High-sensitivity determination of Cd isotopes of low-Cd geological samples by double spike MC-ICP-MS

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Table S1 Reported methods and the total procedural blanks for Cd separation

Reference	Resin*	Sample type	The lowest Cd in Sample (μg g^{-1})	Blank ng	Yield (%)
Single-column purification scheme					
Cloquet *et al.*(2005) [36]	AGMP-1M	Geological samples	4	0.2	>95
Cloquet *et al.*(2006) [30]	AGMP-1M	Soil	2	0.2	-
Gao *et al.*(2008) [37]	AGMP-1M	Sediment	23	0.2	>90
Conway *et al.* (2013) [16]	Nobias PA-1 AGMP-1M	Seawater		0.004	n.d.
Pallavicini *et al.* (2014) [38]	AGMP-1M	Environmental samples	0.07	n.d.	>95
Wei *et al.* (2015) [39]	AGMP-1M	Plant	0.37	n.d.	>95
Zhang *et al.*(2018) [41]	AGMP-1M	Carbonates	33	<0.07	>90
Yang *et al.* (2019) [40]	AGMP-1M	water and Sediment	18	n.d.	>97
Two-column purification scheme					
Wombacher *et al.* (2003) [11]	AG1-X8 TRU Spec	Chondrites, Basalt, etc.	n.d.	<0.02	n.d.
Horner *et al.* (2010) [12]	AG1-X8 TRU Spec	Fe-Mn crusts	1.7	0.005	n.d.
Gault-Ringold *et al.*(2012) [14]	AG1-X8 TRU-Spec	Seawater		0.055	>90
Xue *et al.* (2012) [13]	AG1-X8 TRU Spec	Seawater		0.02-0.03	>85
Kruijer *et al.* (2013) [43]	AG1-X8 TRU-Spec	Meteorite	0.0004	0.03	>80
Martinková *et al.* (2015) [19]	AG-1- X8 TRU Spec	Environmental samples	5.24	n.d.	>94
Wiggenhauser *et al.* (2016) [44]	AG1-X8 TRU Spec	Plant	-	< 0.53	-
Fouskas *et al.* (2018) [45]	AG1-X8 TRU-Spec	Plant	0.1	-	95
Other purification scheme for TIMS					
Schmitt *et al.* (2009)[56]	AG1-X8	Basalt, Sulphides	0.1	<0.16	n.d.
Abouchami *et al.* (2011) [29]	AG1-X8	Seawater	-	0.015	96
Hohl *et al.* (2017) [21]	AG1-X8	Carbonates	0.02		

***** AG-x8 contains two different mesh, such as 100-200 mesh and 200-400 mesh

Table S2 The description of geological reference materials

Sample name	Cd (μg g^{-1})	Description
BCR-2	0.69	Columbia River basalt
BHVO-2	0.15	Hawaiian volcanic basalt
SGR-1b	0.90	Petroleum and carbonate-rich shale from the Mahogany zone of the Green River Formation
NOD-A-1	6.50	Manganese nodules from the Atlantic Oceans at a depth of 788 meters
NOD-P-1	22.30	Manganese nodules from the Pacific Oceans at a depth of 4,300 meters
SRM 2711a	54.10	Montana II Soil
GSS-1	4.30	Brown soil from Xilin Lead-Zinc Mine, Heilongjiang Province, China
GSS-4	0.35	Limestone weathered soil in Yishan, Guangxi Province, China
GSS-5	0.45	Yellow-red soil in Qibaoshan skarn copper polymetallic ore district, Hunan Province, China
GSS-14	0.20	Agricultural soil of a tillage layer form sichuan basin, Sichuan Province, China
GSD-5a	1.37	River sediment from Tongling skarn copper mining area, Anhui Province, China
GSD-6	0.43	River sediment from Zhadou porphyry copper mining area, Qinghai Province, China
GSD-7a	5.60	River sediment from Kaiyuan lead zinc mining area, Liaoning Province, China
GSD-10	1.12	River sediment from Yishan carbonate area, Guangxi Province, China
GSD-11	2.30	River sediment from Shizhuyuan polymetallic mining area, Hunan Province, China
GSD-12	4.00	River sediment from Yangchun polymetallic mining area in Guangdong Province, China
GSD-17	4.30	River sediment from Xiaoxilin lead zinc mining area, Yichun, Heilongjiang Province, China
GSD-21	0.76	River sediment from Xiaorequanzi copper mining area,Turpan, Xinjiang Province, China
GSD-23	4.80	River sediment from Yinshan polymetallic mining area, Dexing, Jiangxi Province, China
GSH-1	0.38	Shrub branches and leaves from Xitieshan lead zinc mining area, Qinghai Province, China
GSV-2	0.11	Human hair from Langfang City, Hebei Province, China

Table S3 Calibrated isotope ratios of the double spike and NIST SRM 3108 using $^{107}Ag/^{109}Ag$ =1.076378 to correct for instrument mass bias.

	$^{106}Cd/^{110}Cd$	$^{108}Cd/^{110}Cd$	$^{111}Cd/^{110}Cd$	$^{112}Cd/^{110}Cd$	$^{113}Cd/^{110}Cd$	$^{114}Cd/^{110}Cd$	$^{116}Cd/^{110}Cd$
Double spike	0.022118	0.03056	59.02343	1.905029	38.08632	0.854083	0.0523
NIST SRM 3108	0.099814	0.071194	1.026207	1.932893	0.980063	2.303989	0.601450

Table S4 Ratios of matrix elements and cadmium in different types of samples

Sample	Data origin	Mg/Cd	Fe/Cd	Zn/Cd	Ga/Cd	Ge/Cd	Zr/Cd	Mo/Cd	Pb/Cd
BHVO-2	Jochum *et al*. (2016) [64]	197727	410455	472	97.1	7.42	778	18.5	7.51
BCR-2	Jochum *et al*. (2016) [64]	67500	301219	405	69	4.56	583	783	34.2
NOD-A-1	USGS	5490	21081	114	-	-	-	86.5	163
NOD-P-1	USGS	5130	15052	415	-	-	-	197	145
SGR-1b	USGS	40985	32631	114	18.5	-	81.5	53.8	58.5
2711a	NIST	5130	15052	415	-	-	-	197	145
GSS-1	GGE	7145	23901	447	12.6	0.88	161	0.92	64.5
GSS-4	IGGE	9188	225313	656	96.9	5.94	1563	8.13	181
GSS-5	IGGE	9385	226513	1267	82.1	6.67	697	11.8	1415
GSS-14	IGGE	60000	196000	505	98.9	7.47	1195	3.42	163
GSD-5a	IGGE	6242	29750	212	15.1	1.28	222	1.32	82.3
GSD-6	IGGE	2896	5649	151	2.78	0.22	35.5	0.16	107
GSD-7a	IGGE	41860	95721	335	38.8	3.02	395	17.9	62.8
GSD-10	IGGE	947	35553	61	24.3	0.53	92.1	1.58	35.5
GSD-11	IGGE	5027	41527	504	25.3	2.45	207	7.97	859
GSD-12	IGGE	1492	18074	263	7.46	0.99	124	4.34	151
GSD-17	IGGE	2005	8850	150	4.59	0.3	56.7	0.41	88.3
GSD-21	IGGE	16986	47324	407	22.1	1.49	252	2.39	36.6
GSD-23	IGGE	1834	12066	214	5.26	0.43	58.9	0.38	30.8
GSH-1	IGGE	0.36	540	1900	-	-	-	0.73	88
GSV-2	GGE	0.92	2058	106	-	-	-	0.54	90.4

Table S5 Cd isotopic compositions of common standard solutions

Standard solution	Reference	$\delta^{114/110}Cd$	2SD	N [b]	Method	Instrument
NIST 3018	This study	0.000	0.064	31	^{111}Cd-^{113}Cd DS	Nu II
	This study	0.000	0.034	181[c]	^{111}Cd-^{113}Cd DS	Nu III/ NP
	Average	**0.000**	**0.040**	**212**		
NIST 3018_{ICL}	This study	0.014	0.048	9	^{111}Cd-^{113}Cd DS	Nu II
	This study	0.003	0.035	13	^{111}Cd-^{113}Cd DS	Nu III/ NP
	Average	**0.007**	**0.041**	**22**		
Münster Cd	This study	4.471	0.072	7	^{111}Cd-^{113}Cd DS	Nu II
	This study	4.457	0.028	12	^{111}Cd-^{113}Cd DS	Nu III/ NP
	Average	**4.461**	**0.047**	**19**		
	Cloquet *et al.*(2005)[36]	4.499[a]	0.004		SSB	GV
	Ripperger and Rehkämper,(2007) [35]	4.497[a]	0.120		^{110}Cd-^{111}Cd DS	Nu I
	Gao *et al.*(2008) [37]	4.467[a]	0.130		SSB	GV
	Schmitt *et al.*(2009a) [36]	4.446[a]	0.017		^{106}Cd-^{108}Cd DS	TIMS
	Schmitt *et al.*(2009b) [62]	4.443[a]	0.017		^{106}Cd-^{108}Cd DS	TIMS
	Abouchami *et al.*(2012) [50]	4.499	0.050			
	Gault-Ringold *et al*. (2012) [14]	4.51	0.130	12	^{110}Cd-^{111}Cd DS	Nu I
	Xue *et al.* (2012) [13]	4.531 [a]	0.050		^{111}Cd-^{113}Cd DS	Nu I
	Conway *et al.* (2013) [16]	4.486	0.060		^{110}Cd-^{111}Cd DS	NP
	Fouskas *et al.* (2018) [35]	4.54	0.130	6	Ag correction	Nu I
	Zhang *et al.* (2018) [41]	4.4.6	0.060		SSB	NP
	Yang *et al.* (2019) [40]	4.4.3	0.060		SSB	NP
	Liu *et al.* (2019) [46]	4.455	0.047		^{111}Cd-^{113}Cd DS	NP
BAM-I012	This study	-1.336	0.064	9	^{111}Cd-^{113}Cd DS	Nu II
	This study	-1.323	0.028	12	^{111}Cd-^{113}Cd DS	Nu III/ NP
	Average	**-1.329**	**0.045**	**21**		
	Ripperger and Rehkämper,(2007) [35]	-1.378 [a]	0.110		^{110}Cd-^{111}Cd DS	Nu I
	Shiel *et al.*(2009) [59]	-1.251	0.035		SSB	Nu I
	Schmitt *et al.*(2009a)[56]	-1.313 [a]	0.013		^{106}Cd-^{108}Cd DS	TIMS
	Horner *et al.*(2011) [12]	-1.296 [a]	0.090		^{111}Cd-^{112}Cd DS	Nu I
	Abouchami *et al.*(2012)[50]	-1.332	0.040			
	Gault-Ringold *et al.*(2012) [14]	-1.360	0.140		^{110}Cd-^{111}Cd DS	Nu I
	Xue *et al.* (2012) [13]	-1.329 [a]	0.080		^{111}Cd-^{113}Cd DS	Nu I
	Gao *et al.*(2013) [37]	-1.260 [a]	0.100		SSB	GV
	Lambelet *et al.(*2013)[17]	-1.330	0.100		^{111}Cd-^{113}Cd DS	Nu I
	Fouskas *et al.* (2018)[45]	-1.340	0.150		Ag correction	Nu I
	Li et al.(2018)[42]	-1.310	0.090		SSB	NP
	Liu *et al.* (2019) [46]	-1.325	0.043		^{111}Cd-^{113}Cd DS	NP

Table S5 (*Contd.*)

Standard solution	Reference	$\delta^{114/110}Cd$	2SD	N [b]	Method	Instrument
Spex Cd-CUGB	This study	-2.138	0.065	5	^{111}Cd-^{113}Cd DS	Nu II
	This study	-2.117	0.040	13	^{111}Cd-^{113}Cd DS	Nu III/ NP
	Average	**-2.121**	**0.0420**	**18**		
	Li *et al.* (2018)[42]	-2.13	0.090	74	SSB	NP

[a]**:** The $\delta^{114/110}Cd$ values in previous studies were recalculated relative to NIST SRM 3108, according to Abouchami *et al*. (2012)[50].

[b]**:** The number repeated measurements.

[c]**:** Data include measuring at concentrations of 5ng mL^{-1}, 10 ng mL^{-1}, 20 ng mL^{-1} and 25 ng mL^{-1}(0.000±0.030‰, 2SD,n=64)for NP, and 25 ng mL^{-1} (0.000±0.030‰, 2SD,n=55)and 50 ng mL^{-1} for Nu III.

Fig. S1 Elution curves of the Cd purification procedures using AG-MP-1M anion exchange resin

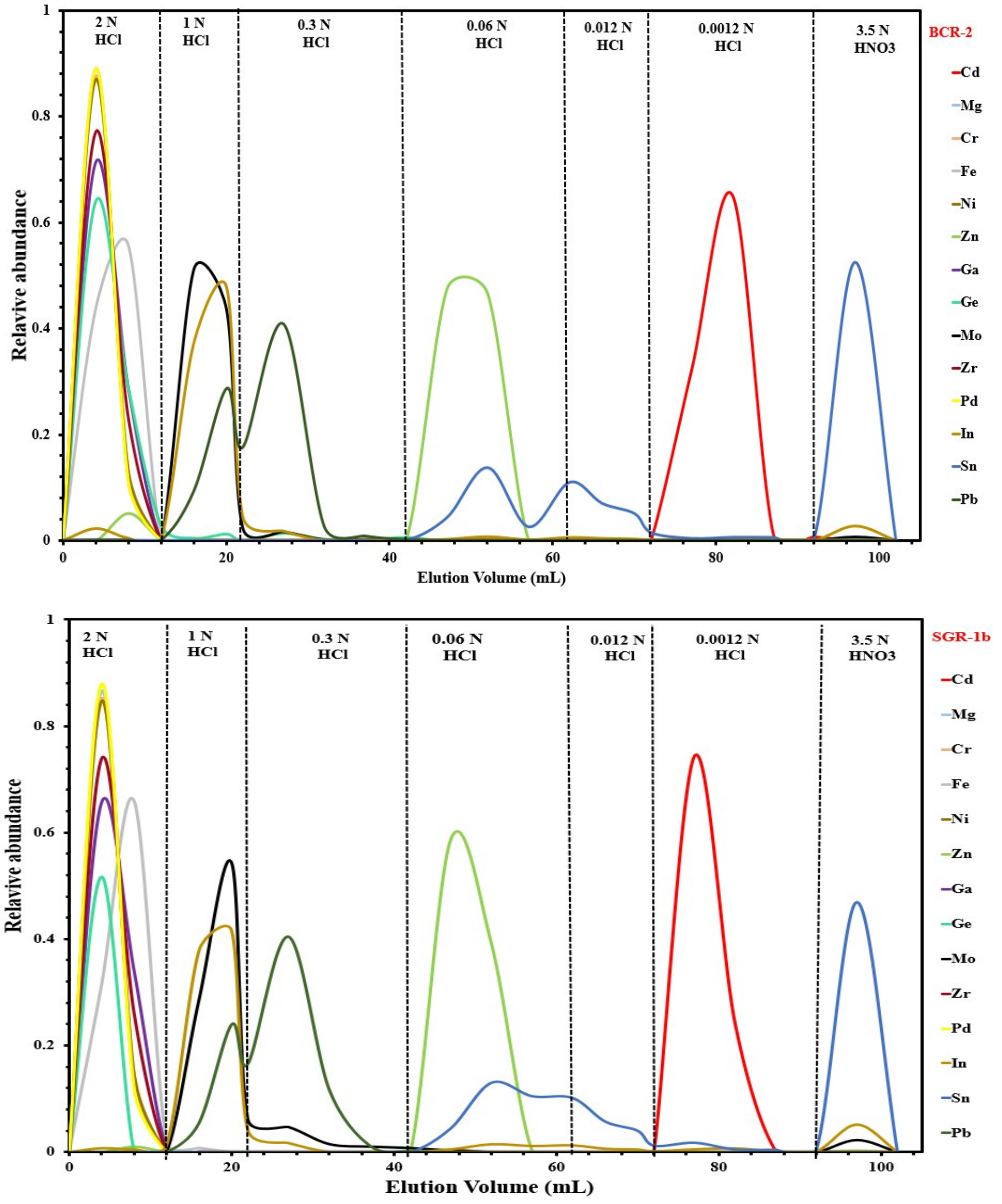

Fig. S2 Effectiveness of purification procedures at removing matrix elements for BHVO-2 (A and B) and SGR-1b (C and D). X denotes a matrix element, and X/Cd is the concentration ratio of matrix elements to Cd. Figures A and C shows the value of X/Cd before purification and figures B and D is the ratios after purification.

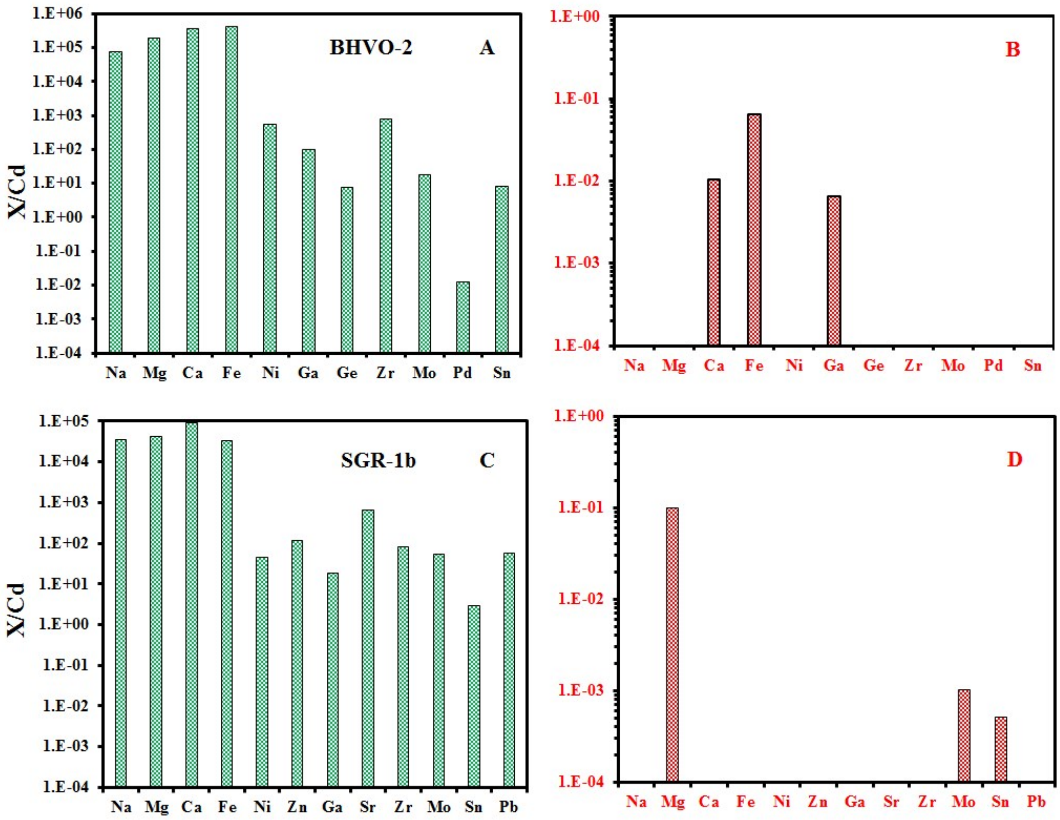

Fig. S3 The effects of Ge and Fe on measured $\delta^{114/110}$Cd. The gray band is the average external precision on Nu II, Nu III and Neptune Plus (±0.040‰)