Electronic Supplementary Material (ESI) for JAAS.

Supplementary information

High-precision measurement of Cd isotopes in ultra-trace Cd samples using double spike-standard addition MC-ICP-MS

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Text S1. Details of Equation (6) for calculating the error propagation of multi-standard addition.

The δ value of sample is calculated from equation (5), and the error propagation can be estimated by the following equation:

$$\sigma_{\delta spl-multi} = \sqrt{\left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta std1}}\right)^2 \times \sigma_{\delta std1}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta std2}}\right)^2 \times \sigma_{\delta std2}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta mix1}}\right)^2 \times \sigma_{\delta mix1}{}^2 + \left(\frac{\partial_{\delta spl-m\cdots}}{\partial_{\delta mix\cdots}}\right. \cdots \atop \left(\frac{\partial_{\delta spl-multi}}{\partial_{Pstd1}}\right)^2 \times \sigma_{Pstd1}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{Pstd2}}\right)^2 \times \sigma_{Pstd2}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{Pmix1}}\right)^2 \times \sigma_{Pmix1}{}^2 + \left(\frac{\partial_{\delta spl-\cdots}}{\partial_{Pm\cdots}}\right. \cdots}$$

Since the uncertainties contributed by $\sigma_{P\text{-}std}$ and $\sigma_{P\text{-}mix}$ account for less than one-thousandth of the total error, the terms containing $\sigma_{P\text{-}std}$ and $\sigma_{P\text{-}mix}$ can be negligible. Thus,

$$\sigma_{\delta spl-multi} = \sqrt{\left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta std1}}\right)^2 \times \sigma_{\delta std1}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta std2}}\right)^2 \times \sigma_{\delta std2}{}^2 + \left(\frac{\partial_{\delta spl-multi}}{\partial_{\delta mix1}}\right)^2 \times \sigma_{\delta mix1}{}^2 + \left(\frac{\partial_{\delta spl-m\cdots}}{\partial_{\delta mix\cdots}}\right. \cdots} \quad (6)$$

Each error term of equation 6 can be reduced by the following equations:

$$\frac{\partial_{\delta spl-multi}}{\partial_{\delta std1}} = 1 - \frac{P_{std1}{}^2 \times \left(\delta^{114/110}Cd_{std1} - \delta^{114/110}Cd_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \cdots\right.}{\left(P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times \left(\delta^{114/110}Cd_{std1} \cdots\right.\right.} - \frac{P_{std1} \times (\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2})}{P_{std1} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times (\delta^{114/110}Cd_{std1} - \delta^{114/\cdots}} \quad (7)$$

$$\frac{\partial_{\delta spl-multi}}{\partial_{\delta mix1}} = \frac{P_{std1} \times (\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2})}{P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times \left(\delta^{114/110}Cd_{std1} - \delta^{1\cdots}\right.} + \frac{P_{std1}{}^2 \times (\delta^{114/110}Cd_{std1} - \delta^{114/100}Cd_{mix1}) \times \left(P_{std2} - P_{mix2}\right) \times \left(\delta^{114/110}Cd_{std2} \cdots\right.}{(P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times (\delta^{114/110}Cd_{std1} - \delta^{114\cdots}} \quad (8)$$

$$\frac{\partial_{\delta spl-multi}}{\partial_{\delta std2}} = \frac{P_{std1} \times P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times (\delta^{114/110}Cd_{std1} - \delta^{114/100}Cd_{mix1})}{\left(P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{\frac{114}{110}}Cd_{std2} - \delta^{\frac{114}{110}}Cd_{mix2}\right) - P_{std1} \times (\delta^{114/110}Cc} - \frac{P_{std1} \times (\delta^{114/110}Cd_{std1} - \delta^{114/100}Cd_{r}}{P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times (\delta^{114/1}} \quad (9)$$

$$\frac{\partial_{\delta spl-multi}}{\partial_{\delta mix2}} = \frac{P_{std1} \times (\delta^{114/110}Cd_{std1} - \delta^{114/110}Cd_{mix1}}{P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times (\delta^{114/110}Cd_{st}} - \frac{P_{std1} \times P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std1} - \delta^{114/110}Cd_{mix1}\right) \times (}{\left(P_{std2} \times \left(P_{std1} - P_{mix1}\right) \times \left(\delta^{114/110}Cd_{std2} - \delta^{114/110}Cd_{mix2}\right) - P_{std1} \times \left(\delta^{114/110}Cd_{st}\right.\right.} \quad (10)$$

Table S1 Instrumental parameters for Cd isotope measurement.

Parameters	**Setting for Neptune**
Cup configuration	L4 (^{107}Ag), L3 (^{108}Cd), L2 (^{109}Ag), L1 (^{110}Cd), C (^{111}Cd), H1 (^{112}Cd, ^{112}Sn), H2 (^{113}Cd), H3 (^{114}Cd, ^{114}Sn), H4 (^{117}Sn)
Inlet system	
cool gas	15 L min^{-1}
aux gas	0.80-1.15 L min^{-1}
sample gas	0.92-1.20 L min^{-1}
RF power	1250W
sample cone	H type, Ni/Pt
skimmer cone	X type, Ni/Pt
resolution mode	low
sample uptake	110 μL min^{-1}
Aridus II	
spray chamber temperature	110°C
desolvator temperature	160°C
Ar_2 sweep gas	4.5-6 L min^{-1}
Nitrogen gas	1-6 mL min^{-1}
sensitivity	460 V ppm^{-1} of ^{112}Cd
injecting concentration	5-10 μg L^{-1}

number of cycles	45 (3 blocks ×15 cycles) for 10 ppb; 60 (3 blocks ×20 cycles) for 5 ppb
Integration time	4.194s

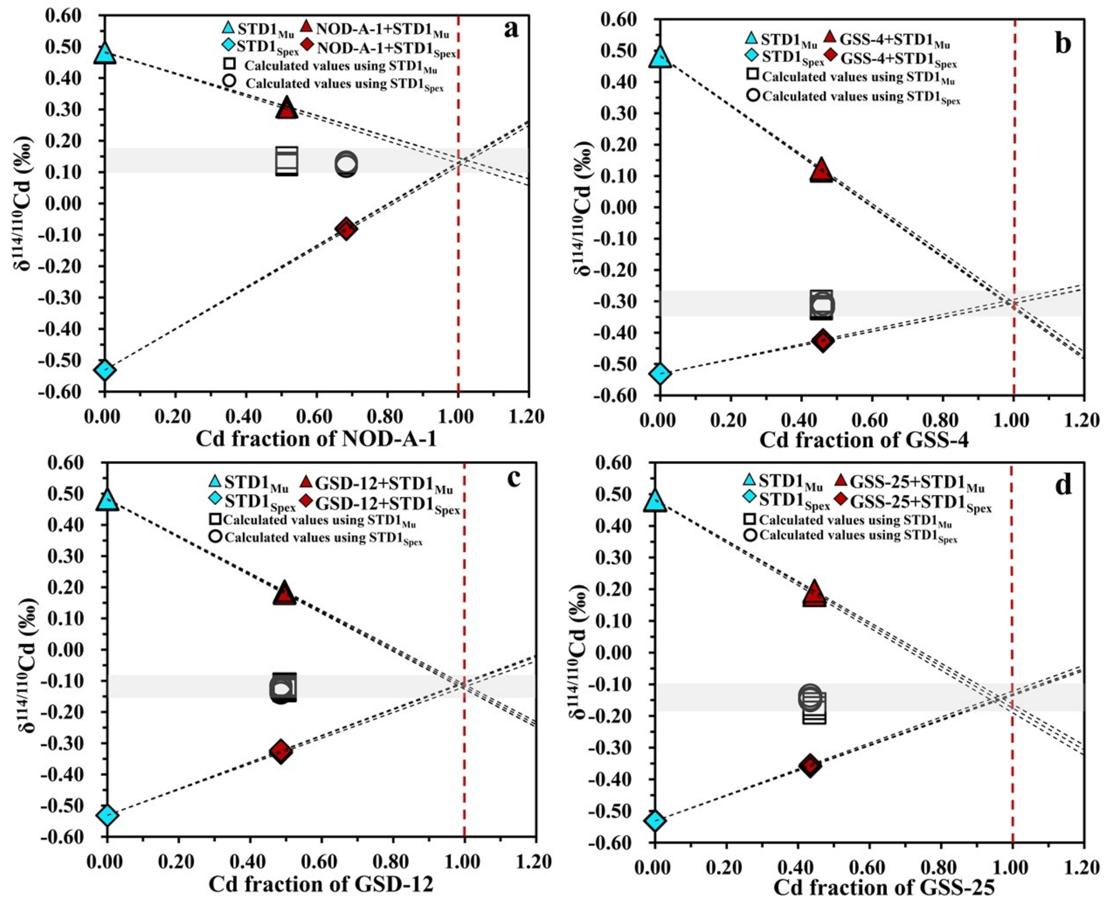

Fig. S1 The $\delta^{114/110}$Cd values of mixed solutions (sample + standard) and calculated values for geological reference materials. The gray bar denotes 2SD of those values calculated by single-standard method; the red vertical line represents the pure sample (with no standard added).

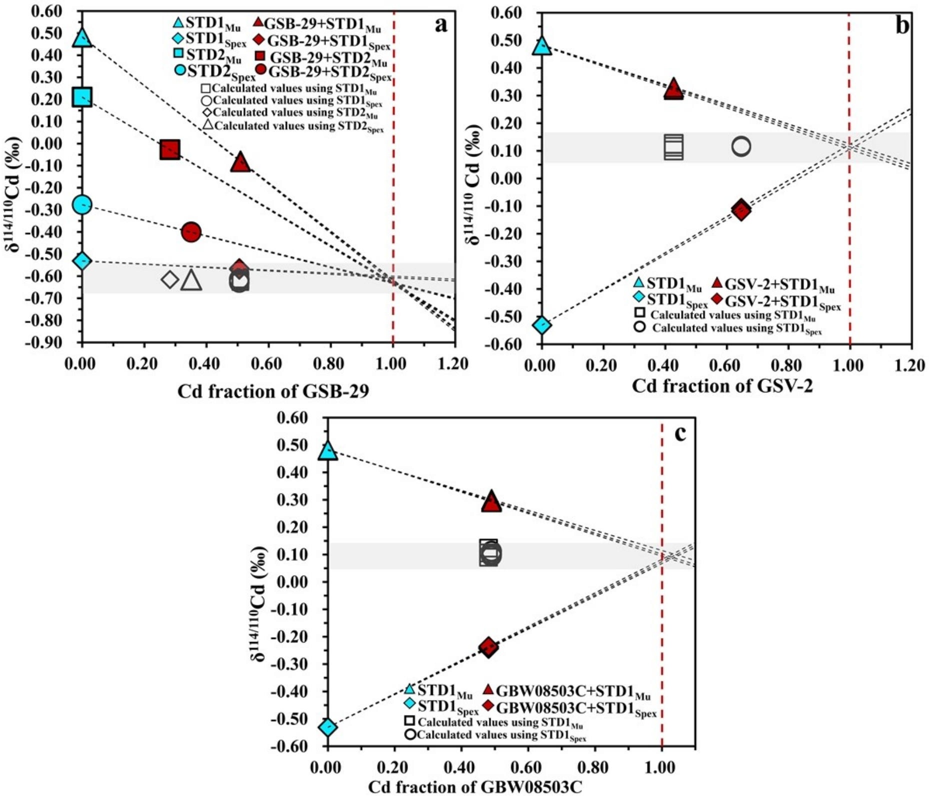

Fig. S2 The $\delta^{114/110}$Cd values of mixed solutions (sample + standard) and calculated values for biological reference materials. The gray bar denotes 2SD of those values calculated by a single-standard; the red vertical line represents pure sample (with no standard added).

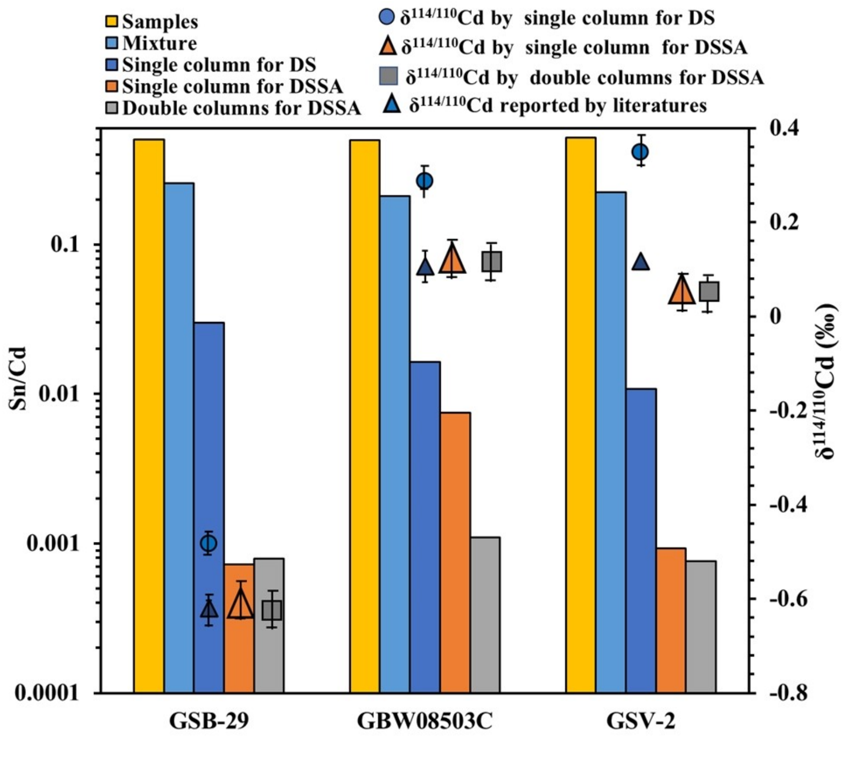

Fig. S3 Comparison of the effects on removing matrix elements (Sn) in single column purification using traditional DS and DSSA methods.

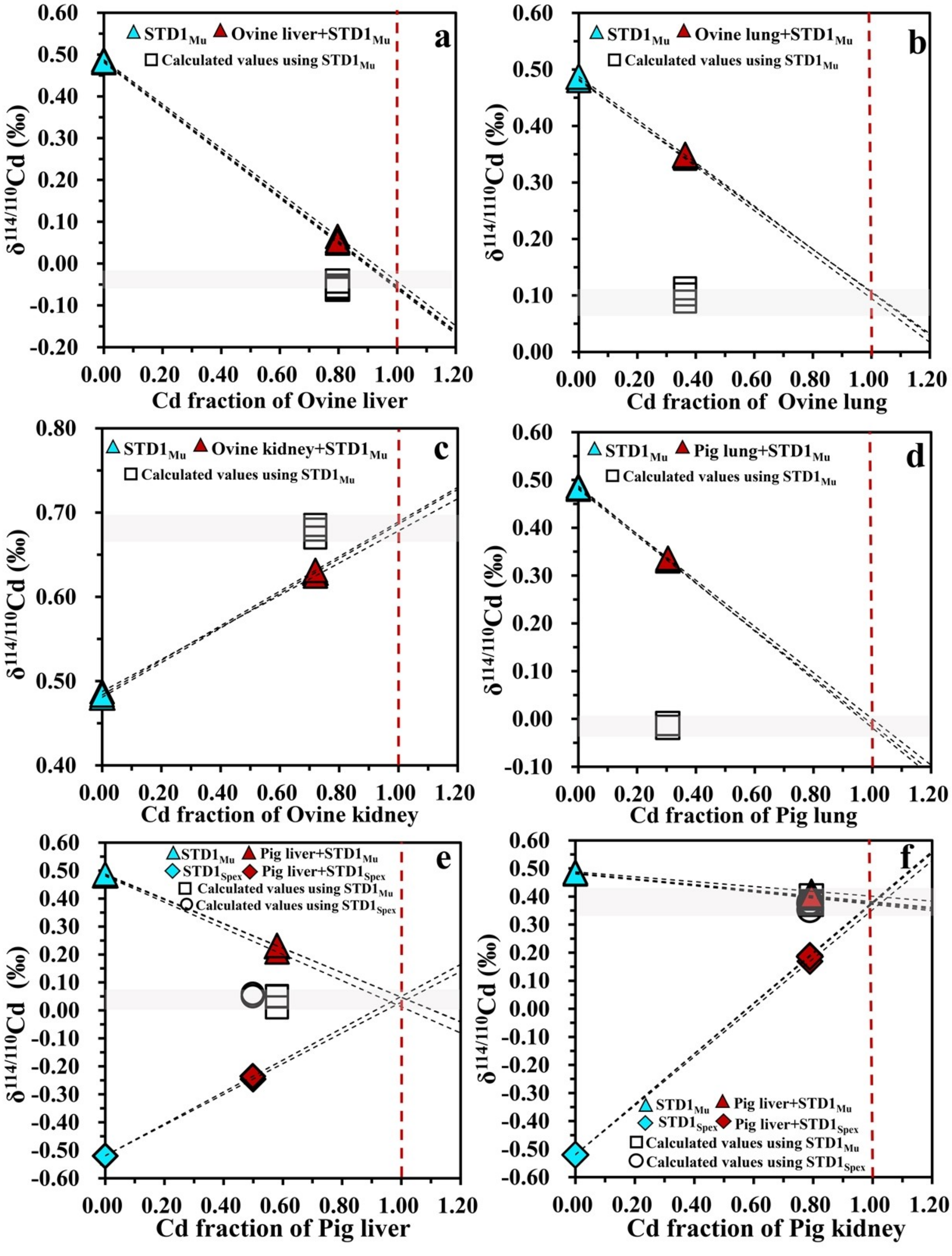

Fig. S4 The $\delta^{114/110}Cd$ values of mixed solutions (sample + standard) and calculated values for ovine and pig organs. The gray bar denotes 2SD of those values calculated by a single-standard; the red vertical line represents the 100% sample. (a) ovine liver; (b) ovine lung; (c) ovine kidney; (d) pig lung; (e) pig liver; (f) pig kidney.