Electronic Supplementary Material (ESI) for JAAS.

Supplementary Material

Table S1: Nu Plasma II settings

	Sn analysis		**Cd analysis**	
Desolvating nebuliser system	DSN 100		DSN 100	
Argon membrane gas flow	2.3-2.7	L/min	2.3-2.9	L/min
Hot gas flow	0.23	L/min	0.23	L/min
Nitrogen gas flow	0	ml/min	0	ml/min
Nebuliser pressure	24	psi	15.3-34	psi
Spray chamber temperature	110	°C	110	°C
Membrane temperature	110	°C	110	°C
Solution uptake rate	50-60	µl	50-60	µl
Inlet system				
Cooling gas	13	L/min	13-20	L/min
Auxiliary gas	0.82	L/min	0.77-1.1	L/min
RF power	1300	W	1300	W
Analysis parameter				
Number of blocks	1		1	
Number of integrations per block	20		30	
Magnet delay time	3	s	2	s
Integration time	10s for line 1, 5s for line 2		10s for line 1, 5s for line 2	
Concentration	100 - 200 ppb		200 ppb	
Medium	0.5 M HNO_3 - 0.005 M HF		0.5 M HNO_3	

Table S2: Comparison of Te correction with ^{125}Te or ^{126}Te on the isotopic ratio ^{124}Sn/^{120}Sn.

			^{125}Te correction				^{126}Te correction			
Sample	n	Te/Sn	^{124}Sn/^{120}Sn	2SD	ε^{124}Sn	2SD	^{124}Sn/^{120}Sn	2SD	ε^{124}Sn	2SD
NIST 40 ppb	36	0.000019	0.177600	(10)	0.01	0.40	0.177602	(10)	0.01	0.55
NIST 5.5 ppb	23	0.000013	0.177595	(45)	-0.01	2.51	0.177596	(54)	-0.01	3.16
NIST 5.5 ppb + Te	1	0.003603	0.177568		-0.37		0.177587		0.79	
NIST 5.5 ppb + Te	1	0.003603	0.177626		-0.30		0.177631		-1.02	
NIST 9 ppb	26	0.000020	0.177595	(31)	-0.81	2.93	0.177598	(31)	0.30	1.65
NIST 9 ppb + Te	1	0.003273	0.177565		-0.17		0.177568		-0.34	
NIST 100 ppb	43	0.000035	0.177610	(11)	0.01	0.33	0.177614	(10)	0.02	0.37
NIST 200 ppb	58	0.000037	0.177609	(9)	-0.02	0.39	0.177613	(9)	-0.02	0.38
NIST 200 ppb + Te	1	0.001073	0.177611		-0.10		0.177615		-0.07	

2SD on ^{124}Sn/^{120}Sn refer to last digits; NIST: Sn NIST SRM3161a.
Please note that the ε^{124}Sn values are calculated relative to the bracketing standards. They do not directly relate to the absolute ^{124}Sn/^{120}Sn ratios reported here.

Table S3: Cadmium isotope ratios of column processed standards and samples

Sample	Cd (ppb)	$^{118}Sn/^{111}Cd$	$^{115}In/^{111}Cd$	$^{105}Pd/^{111}Cd$	$^{66}Zn/^{111}Cd$	N	$\varepsilon^{106}Cd$			$\varepsilon^{108}Cd$			$\varepsilon^{110}Cd$			$\varepsilon^{112}Cd$			$\varepsilon^{113}Cd$			$\varepsilon^{114}Cd$		
Cd standard solutions																								
Alfa Aesar	200	8.9E-05	1.6E-05	2.7E-05		40	0.0	±	1.0	0.0	±	1.1	0.00	±	0.28	0.00	±	0.16	0.00	±	0.20	0.00	±	0.17
NIST SRM 3108	200	9.8E-05	9.8E-06	2.7E-05		2	-0.1	±	0.9	0.2	±	1.0	-0.06	±	0.21	-0.01	±	0.29	0.07	±	0.39	0.03	±	0.27
Column processed Alfa Aesar Cd standard solutions																								
Cd Std 1 (Main Cd)*	200	7.3E-04	2.2E-05	4.3E-05	3.2E-03	1	0.6	±	0.7	0.1	±	0.9	-0.04	±	0.21	-0.07	±	0.11	-0.09	±	0.09	-0.06	±	0.14
	200	7.5E-04	3.6E-05	6.0E-05	3.0E-02	1	1.3	±	2.2	0.7	±	3.0	-0.01	±	0.37	-0.01	±	0.25	-0.03	±	0.27	-0.01	±	0.18
	200	7.1E-04	1.7E-05	3.2E-05	2.5E-02	1	4.5	±	1.0	3.6	±	1.4	0.40	±	0.56	0.20	±	0.35	0.02	±	0.37	0.15	±	0.29
	200	7.3E-04	2.2E-05	3.6E-05	3.0E-02	1	2.9	±	1.0	1.7	±	1.0	0.26	±	0.32	0.19	±	0.20	-0.13	±	0.24	0.04	±	0.16
Cd Std 2 (Main Cd)*	200	6.6E-03	1.0E-04	2.4E-04	8.3E-03	1	0.3	±	0.7	-0.3	±	0.9	0.02	±	0.21	0.02	±	0.11	-0.10	±	0.09	-0.23	±	0.14
	200	1.0E-03	1.8E-05	4.5E-05	5.2E-03	1	1.3	±	0.8	0.3	±	1.2	0.36	±	0.27	0.17	±	0.14	0.01	±	0.15	-0.01	±	0.11
Cd Std 3 (Full chemistry)*	200	1.1E-04	1.1E-05	2.4E-05	1.8E-03	1	-0.3	±	1.0	0.4	±	1.0	0.22	±	0.32	0.20	±	0.20	-0.01	±	0.24	0.16	±	0.16
	200	3.4E-04	1.1E-05	3.4E-05		1	-0.1	±	0.7	-1.1	±	1.0	0.17	±	0.28	0.16	±	0.20	0.11	±	0.26	0.11	±	0.24
	200	1.2E-04	8.8E-06	2.7E-05		1	-1.2	±	0.8	-1.1	±	1.2	0.00	±	0.28	0.12	±	0.15	0.01	±	0.18	0.10	±	0.15
average	200					9	1.0	±	3.5	0.5	±	2.9	0.15	±	0.33	0.11	±	0.21	-0.02	±	0.15	0.03	±	0.24
Column processed Alfa Aesar Cd-Zn standard solutions																								
Cd-Zn Std 1 (Main + Short Cd)*	200	1.9E-04	1.3E-05	3.8E-05	7.9E-03	1	0.0	±	0.8	-0.4	±	1.2	-0.02	±	0.27	0.08	±	0.14	-0.17	±	0.15	0.02	±	0.11
Cd-Zn Std 2 (Main Cd)*	200	1.8E-03	5.0E-05	5.5E-05	1.4E-02	1	0.6	±	0.7	-0.5	±	0.9	-0.13	±	0.21	0.00	±	0.11	-0.14	±	0.09	-0.10	±	0.14
Cd-Zn Std 3 (Main Cd)*	200	1.4E-03	4.0E-05	5.7E-05	1.8E-02	1	1.4	±	0.7	0.1	±	0.9	0.14	±	0.21	0.00	±	0.11	0.02	±	0.09	-0.04	±	0.14
Cd-Zn Std 4 (Main Cd)*	200	1.2E-03	3.2E-05	5.0E-05	1.4E-02	1	0.7	±	0.7	0.0	±	0.9	-0.09	±	0.21	-0.06	±	0.11	0.00	±	0.09	-0.03	±	0.14
Cd-Zn Std 5 (Short Cd)*	200	1.4E-04	1.7E-05	4.1E-05	3.2E-03	1	-0.8	±	1.1	-1.0	±	1.1	0.01	±	0.26	0.05	±	0.15	0.05	±	0.14	0.02	±	0.15
average	200					5	0.4	±	1.7	-0.3	±	0.9	-0.02	±	0.21	0.02	±	0.10	-0.05	±	0.20	-0.02	±	0.10
Lake Sediment																								
Lake Zürich Ia	200	2.9E-04	1.3E-05	4.7E-05	8.3E-03	1	-0.1	±	0.8	-0.5	±	1.2	0.18	±	0.27	0.13	±	0.14	-0.09	±	0.15	0.06	±	0.11
Lake Zürich Ib	200	2.1E-04	7.3E-06	3.9E-05	2.3E-03	1	-0.2	±	0.8	-1.0	±	1.2	0.04	±	0.27	0.08	±	0.14	-0.01	±	0.15	0.03	±	0.11
Lake Zürich Ic	200	9.6E-04	1.4E-05	3.2E-05	6.3E-03	1	0.4	±	0.8	-0.3	±	0.9	0.21	±	0.16	0.14	±	0.13	-0.18	±	0.18	-0.12	±	0.15
Lake Zürich Id + Ie	200	2.6E-04	1.5E-05	2.5E-05	7.1E-03	1	0.5	±	0.9	1.0	±	1.1	0.19	±	0.24	0.06	±	0.19	0.06	±	0.22	0.09	±	0.18
Lake Zürich If	200	6.4E-04	4.2E-05	5.0E-05	5.6E-03	1	-0.1	±	2.2	-0.5	±	3.0	-0.11	±	0.37	-0.11	±	0.25	-0.21	±	0.27	-0.06	±	0.18
Lake Zürich If	200	9.2E-04	2.4E-05	2.9E-05	1.1E-02	1	1.8	±	0.7	1.8	±	1.0	0.24	±	0.28	0.11	±	0.20	0.01	±	0.26	0.01	±	0.24
Lake Zürich I bomb a	200	1.7E-04	6.0E-06	2.3E-05	1.9E-03	1	0.1	±	0.9	0.1	±	1.3	0.04	±	0.22	0.03	±	0.12	-0.10	±	0.24	0.00	±	0.25
Lake Zürich I bomb b	200	2.1E-04	1.5E-05	2.8E-05	1.6E-03	1	-1.2	±	0.7	-1.5	±	0.8	-0.21	±	0.22	-0.07	±	0.17	-0.32	±	0.24	-0.11	±	0.14
Lake Zürich I bomb c	200	6.6E-05	2.6E-06	2.1E-05	2.6E-03	1	0.7	±	0.8	0.7	±	0.9	0.30	±	0.16	0.13	±	0.13	-0.07	±	0.18	0.03	±	0.15
average	200					9	0.2	±	1.7	0.0	±	2.0	0.10	±	0.34	0.06	±	0.18	-0.10	±	0.24	-0.01	±	0.15

Uncertainty quoted is the drift corrected reproducibility (2SD) of the Alfa Aesar Cd standard in the same measurement session except for averages, where the 2SD of the repeat analyses are shown. The Cd (ppb) refers to the concentration of the measured solution.

"N" refers to the number of measurement sessions (Cd standard solutions) or individual analysis (column processed standards and samples).

*Brackets refer to the column chemistry samples were passed through:

"Main Cd" – first Cd column, "Short Cd" – second down-scaled Cd column, "Full chemistry" – entire separation procedure performed using all four stages.

Table S4: Comparison of Cd isotope data for Cd standard solutions with previous data.

Ratio	Reagent Cd *Rosman et al. 1980* [52]			Cd metal, Vacuum Technology Aalen *Wombacher et al., 2004* [42]			JMC Cd Münster and Alfa Cd Zürich *Ripperger and Rehkämper, 2007* [51]			Alfa Aesar Cd *200 ppb, ETH*		
	mean	95% CL	95% CL ppm	mean	2SD	2SD ppm	mean	2SD	2SD ppm	mean	2SD	2SD ppm
$^{106}Cd/^{114}Cd$	0.044247	0.00027	6102	0.044206	0.000004	90	-			0.044231	0.000007	158
$^{108}Cd/^{114}Cd$	0.031374	0.000025	797	0.031364	0.000003	96	-			0.031381	0.000004	128
$^{110}Cd/^{114}Cd^{*}$	0.438564			0.438564			0.438564			0.438564		
$^{111}Cd/^{114}Cd$	0.44845	0.00011	245	0.448848	0.000007	16	0.448867	0.000050	111	0.448881	0.000023	52
$^{112}Cd/^{114}Cd$	0.84324	0.00012	142	0.843259	0.000020	24	0.843269	0.000132	157	0.843266	0.000031	37
$^{113}Cd/^{114}Cd$	0.426046	0.000058	136	0.42645	0.00007	164	-			0.426483	0.000040	93
$^{116}Cd/^{114}Cd$	0.259629	0.000029	112	0.259661	0.000019	73	-			0.259704	0.000022	83
n	6			5			93			1061		

*All data are normalised to $^{110}Cd/^{114}Cd = 0.438564$ [52]
"n" refers to the number of data points

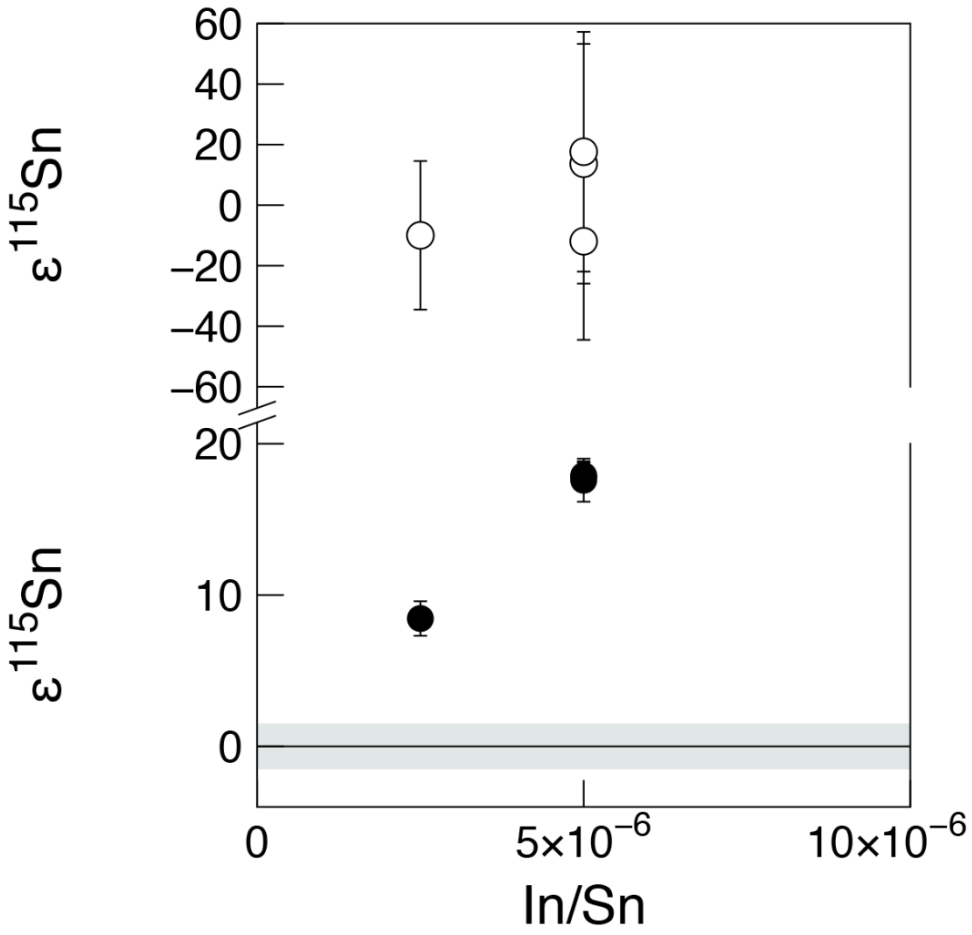

Figure S1: Tin isotope ratios for a 100 pbb NIST SRM 3161a standard solution doped with In. Open symbols show interference corrected data, while closed symbols data without interference correction. Data points are single analyses and error bars represent the analytical precision of the NIST bracketing standard during the measurement session. The grey band represents the reproducibility (2SD) of NIST SRM 3161a at 100 ppb.

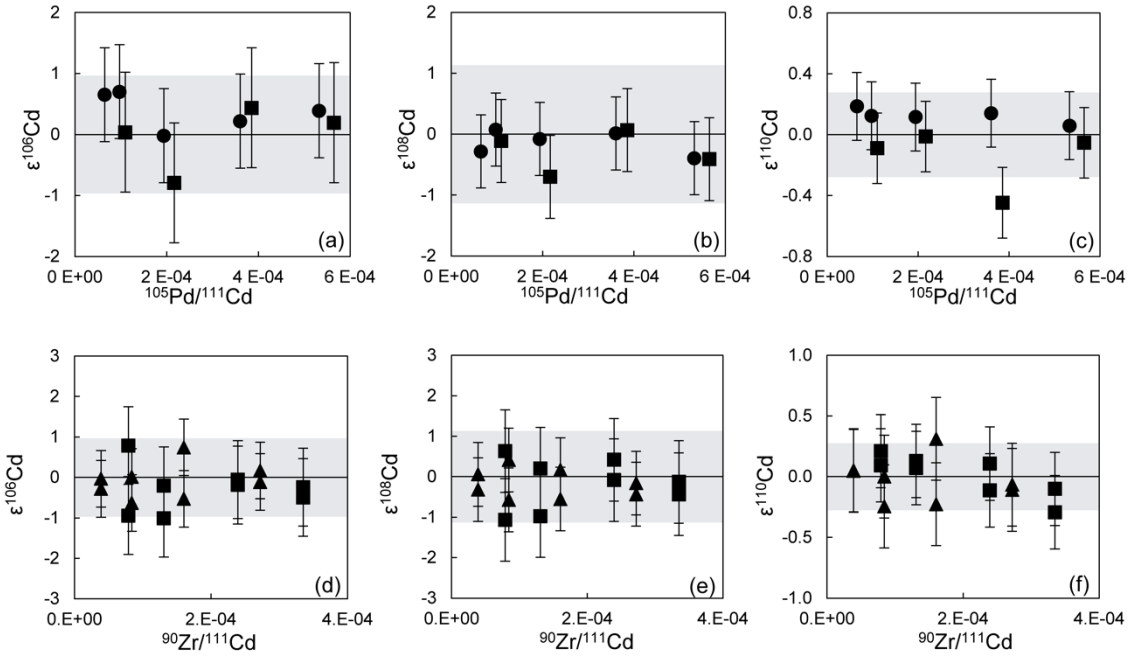

Figure S2: Cadmium isotope ratios measured for a 200 ppb Alfa Aesar Cd standard solution doped with Pd and Zr after interference correction. Symbols and grey bands are the same as in Fig. 2. The $^{105}Pd/^{111}Cd$ ratios were determined from the measured signal intensities during isotope analysis, the $^{90}Zr/^{111}Cd$ ratios from mass-scans performed prior to analysis.