0.15mM CuSO ₄ + 0.25mM Na ₂ S	0.5
4	0.2mM cysteine + 0.05mM FeSO ₄ + 0.1mM CuSO ₄ + 0.25mM Na ₂ S	0.7
5	0.4mM NH ₂ OH•HCl + 0.1mM FeSO ₄ + 0.1mM CuSO ₄ + 0.1mM Na ₂ S	0.4
6	3mM NH ₂ OH•HCl + 0.2mM cysteine + 0.2mM FeSO ₄ + 0.1mM CuSO ₄ + 0.1mM Na ₂ S	0.4
7 ^a	3mM NH ₂ OH•HCl + 0.2mM cysteine + 0.2mM FeSO ₄ + 0.1mM CuSO ₄ + 0.1mM Na ₂ S	0.6
8	0.4mM cysteine + 1.4mM FeSO ₄ + 2mM Na ₂ S	0.6
9	3mM NH ₂ OH•HCl + 0.2mM cysteine + 0.1mM FeSO ₄ + 0.2mM CuSO ₄ + 0.2mM Na ₂ S + 1g/L montmorillonite	4.5
10	3mM NH ₂ OH•HCl + 0.2mM cysteine + 0.1mM FeSO ₄ + 0.2mM CuSO ₄ + 0.2mM Na ₂ S + 1g/L kaolinite	3.6

^a The solution remained undisturbed for 18 hours before filtration.

Table S4. Rhenium recoveries and isotopic results for synthetic solutions. The doped AAS Re exhibits $\delta^{187}\text{Re}$ of $-0.50\pm 0.05\%$ (2SD, n=28).

number	matrix	recovery (%)	$\delta^{187}\text{Re}$ (‰)
1	MQ	100.0	-0.46 ± 0.04
2	MQ	101.2	-0.47 ± 0.03
3	DS ^a	96.3	-0.47 ± 0.04
4	DS	95.1	-0.49 ± 0.04
5	DS	97.0	-0.48 ± 0.03
6	Seawater	102.1	-0.51 ± 0.04
7	Seawater	98.9	-0.51 ± 0.04
8	Seawater	105.5	-0.50 ± 0.04
9	Seawater	103.3	-0.51 ± 0.04
10	Seawater	97.0	-0.49 ± 0.05

^a DS refers to the BHVO-2 digested solution.

Table S5. Rhenium isotopic results for geological materials. The analyte concentration of ~2 ppb corresponded to internal errors of ~0.12‰ (2 SE). Increasing the analyte concentration to ~4 ppb reduced the internal error to ~0.08‰ (2 SE).

materials	$\delta^{187}\text{Re}$ (‰)
MAG-1	-0.33±0.13, -0.37±0.13, -0.31±0.10, -0.20±0.13, -0.35±0.16, -0.25±0.13
SBC-1	-0.47±0.09, -0.46±0.14, -0.47±0.14, -0.41±0.11
SGR-1	-0.29±0.13, -0.30±0.11, -0.23±0.12, -0.20±0.13, -0.32±0.12
SDO-1	-0.06±0.12, -0.13±0.11, -0.14±0.11, -0.12±0.08, -0.10±0.08, -0.03±0.12, -0.14±0.12, -0.12±0.07
BCR-2	-0.36±0.14, -0.35±0.11, -0.37±0.13, -0.29±0.15, -0.23±0.11, -0.37±0.12
BHVO-2	-0.40±0.12, -0.39±0.17, -0.28±0.15
BIR-1	-0.32±0.10
Seawater	-0.21±0.12, -0.22±0.10, -0.25±0.11, -0.19±0.08, -0.16±0.06, -0.22±0.08, -0.23±0.10, -0.20±0.10

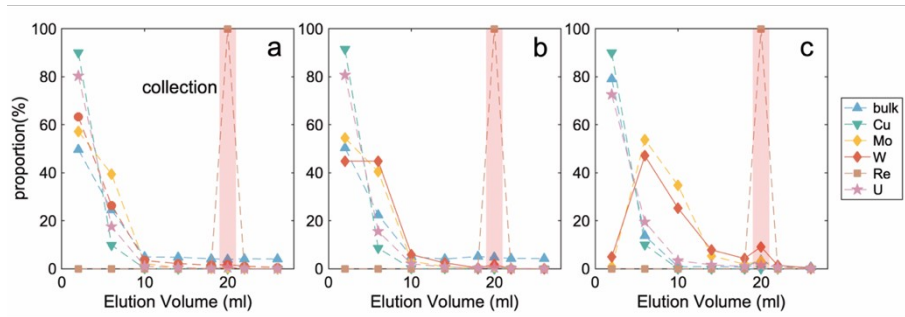


Fig. S1. Elution curves of the column chemistry. Preconcentrated BCR-2 (a), SDO-1 (b), and seawater (c) were tested, respectively.

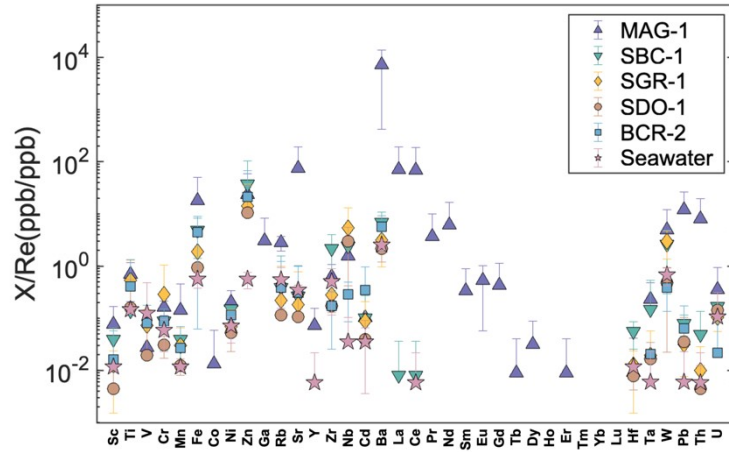


Fig. S2. Element/Re ratios after one column separation. Major elements like Na, Mg, Al, K, and Ca were not measured. The error bar was 2SD for repeated measurements (3 for MAG-1, 3 for SBC-1, 3 for SGR-1, 3 for SDO-1, 4 for BCR-2, and 2 for seawater). Ratios less than 0.001 were not shown in this figure.

References

- (1) Dellinger, M.; Hilton, R. G.; Nowell, G. M. Measurements of rhenium isotopic composition in low-abundance samples. *Journal of Analytical Atomic Spectrometry* **2020**, *35* (2), 377-387, 10.1039/C9JA00288J. DOI: 10.1039/C9JA00288J.