Fast and Highly Sensitive Cd Isotopic Analyses in low-Cd Complex Samples with MC-ICPMS Based on Plasma Electrochemical Vapor Generation

Xing Liu,[1] Linjie Chen,[1] Huan Peng,[1] Guan Wang,[1] Nicholas Stanley Belshaw,[1, 3] Hongtao Zheng,[2] Shenghong Hu,[1] and Zhenli Zhu* [1, 2, 4]

[1] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, Hubei 430074, China

[2] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan, Hubei 430074, China

[3] Department of Earth Sciences, Oxford University, Oxford, UK, OX1 3PR

[4] State Environmental Protection Key Laboratory of Source Apportionment and Control of Aquatic Pollution, Ministry of Ecology and Environment, Wuhan, Hubei 430074, China

Corresponding Author: Zhenli Zhu

* Phone: +86-27-6788-3452. Fax: +86-27-6788-3456. E-mail: zlzhu@cug.edu.cn

ABSTRACT: Cd isotopes have provided a powerful tool for better understanding Cd geochemical cycling in soil, water and biological systems. Conventional solution-based MC-ICPMS techniques used for Cd isotopic analysis typically requires time-consuming purification, which greatly limits the wide application of Cd isotope. In this work, a fast, highly sensitive and cost-effective Cd isotopic analysis method has been developed based on plasma electrochemical vapor generation (PEVG) coupled with MC-ICPMS. PEVG enhances sensitivity by more than 6 times compared with conventional pneumatic nebulization (PN) system, allowing Cd analysis to be carried out with samples as low as ~ 13 ng. Usefully, the tolerance level for organic resin materials and matrix elements (Sn/In/Pd/Zr/Mo/Zn:Cd > 250:1) is greatly improved because of the excellent matrix separation capability inherent to PEVG. This allows simplification of the complex and time-consuming ion-exchange chromatography purification process, achieving a reduction of time by >20 times compared to conventional two-step Cd purification process. The precision and accuracy of this method were first assessed by measuring NIST 3108 and BGEG-Cd standard under optimum conditions ($\delta^{114/110}$Cd of 0.00 ± 0.06 ‰ and -1.00 ± 0.06 ‰ (2sd, n=25)). The method was also successfully applied to sensitive and fast determination of $\delta^{114/110}$Cd in various reference materials (soil, sediment, and basalt) and environmental samples (pyrite, galena, sphalerite, soils and tap water), validating the applicability of the proposed technique. Owing to the sensitivity, selectivity, low power, and low gas consumption of the PEVG, the proposed PEVG-MC-ICPMS technique provides a much faster and cost-effective approach for the accurate measurement of Cd isotopic compositions in low-Cd complex samples.

Keywords: Cadmium isotopes, plasma, vapor generation, MC-ICPMS, ion-exchange chromatography

1. Introduction

Cadmium (Cd) isotope system has been increasingly used in cosmochemistry, oceanography, ore deposit geology, and biogeochemistry processes as a novel and powerful tracer to track Cd cycling, oceanic nutrition cycle, paleo-primary productivity, and paleo-environment changes, deposit evolution, etc [1-5]. Studies have shown that Cd isotopic fractionation ($\delta^{114/110}$Cd) is very limited (such as wheat with 0.10 to 0.51‰ [6], sulfide ores with -0.71 to 0.23 ‰ [7], upper continental crust with -0.01±0.04 ‰ [8], and rivers with 0.1 to 0.3 ‰ [9]) during the transfer processes at a global scale. The rapid development of MC-ICPMS technology now allows precise measurement of Cd isotopes in environmental samples, and has improved the understanding of the Cd geochemical cycle [7, 10-12]. However, the use of Cd isotopes is hampered by the relatively low efficiency of Cd isotopic analysis. In addition, isobaric/polyatomic interferences and inefficient analytical sensitivity can also be problematic for Cd isotopic analysis by conventional solution-based MC-ICPMS, especially in low-Cd complex geological samples [13-16]. The presently reported highest tolerances for coexisting ions during measurement are at the level of Sn/Cd < 0.5 [15], Mo/Cd < 10 [15], Zr/Cd < 0.01 [15], Pd/Cd < 0.05 [14], and In/Cd < 0.02 [14], but the content of these elements in many geological samples is dozens to thousands of times higher than that of Cd [13].

Separation of Cd by means of ionic exchange resins is a prerequisite to minimize isobaric/polyatomic interference and matrix effects for accurate Cd isotopic analysis [11, 15, 16]. In 1975, Rosman et al. first developed an anion exchange resin AG1-X8 purification scheme for separating Cd from the sample matrix [17]. Since then, a number of procedures have been proposed for the separation and purification of Cd (either by AG1-X8, AG-MP-1 M and/or Eichrom TRU Spec resins), varying in complexity from a single pass through one column to elaborate, multiple-stage schemes, depending on the sample matrix [7, 14-24]. For low-Cd complex samples (soils, living organisms, sedimentary, mantle-derived, and igneous rocks etc), residual Sn, Mo, Zr and In may still remain in the Cd fraction after a one-step column procedure, which would produce serious isobaric/polyatomic interference in any Cd isotopic analysis, and thus two-step or three-step column procedures for adequate separation of Cd from the matrix are required [10, 22, 25-27]. However, these purification processes are complicated and extremely time-consuming, the entire procedure usually taking at least 48 hours [15]. It should be noted that additional $HClO_4/HNO_3$ or H_2O_2/HNO_3 oxidative digestion steps are typically needed to eliminate residual resin-derived organics which may cause anomalous isotopic shifts and further extends the pretreatment time by at least 24 hours [12, 24, 28]. Improving analytical sensitivity is also helpful to obtain high-precision Cd isotopic data, particularly for low-Cd samples. The most popular approach to improve the sensitivity of MC-ICPMS is the uses of membrane desolvation (MD) technology, which has some limitations, including no matrix separation capability, memory effects, high costs and dubious stability [29, 30]. In this context it would be desirable to develop a fast Cd isotopic analysis procedure with high matrix tolerance and good analytical sensitivity, making it more accurate, fast, and cost-effective.

Chemical vapor generation (CVG) technology is well suited to address these issues, as its efficient sample introduction and matrix separation capabilities can significantly reduce sample consumption while reducing matrix element interference during Cd isotopic analysis [31, 32]. To date, CVG has been successfully applied to measure isotopic compositions of Hg [33], Se [34], Ge [35], Sb [36], Os [37], and Pb [29, 38]. Despite these advantages, CVG techniques have not been used in producing published Cd isotopic data. To operate successfully CVG must overcome several challenges. The vapor generation efficiency of Cd using CVG is typically inefficient, and enhancing reagents (such as iodate and hexacyanochromate) are often required to improve the efficiency [39, 40]. In addition to Cd, Sn is also simultaneously converted to volatile species during CVG [41, 42]. Moreover, Cd analyses suffers interferences from transition metals and also the negative impact of hydrogen co-produced by CVG on isotope precision [43]. The developed plasma electrochemical vapor generation technique (PEVG) was shown to improve the Cd vapor generation efficiency 2-fold to that of conventional CVG method by consuming only a small amount of acid and operating at low power (< 6 W) [44]. More importantly, this method also offers excellent selectivity and good tolerance to matrix elements. Therefore, it is expected that coupling PEVG with MC-ICPMS can deliver the advantages of high sample introduction efficiency while also reducing the interference caused by coexisting ions, especially Sn, Mo, Zr, and In.

In this study, we integrate PEVG and MC-ICPMS to construct a simple, rapid, accurate, and sensitive system for the Cd isotopes in low-Cd complex samples. Cd in solution is efficiently converted into volatile species at the plasma-liquid interface, enhancing the sensitivity and achieving good matrix separation. This process has excellent tolerance to coexisting ions and consumes only a small amount of electric energy. Moreover, the time-consuming and laborious anion resin purification process is simplified greatly taking advantage of the good matrix separation capability of PEVG. The PEVG-MC-ICPMS system assay and setup development is presented. We demonstrate that the PEVG-MC-ICPMS with the simplified purification method can be reliably used for the Cd isotopic analysis in various reference materials and environmental samples with low Cd contents and complex matrix. PEVG has the potential to be coupled with MC-ICPMS to accomplish the fast, sensitive and inexpensive analysis of Cd isotope, attributed to its sensitivity, selectivity, low power, and low gas consumption, thereby enables to accumulate massive Cd isotopes data and improve the understanding of the Cd geochemical cycle. To our knowledge, this is the first work to determine Cd isotope ratios by coupling a vapor generation method with MC-ICPMS.

2. Experimental section

2.1. Instrumentation

Cd isotopic analysis was performed at the State Key Laboratory of Biogeology and Environmental Geology (BGEG) using a Nu Plasma II MC-ICPMS, equipped with 16 fixed Faraday cups (10^{11} Ω) and 5 ion counting channels. Nine of the Faraday collectors were employed for the measurement of masses ranging from 108 to 117, for isotopes of Cd (108, 110, 111, 113, 114, and 116), Pd (105), In (115), and Sn (117). Elemental concentrations were measured using an Agilent 7700x ICP-MS instrument (Agilent Technologies, USA).

The experimental setup is illustrated schematically in Figure 1. The Cd in solution was first converted into volatile species in a plasma electrochemistry vapor generation (PEVG) reactor, and then was carried into the ICP for measurement with MC-ICPMS. The new reactor (cf. Figure 1) was modified from our previous reported reactors (an H-type divided cell) [44], aiming to improve signal stability, reduce sample consumption and minimize memory effects. It contains a glass tube (25 mm o.d. × 20 mm i.d. × 50 mm length), a cathode assembly, and a titanium (Ti) tube (1.5 mm o.d. × 1.1 mm i.d.× 40 mm length). In this design, the cathode assembly consists of a stainless steel tube (2 mm o.d. × 1 mm i.d. × 40 mm length) with a tungsten rod (1 mm o.d.× 8 mm length) embedded at one end, which is more effective at sustaining a stable discharge compared with previous designs using only stainless steel tubes. The solution is delivered through a PTFE capillary (i.d., 0.38 mm; o.d., 1.1 mm) inserted into the Ti tube (anode), which is connected to a high voltage power supply(DW-P152-150ACDE, Dongwen High Voltage Power Supply (Tianjian) Limited Company, China). This anode arrangement sustains the PEVG without discharge breakdowns at lower sample solution flow rates, even if the solution is cut off during sample switching. In addition, the use of PTFE capillary avoids the generation of oxygen on the inner wall of the Ti tube anode, which reduces the negative impact of any generated oxygen on the discharge system. The distance between the W rod tip and the Ti tube is approximately 2 mm. Argon flows through 4 symmetrically placed holes near the end of the stainless-steel tube, which cools the W cathode and reduces the effect of sputtering. Additionally, a makeup gas was supplied from the upper left tangential channel of the generator to improve the stability of the signal. During operation, the sample is introduced through a peristaltic pump at an uptake rate of ~ 0.8 mL min^{-1}, and the plasma is initiated by temporarily reducing the distance between the W cathode tip and the anode solution. The generated volatile species produced from the PEVG process are then swept by an argon stream through a glass valve to the ICP for measurement by MC-ICPMS. The inclusion of the glass valve allows us to adjust the vapor generator without worrying about the ICP plasma being extinguished. Double spike (DS, ^{111}Cd:^{113}Cd=54.52%:45.48%, sample:DS=4:6) technique was used to correct Cd isotopic fractionation during column separation, PEVG and instrument measurement. [14] Details of the instrumental operating conditions and key parameters of the PEVG-MC-ICPMS are summarized in Table S1.

2.2. Reagents and Sample Pretreatment.

The details of the reagents and sample pretreatment are shown in the Supporting Information.

3. Results and discussion

3.1 Feasibility of PEVG-MC-ICPMS for Cd isotopic analysis.

High analytical sensitivity and good tolerance of interferences are critical in achieving high precision and accurate isotopic analysis [7, 14-16]. The PEVG method can readily achieve efficient vapor generation and separation of Cd from coexisting elements making it well-suited to be developed as an alternative sensitive sampling method for Cd isotopic analysis [44]. To investigate the feasibility and practicality of PEVG for Cd isotopic analysis, an improved PEVG generator was developed and coupled to MC-ICPMS. As shown in Figure 2, an intense Cd signal was immediately obtained when Cd solution was introduced into the PEVG reactor without using any unstable and costly tetrahydridoborate. Compared with conventional dry/wet-plasma (a 0.1 mL min^{-1} microconcentric nebulizer combined with a CETAC Aridus II/cyclonic spray chamber), the Cd signal intensity obtained using PEVG was significantly improved (more than 8 and 48 times). A sensitivity comparison of the three approaches with the same rate of Cd consumption showed the Cd signal from PEVG is about 6 times higher compared with the wet-plasma mode, and comparable with dry-plasma mode. Further measurements showed that the vapor generation efficiency of Cd in the PEVG system was 66 ± 5%, which is much higher than that obtained with pneumatic nebulization (PN), indicating that PEVG has the potential to be an efficient sampling method for Cd isotopic analysis. The modified device also offers excellent signal stability, and the relative standard deviation (RSD) of the ^{110}Cd signal for continuous measurement of 20 μg L^{-1} Cd can be as low as 0.5%, which is comparable to dry-plasma mode. The memory effect of the PEVG generator is also small, and the signal from any Cd solution falls to below 0.1 % by cleaning with blank for 20 seconds in contrast to more than 40 seconds of cleaning with the membrane desolvation techniques.

In addition to the improved sensitivity and low memory effect, our proposed PEVG sample introduction system offers the advantage of good selectivity. Unlike aerosols generated using pneumatic nebulization in conventional systems, the Cd signal obtained in PEVG comes from the formation of Cd volatile species. Elements which cannot be converted into volatile species will not be introduced into the ICP source. Therefore, even operating the PEVG with Sn, Mo, Zr, Pd and Na solution at 1 mg L^{-1}, the signals of these elements can barely be detected.

Isotopic fractionation can occur during plasma-chemical vapor generation processes, according to some similar studies including chemical vapor generation [29, 45, 46], and knowing the degree of PEVG-induced isotopic fractionation is crucial for obtaining precise Cd isotope ratios. The fractionation during PEVG was evaluated as detailed in the supporting information (Figure S2). It was found that lighter Cd isotopes are preferentially vaporized. Cd isotopic fractionation in PEVG is mass dependent, where Ln($^{114/110}$Cd) plotted linearly along the line with a slope of 0.5356 (R^2=0.9921) on plots of Ln($^{112/110}$Cd)-Ln($^{114/110}$Cd), allowing the previously established DS correction method to be used for mass bias correction in Cd isotopic analysis with PEVG [14].

3.2. Optimization of PEVG-MC-ICPMS

To obtain the optimal analytical performance, the main parameters of PEVG-MC-ICPMS including electrolyte pH, discharge current, discharge gap and sample flow rate were investigated. The electrolyte pH significantly affects the formation of reactive species in the process of liquid-plasma interaction [44, 47]. Only HCl was used to purify Cd, and the effects of different concentrations of HCl on PEVG was investigated. As shown in Figure S3a, optimum Cd responses were obtained at pH 2.8~3.2. Beyond this range of pH, the signal intensity of Cd decreased significantly. This optimum pH range can easily be obtained by simply diluting the collected Cd fraction from column purification (HCl, 0.0012 mol L^{-1}), which allows direct Cd isotopic analysis by PEVG-MC-ICPMS, avoiding laborious and time-consuming evaporation and redissolution steps normally required for Cd solutions in dry/wet-plasma mode. Discharge current is another key parameter as it controls the electron flux and also the plasma intensity, and accordingly the effect of the discharge current was evaluated in the range of 5−25 mA (Figure S3b). The Cd signal reached a maximum value at 20 mA and then declined. The power consumption with this discharge current is only about 15 W. Varying sample flow rate showed that, Cd signals increased significantly as flow rate is increased from 0.2 to 0.8 mL min^{-1}, and then leveled off with further increase from 0.8 to 2 mL min^{-1}, as can be seen in Figure S3c. It is worth noting that the Cd signal increases almost linearly with flow rate from 0.2 to 0.8 mL min^{-1}, which suggest the vapor generation (sample introduction) efficiency remains constant in this flow rate range. This allows us to tune the Cd signal intensity simply by adjusting the flow rate of the solution. Usefully, for large samples with low-Cd content, preconcentration by evaporation is not needed, because sufficient analytical sensitivity can be met by increasing the flow rate. The influence of the discharge gap was investigated in the range of 1-4 mm, and it was observed that the Cd signal reached its maximum value at 2 mm and then fell (Figure S3d). Based on all these results optimal conditions for subsequent PEVG-MC-ICPMS experiments were determined to be a solution pH of 3.0, discharge current of 20 mA, sample flow rate of 0.8 mL min^{-1} and discharge gap of 2 mm.

3.3. Effect of Cd concentration on the isotopic ratio precision

It is highly desirable to reduce the amount of analytes for measuring isotopes with low concentration samples. However, reducing the analyte concentration typically leads to the degradation of the precision and even the accuracy of isotope ratios [29, 48]. Therefore, the effect of Cd concentration on the accuracy and precision of Cd isotope ratios obtained with PEVG-MC-ICPMS was investigated using a laboratory internal standard, BGEG-Cd. Figure 3 shows the relationship between the accuracy and precision of $\delta^{114/110}$Cd and Cd concentrations ranging from 2 and 16 μg L^{-1}. It was observed that measured $\delta^{114/110}$Cd values were in excellent agreement with those previously reported at -1.00±0.04 ‰ [14] whilst decreasing Cd concentration from 16 to 6 μg L^{-1}. Values then shifted slightly becoming more negative, and finally deviated significantly from -1.06 to -1.32 as the Cd concentration decreased from 4 to 2 μg L^{-1}. It was also found that the precision became poorer going from 0.05 ‰ to 0.15 ‰ (repeated measurements of the same treated sample, 2sd, n=3) with reducing the Cd concentration from 4 μg L^{-1} to 2 μg L^{-1}. Considering possible matrix in real samples, which may interfere with the Cd isotopic analysis in PEVG-MC-ICPMS, 8 μg L^{-1} (~ 50 ng, based on 8 μg L^{-1} × 0.8 mL min^{-1} uptake rate × ~ 8 min measuring time) was determined as the optimal concentration for obtaining accurate data while achieving a balance in analyte consumption. This is comparable to that of conventional dry-plasma mode (Nu plasma II equipped with Aridus II: ~ 45 ng, based on 50 μg L^{-1} × 0.1 mL min^{-1} uptake rate × ~ 9 min measuring time) [15]. Notably, with a Cd concentration of 4 μg L^{-1}, the obtained analytical precision is ~0.07 ‰, which is still acceptable for the measurement of most samples. Sample consumption can further be reduced by increasing the DS: sample ratio from 3:2 to 4:1, which has been demonstrated in our previous work [14], meaning that 2 μg L^{-1} (~13 ng) samples can also be measured reliably.

3.4. Influence of matrix elements and resin-derived organic material

The determination of Cd isotope ratios by MC-ICPMS is susceptible to matrix effects, both isobaric (e.g., Sn, Pd, and In) and polyatomic interferences (e.g., MoO and ZrO etc.) interference [14-16, 49]. This is a great challenge for low-Cd environmental samples with complex matrices. It has been confirmed that PEVG can convert Cd into volatile species without introducing other matrix elements into the MC-ICPMS, which gives a useful reduction of isobaric and matrix interferences on Cd isotopic analyses.

Of potential interferences, Sn may present significant problems when attempting to analyse Cd, with ^{116}Sn, ^{114}Sn, and ^{112}Sn on ^{116}Cd, ^{114}Cd, and ^{112}Cd, respectively. It was therefore important to assess the effect of Sn on $\delta^{114/110}$Cd measurements in our proposed PEVG-MC-ICPMS method. As shown in Figure 4, the addition of Sn during PEVG does not affect the analytical sensitivity of Cd, even with Sn concentration 2500 times higher than that of Cd. In addition, the presence of high concentration of Sn does not interfere with the measurement of $\delta^{114/110}$Cd. ^{117}Sn signal levels of only 0.006 V was observed with Sn concentration of 20000 μg L^{-1}. In contrast to conventional CVG of Sn and Cd where both elements are vapor generated, in the PEVG cell, the small Sn signal observed mainly comes from a minor amount of aerosol generated during the plasma-liquid interaction (Figure S4). Therefore, the proposed PEVG-MC-ICPMS provides excellent tolerance to Sn, and at levels as high as 2500x higher than Cd did not affect the accuracy of $\delta^{114/110}$Cd. This is almost impossible in other reported methods, as the best tolerance for Sn/Cd reported are in the range from 0.001 to 0.5 [14, 16]. The interference of other isobaric ions (In and Pd) and elements producing polyatomic interferences (MoO and ZrO) was also evaluated at a concentration of 2000 μg L^{-1}. Negligible interference effects from these elements were observed on the Cd signals or the accuracy of Cd isotopic analysis. This is predictable since PEVG cannot introduce these non-hydride forming elements into the ICP. It can also be predicted that the tolerance of matrix elements (e.g. K, Ca, Na, and Mg) can also be greatly improved by this method. However, it should be noted that the effect of Zn on the measurement of $\delta^{114/110}$Cd was also explored here, knowing the high vapor generation efficiency of Zn in PEVG and its affect on Cd [44]. Intense Zn (500 μg L^{-1}) isotope signals can clearly be detected, but the yield of ZnAr is observed to be very low and thus does not interfere with Cd isotopic analysis (Figure 4b and S4). From these results, we can be confident that Cd isotopic analysis will not be affected by these matrix elements at concentration levels up to 250x that of Cd. Remarkably, the results show that PEVG can be directly applied to the detection of simple matrix samples (such as tap water, rainwater) without complex separation and purification processes (Figure S5).

Several studies have pointed out that oxidative digestion (H_2O_2/HNO_3 or $HClO_4/HNO_3$) or liquid-liquid extraction (n-heptane) is necessary to eliminate anomalous Cd isotopic shifts associated with organic resin residues, especially for the low-Cd complex matrix samples [12, 24, 27]. Therefore, the effects of resin-derived organic material (AG-MP-1 M) on Cd measurements were also evaluated. Figure 5a shows that the $\delta^{114/110}$Cd of NIST 3108 with inclusion of resin-derived organic material can be accurately measured by PEVG-MC-ICPMS. This indicates that any residual resin does not affect the vapor generation of Cd and so does not enter into the ICP to interfere with analysis. Notably, although no highly anomalous isotopic shifts reported by Gault-Ringold [24] and Murphy et al. [28] were found, the precision in dry plasma mode got worse compared to PEVG.

3.5. Efficiency of the proposed PEVG-MC-ICPMS.

The efficiency of making Cd isotopic analyses by MC-ICPMS is mainly limited by lengthy chemical purification procedures [50]. The high tolerance for matrix elements and residual organics demonstrated by PEVG-MC-ICPMS enables simplification of the purification process without compromising measurement accuracy and precision, giving a rapid and accurate Cd isotopic analysis method.

A simpler Cd purification procedure matched for the needs of PEVG was developed using AG-MP-1M anionic exchange resin, modified according to our previous purification procedure [14]. As shown in Table S2, the overall framework of the original procedure including resin cleaning, sample loading, matrix elution and Cd collection was retained but the acid consumption was reduced. Usefully, the second step for further purification of Cd is not needed. To evaluate the performance of this simplified process, a synthetic solution prepared with NIST 3108 Cd (300ng; DS, 450 ng) and other elements including Fe, Mn, Zr, Mo, Ni, Cu, Zn, Sr, In, Sn, and Pb (30000 ng each) was processed. The elution curve (Figure S1) was redrawn and the purified solution was measured with both PEVG and dry-MC-ICPMS techniques, respectively. The results show that although the consumption of hydrochloric acid is reduced, most matrix elements were removed, and the contaminants Fe, Mn, Zr, Mo, Ni, Cu, Zn, Sr, In, and Pb were not detected in the collected Cd fraction. However, the simplified purification procedure allows a significant proportion of Sn (1500 ng, about 5 % of loaded Sn) to remain in the Cd fraction, leading relative proportions of Sn/Cd of ~ 5/1 in the final Cd solution. Although such levels are much higher than that can be tolerated in previously reported methods [14-16], its effect on the $\delta^{114/110}$Cd is negligible for the measurement with PEVG-MC-ICPMS (Figure 5b). In contrast, the $\delta^{114/110}$Cd deviates significantly when measured by dry-plasma mode, which demonstrates the importance of the two-step purification process for most current Cd isotope analyses. The results confirm that the use of a simplified purification procedure for rapid and precise Cd isotopic analysis is acceptable with PEVG-MC-ICPMS. The measurements also indicate that our proposed PEVG-MC-ICPMS provides much better tolerance to elution curve drifts, which are often encountered in real sample purification, especially for complex matrix samples.

Besides column purification, the evaporation and redissolution steps typically required for conventional dry/wet plasma analysis modes are also time-consuming. In addition, secondary purification and oxidative digestion of resin derived organic materials may also be necessary [24], which further increases the preparation time. Our proposed PEVG method offers good tolerance to matrix elements and residual organics, and at a pH of 2.8~3.2, is well-matched with the pH of eluted Cd. These aspects allow Cd to be analyzed directly with PEVG, without any evaporation, re-dissolution and digestion, such that the total analysis time for a Cd analysis could be dramatically reduced. Shown in Table 1, purified Cd can be separated from a sample within 3 hours, reducing by more than a factor of 20, the time required for the conventional two-step approach. PEVG-MC-ICPMS is a promising method for making rapid and sensitive Cd analyses, which would be especially helpful for high throughput Cd isotopic analysis for large numbers of geological and environmental samples.

3.6. The precision and accuracy of the proposed PEVG-MC-ICPMS

To evaluate the long-term precision and accuracy of the presented method, two Cd standard solutions were measured repeatedly. Figure 5c shows the long-term reproducibility of analyses of the 8 μg L^{-1} NIST 3108 and BGEG-Cd during four individual measuring sessions over a time period of 10 months (December 2020 to September 2021). The $\delta^{114/110}$Cd values of BGEG-Cd relative to NIST 3108 is -1.00 ± 0.06 ‰ (2sd, n=25), and both standards present the same precision (0.06 ‰). The values of BGEG-Cd are in excellent agreement with our calibrated value [14].

Since the objective of this work was to develop a sensitive method with excellent tolerance to matrix elements to meet the requirement for rapid, accurate and inexpensive measure Cd isotopes in low-Cd samples. Six geological standard materials were analysed to further validate the accuracy of the proposed method, including two soil reference materials (GSS-5 and GSS-6a), three sediment reference materials (GSD-5a, GSD-11, and GSD-12) and a basalt reference BHVO-2. These standard samples contain relatively low concentrations of Cd, and the Sn/Cd ratio ranges from 4 to >800, which is useful to assess the PEVG-MC-ICPMS method. The determined values from PEVG-MC-ICPMS were compared with those obtained in dry-plasma mode after a two-step purification or the simplified purification process (Figure 6 and Table S3). Results are in good agreement in terms of accuracy of the method compared to dry-plasma mode with a two-step purification process, and also agrees well with published data. However, the results in dry-plasma mode with the one-step simplified purification process show some variation. For example, the $\delta^{114/110}$Cd of GSD-5a and GSD-12 shifted to 0.10±0.05 ‰ and 0.09±0.06 ‰, which was higher than the reported value of 0.01±0.02 ‰ and, -0.10±0.06 ‰ [14]. The $\delta^{114/110}$Cd of GSS-5 and GSD-11 shows an even larger offset, where measured values of -0.85±0.05‰ and -0.51±0.07‰ were much lower than the reported values of -0.54±0.06‰ and -0.34±0.06‰. As previously discussed, the shift seen in the $\delta^{114/110}$Cd values is most likely caused by matrix ions (especially Sn) in the sample solution resulting from the simplified purification procedure. These results confirm the excellent matrix tolerance and reliability of the developed method.

The Cd isotopic composition of GSS-6a is reported for the first time in this study, with a $\delta^{114/110}$Cd of -0.76±0.05‰. Due to the high Sn/Cd ratio (878:1), it is almost impossible to obtain accurate Cd isotopic composition of GSS-6a by the one-step simplified purification method in dry-plasma mode (-1.52±0.34‰). It should be noted that it is also challenging to obtain accurate analyses even with a two-stage purification.

To further demonstrate usability for real samples, the developed method was applied to the analysis of four real environmental samples with complex matrices. The measured $\delta^{114/110}$Cd values were 0.24±0.06‰ (pyrite), -0.63±0.05‰ (galena), 0.48±0.04‰ (sphalerite), and 0.07±0.05‰ (soil), respectively, which all agreed well with the values obtained with dry-plasma mode with a two-step purification (Figure 6 and Table S4). All results demonstrate that the proposed PEVG-MC-ICPMS method can rapidly deliver accurate high-precision Cd isotopic compositions in low-Cd materials showing high sensitivity and excellent tolerance to matrix elements.

4. Conclusion

In summary, a novel, rapid, simple, and highly selective PEVG-MC-ICPMS technique for the accurate and sensitive determination of Cd isotopic compositions in low-Cd complex materials was developed. It enables selective and efficient conversion of Cd into volatile species with a low energy plasma (~ 15 W), thus achieving a greatly simplified purification process in contrast to the rather arduous purification procedure needed for expensive membrane-desolvation systems. This new PEVG sampling strategy for Cd isotopic analysis is attractive in consuming less sample, having shorter purification time and lower analytical cost. Compared to the conventional wet/dry-plasma modes, the sensitivity of the PEVG system is more than 6 times higher than that of wet-plasma mode, while the total time needed for sample purification and preparation is reduced by at least 20 times (< 3 hours). Tolerance to organics and matrix elements such as Sn, In, Pd, Zr, Mo, and Zn is significantly improved, which could handle matrix elements at levels of ~250 times higher to Cd being measured. The accuracy and precision of the proposed method are demonstrated with the analysis of the international reference standards and real samples. This rapid, simple, accurate, and sensitive Cd isotopic analysis method provides a promising approach for Cd isotope applications in environmental sciences, where complex and low concentration samples are always encountered.

ACKNOWLEDGMENTS

This research is supported by the financial support from National Natural Science Foundation of China (No. 21822405, 42003018, 22061130207 and 41673014), and

Frontier project for application basic research of Wuhan (2020020601012280).

REFERENCES:

[1] F. Wombacher, M. Rehkämper, K. Mezger, A. Bischoff, C. Münker, Cadmium stable isotope cosmochemistry. Geochim. Cosmochim. Acta 72 (2008) 646-667.

[2] D. Janssen, T. Conway, S. John, J. Christian, D. Kramer, T. Pedersen, J. Cullen, Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. Proc Natl Acad Sci USA 111 (2014) 6888-6893.

[3] C. Zhu, H. Wen, Y. Zhang, Z. Huang, C. Cloquet, B. Luais, T. Yang, Cadmium isotopic constraints on metal sources in the huize Zn–Pb deposit, SW China. Geosci Front 12 (2021) 101241.

[4] T. Sweere, A. Dickson, H. Jenkyns, D. Porcelli, M. Ruhl, M. Murphy, E. Idiz, S. van den Boorn, J. Eldrett, G. Henderson, Controls on the Cd-isotope composition of upper cretaceous (cenomanian–turonian) organic-rich mudrocks from south texas (eagle ford group). Geochim. Cosmochim. Acta 287 (2020) 251-262.

[5] J. G. Wiederhold, Metal stable isotope signatures as tracers in environmental geochemistry. Environ. Sci. Technol. 49 (2015) 2606-2624.

[6] M. Wiggenhauser, M. Bigalke, M. Imseng, M. Müller, A. Keller, K. Murphy, K. Kreissig, M. Rehkämper, W. Wilcke, E. Frossard, Cadmium isotope fractionation in soil–wheat systems. Environ. Sci. Technol. 50 (2016) 9223-9231.

[7] Q. Zhong, Y. Zhou, D. Tsang, J. Liu, X. Yang, M. Yin, S. Wu, J. Wang, T. Xiao, Z. Zhang, Cadmium isotopes as tracers in environmental studies: A review. Sci. Total Environ. 736 (2020) 139585.

[8] A. Schmitt, S. Galer, W. Abouchami, Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. Earth. Planet. Sci. Lett. 277 (2009) 262-272.

[9] M. Lambelet, M. Rehkämper, T. Flierdt, Z. Xue, K. Kreissig, B. Coles, D. Porcelli, P. Andersson, Isotopic analysis of Cd in the mixing zone of Siberian rivers with the Arctic Ocean—new constraints on marine Cd cycling and the isotope composition of riverine Cd. Earth. Planet. Sci. Lett. 361 (2013) 64-73.

[10] T. Gao, Y. Liu, Y. Xia, J. Zhu, Z. Wang, M. Qi, Y. Liu, Z. Ning, Q. Wu, W. Xu, C. Liu, Cadmium isotope compositions of Fe-Mn nodules and surrounding soils: implications for tracing Cd sources. Funda Res 1 (2021) 269-276.

[11] Z. Lu, J. Zhu, D. Tan, X. Wang, Z. Zheng, $\delta^{114/110}$Cd Values of a suite of different reference materials. Geostand Geoanal Res, 45 (2021) 565-581.

[12] A. Shiel, J. Barling, K. Orians, D. Weis, Matrix effects on the multi-collector inductively coupled plasma mass spectrometric analysis of high-precision cadmium and zinc isotope ratios. Anal. Chim. Acta 633 (2009) 29-37.

[13] R. Rudnick, S. Gao, Composition of the continental crust. Treat. Geochem. 2nd Ed. 2014, pp 1-51.

[14] H. Peng, D. He, R. Guo, X. Liu, N. Belshaw, H. Zheng, S. Hu, Z. Zhu, High precision cadmium isotope analysis of geological reference materials by double spike MC-ICP-MS. J. Anal. At. Spectrom. 36 (2021) 390-398.

[15] D. Tan, J. Zhu, X. Wang, G. Han, Z. Lu, W. Xu, High-sensitivity determination of Cd isotopes in low-Cd geological samples by double spike MC-ICP-MS. J. Anal. At. Spectrom. 35 (2020) 713-727.

[16] M. Liu, Q. Zhang, Y. Zhang, Z. Zhang, F. Huang, H. Yu, High-precision Cd isotope measurements of soil and rock reference materials by MC-ICP-MS with double spike correction. Geostand Geoanal Res 44 (2020) 169-182.

[17] K. Rosman, J. De Laeter, The isotopic composition of cadmium in terrestrial minerals. Int. J. Mass Spectrom. Ion Processes 16 (1975) 385-394.

[18] S. Yang, D. Lee, T. Ho, The isotopic composition of cadmium in the water column of the South China Sea. Geochim. Cosmochim. Acta 98 (2012) 66-77.

[19] E. Martinková, V. Chrastný, M. Francová, A. Šípková, J. Čuřík, O. Myška, L. Mižič, Cadmium isotope fractionation of materials derived from various industrial processes. J. Hazard. Mater. 302 (2016) 114-119.

[20] C. Cloquet, O. Rouxel, J. Carignan, G. Libourel, Natural cadmium isotopic variations in eight geological reference materials (NIST SRM 2711, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-P-1, Nod-A-1) and anthropogenic samples, measured by MC-ICP-MS. Geostand Geoanal Res 29 (2005) 95-106.

[21] F. Wombacher, M. Rehkämper, K. Mezger, C. Münker, Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. Geochim. Cosmochim. Acta 67 (2003) 4639-4654.

[22] N. Pallavicini, E. Engström, D. C. Baxter, B. Öhlander, J. Ingri, I. Rodushkin, Cadmium isotope ratio measurements in environmental matrices by MC-ICP-MS. J. Anal. At. Spectrom. 29 (2014) 1570-1584.

[23] B. Gao, Y. Liu, K. Sun, X. Liang, P.. Peng, G. Sheng, J. Fu, Precise determination of cadmium and lead isotopic compositions in river sediments. Anal. Chim. Acta 612 (2008) 114-120.

[24] M. Gault-Ringold, C. Stirling, Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS. J. Anal. At. Spectrom. 27 (2012) 449-459.

[25] C. Zhu, H. Wen, Y. Zhang, Z. Huang, C. Cloquet, B. Luais, T. Yang, Cadmium isotopic constraints on metal sources in the Huize Zn–Pb deposit, SW China. Geosci Front 12 (2021) 101241.

[26] A. Bryan, A. Dickson, F. Dowdall, W. Homoky, D. Porcelli, G. Henderson, Controls on the cadmium isotope composition of modern marine sediments. Earth. Planet. Sci. Lett. 565 (2021) 116946.

[27] R. Xie, S. Galer, W. Abouchami, M. Rijkenberg, H. de Baar, J. De Jong, M. Andreae, Non-rayleigh control of upper-ocean Cd isotope fractionation in the western south atlantic. Earth. Planet. Sci. Lett. 471 (2017) 94-103.

[28] K. Murphy, M. Rehkämper, K. Kreissig, B. Coles, T. van de Flierdt, Improvements in Cd stable isotope analysis achieved through use of liquid–liquid extraction to remove organic residues from Cd separates obtained by extraction chromatography. J. Anal. At. Spectrom. 31 (2016) 319-327.

[29] X. Liu, Z. Zhu, C. Yang, G. Wang, H. Zheng, S. Hu, Sensitivity and high-precision lead isotopic analysis by multicollector inductively coupled plasma mass spectrometry based on liquid spray dielectric barrier discharge plasma-induced chemical vapor generation. ACS Earth Space Chem 5 (2021) 1762-1771.

[30] C. Gallon, J. Aggarwal, A. R. Flegal, Comparison of mass discrimination correction methods and sample introduction systems for the determination of lead isotopic composition using a multicollector inductively coupled plasma mass spectrometer. Anal. Chem. 80 (2008) 8355-8363.

[31] Y. Gao, R. Liu, L. Yang, Application of chemical vapor generation in ICP-MS: A review. Chin. Sci. Bull. 58 (2013) 1980-1991.

[32] P. Pohl, P. Jamroz, M. Welna, A. Szymczycha-Madeja, K. Greda, Chemical-vapor generation of transition metals through the reaction with tetrahydroborate in recent achievements in analytical atomic spectrometry. TrAC, Trends Anal. Chem. 59 (2014) 144-155.

[33] D. Foucher, H. Hintelmann, High-precision measurement of mercury isotope ratios in sediments using cold-vapor generation multi-collector inductively coupled plasma mass spectrometry. Anal.

Bioanal. Chem. 384 (2006) 1470-1478.

[34] O. Rouxel, J. Ludden, J. Carignan, L. Marin, Y. Fouquet, Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry. Geochim. Cosmochim. Acta 66 (2002) 3191-3199.

[35] O. Rouxel, A. Galy, H. Elderfield, Germanium isotopic variations in igneous rocks and marine sediments. Geochim. Cosmochim. Acta 70 (2006) 3387-3400.

[36] O. Rouxel, J. Ludden, Y. Fouquet, Antimony isotope variations in natural systems and implications for their use as geochemical tracers. Chem. Geol. 200 (2003) 25-40.

[37] M. Norman, V. Bennett, M. McCulloch, L. Kinsley, Osmium isotopic compositions by vapor phase sample introduction using a multi-collector ICP-MS. J. Anal. At. Spectrom. 17 (2002) 1394-1397.

[38] G. Sanabria-Ortega, C. Pécheyran, S. Bérail, O. F. X. Donard, Fast and precise method for Pb isotope ratio determination in complex matrices using GC-MC-ICPMS: application to crude oil, kerogen, and asphaltene samples. Anal. Chem. 84 (2012) 7874-7880.

[39] X. Guo, X. Guo, Studies on the reaction between cadmium and potassium tetrahydroborate in aqueous solution and its application in atomic fluorescence spectrometry. Anal. Chim. Acta 310 (1995) 377-385.

[40] H. Sun, R. Suo, Enhancement reagents for simultaneous vapor generation of zinc and cadmium with intermittent flow system coupled to atomic fluorescence spectrometry. Anal. Chim. Acta 509 (2004) 71-76.

[41] R. Li, H. Yan, X. Yang, Z. Li, Y. Guo, Simultaneous determination of trace lead, tin and cadmium in biological samples by a chemical vapor generation-four-channel atomic fluorescence spectrometry dual gas–liquid separator system. J. Anal. At. Spectrom. 26 (2011) 1488-1493.

[42] M. Guerrero, E. Alonso, J. Pavón, M. Cordero, A. García de Torres, Simultaneous determination of chemical vapour generation forming elements (As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg) and non-chemical vapour forming elements (Cu, Cr, Mn, Zn, Co) by ICP-OES. J. Anal. At. Spectrom. 31 (2016) 975-984.

[43] F. Colin, R. Eléonore, F. Rémi, C. Corinne, A single-step purification method for the precise determination of the antimony isotopic composition of environmental, geological and biological samples by HG-MC-ICP-MS. J. Anal. At. Spectrom. 36 (2021) 776-785.

[44] X. Liu, Z. Liu, Z. Zhu, D. He, S. Yao, H. Zheng, S. Hu, Generation of volatile cadmium and zinc species based on solution anode glow discharge induced plasma electrochemical processes. Anal. Chem. 89 (2017) 3739-3746.

[45] M. H. Thiemens, J. E. Heidenreich, The mass-independent fractionation of oxygen: A novel isotope effect and its possible cosmochemical implications. Science 219 (1983) 1073-1075.

[46] F. Robert, S. Derenne, G. Lombardi, K. Hassouni, A. Michau, P. Reinhardt, R. Duhamel, A. Gonzalez, K. Biron, Hydrogen isotope fractionation in methane plasma. Proc Natl Acad Sci USA 114 (2017) 870-874.

[47] X. Liu, Z. Zhu, P. Xing, H. Zheng, S. Hu, Plasma induced chemical vapor generation for atomic spectrometry: a review. Spectrochim. Acta, Part B. 167 (2020) 105822.

[48] M. Pons, M. Millet, G. Nowell, S. Misra, H. Williams, Precise measurement of selenium isotopes by HG-MC-ICPMS using a 76–78 double-spike. J. Anal. At. Spectrom. 35 (2020) 320-330.

[49] M. Friebel, E. Toth, M. Fehr, M. Schönbächler, Efficient separation and high-precision analyses of tin and cadmium isotopes in geological materials. J. Anal. At. Spectrom. 35 (2020) 273-292.

[50] F. Zhou, D. He, X. Miao, C. Yang, J. Dong, H. Zheng, Z. Cheng, X. Liu, Z. Zhu, Development of an automatic column chromatography separation device for metal isotope analysis based on droplet

counting. Anal. Chem. 93 (2021) 7196-7203.

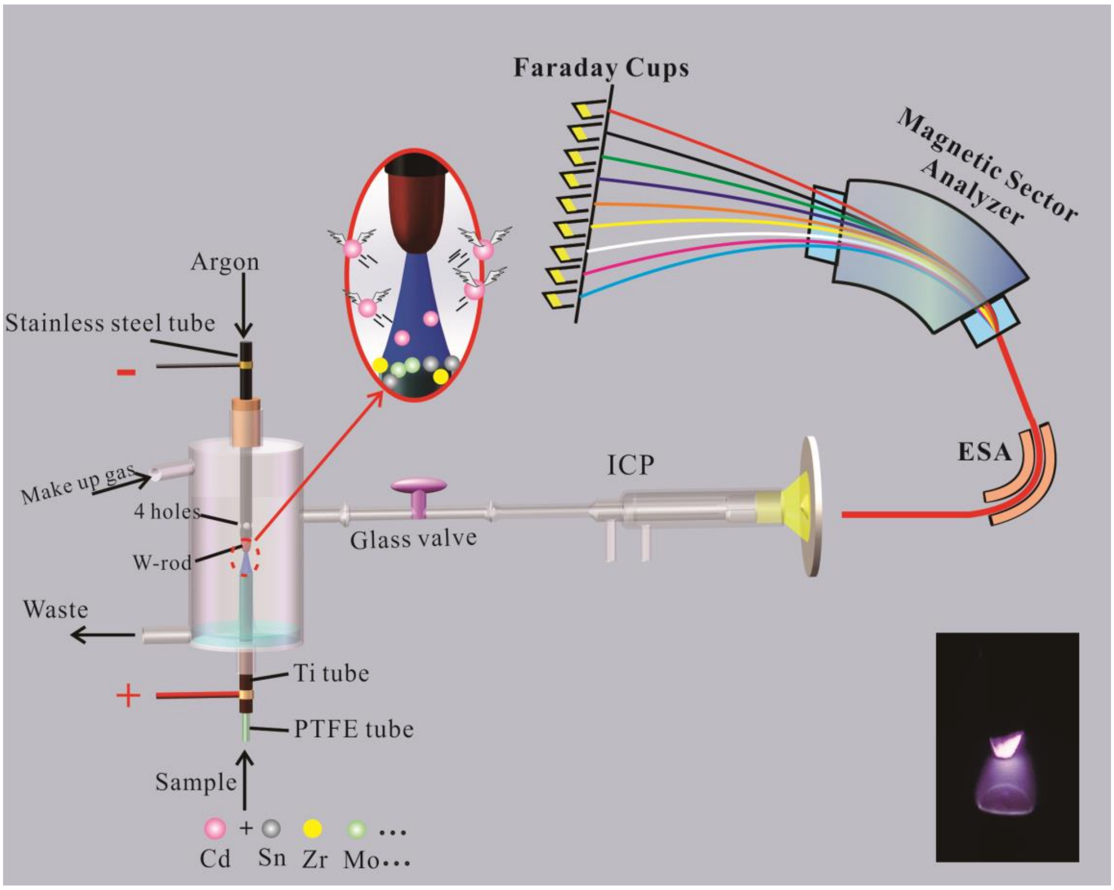

Figure 1. Schematics diagram of the instrumental setup of PEVG-MC-ICPMS.

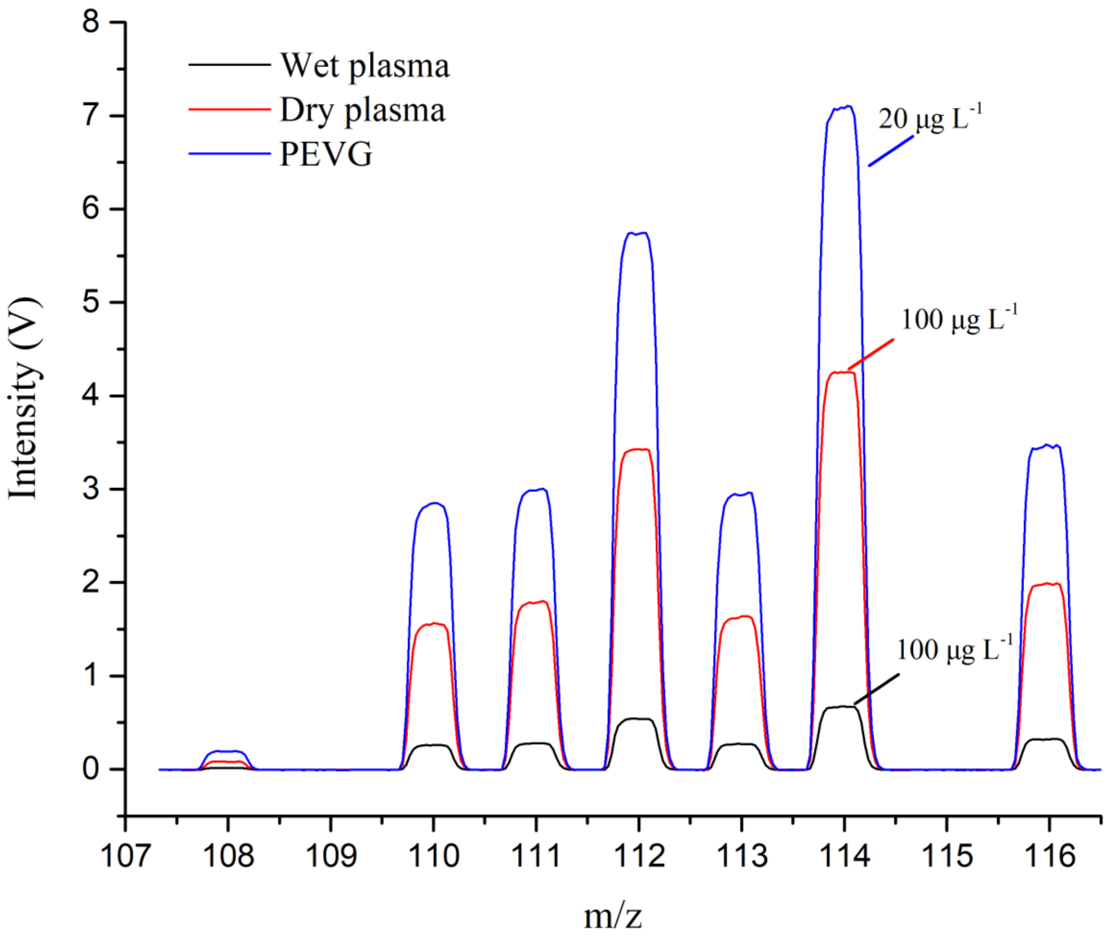

Figure 2. Typical mass spectrum of Cd in MC-ICPMS obtained with three sample introduction modes. Sample flow rate of 0.8 mL min^{-1}, 0.1 mL min^{-1} and 0.1 mL min^{-1} was used for PEVG, dry plasma and wet plasma, respectively.

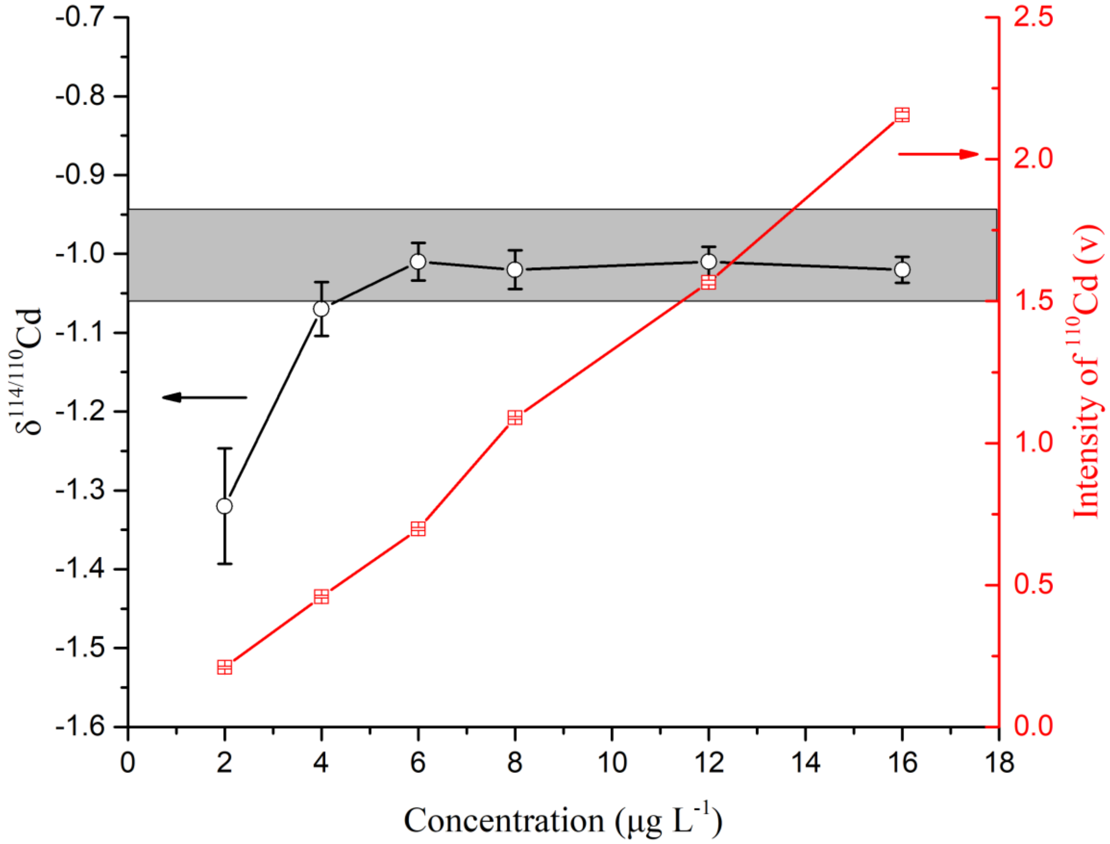

Figure 3. Effect of Cd concentration on the external precision (2 sd, n=3) of $\delta^{114/110}$Cd obtained by PEVG-MC-ICPMS. The gray band represents the analytical uncertainty range of BGEG-Cd.

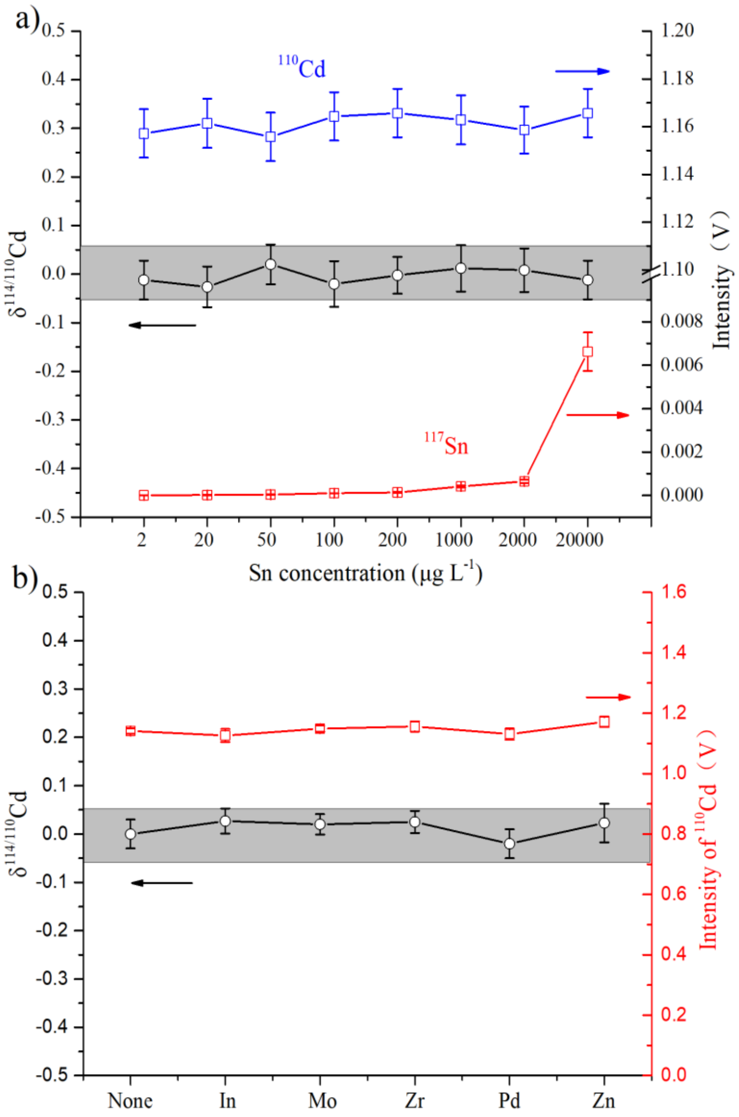

Figure 4. The interference of Sn (a), and In, Mo, Zr, Pd and Zn (b) on the $\delta^{114/110}$Cd of 8 μg L^{-1} NIST 3108 standard solutions obtained by PEVG-MC-ICPMS (n=3). In (b), the interference of In, Mo, Zr, Pd and Zn was also evaluated at concentration of 2000 μg L^{-1}. The gray band represents the analytical uncertainty range of Cd NIST 3108.

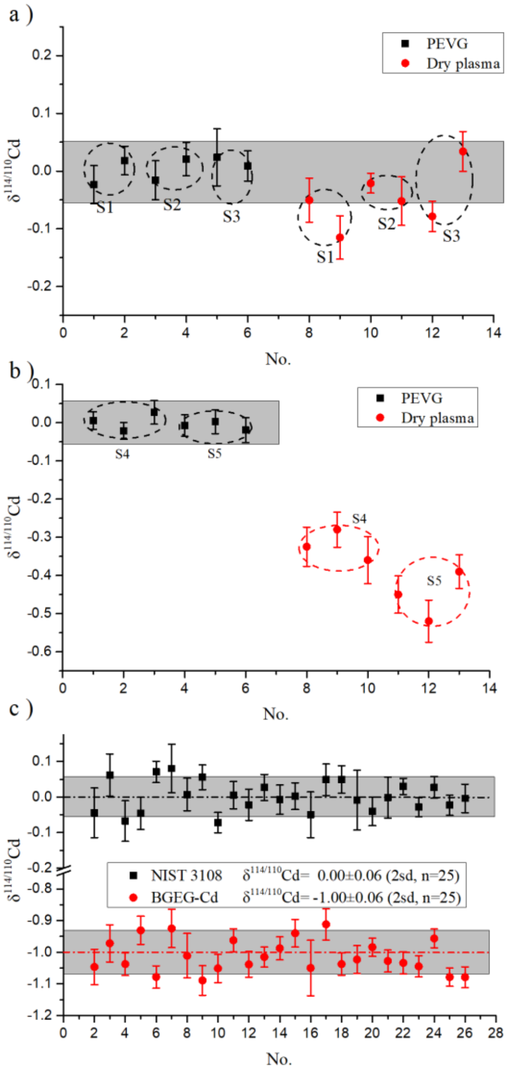

Figure 5. (a) The influence of resin-derived organic material on the $\delta^{114/110}$Cd measurement using PEVG, and dry-plasma mode. (b) Repeat $\delta^{114/110}$Cd measurements of synthetic Cd isotopic solutions processed with the simplified purification process using PEVG, and dry-plasma mode. (c) The long-term precision of $\delta^{114/110}$Cd for the measurement of NIST 3108 and BGEG-Cd. The gray bands represents the analytical uncertainty range. In (a) and (b), S1−5 represent parallel experiments, respectively.

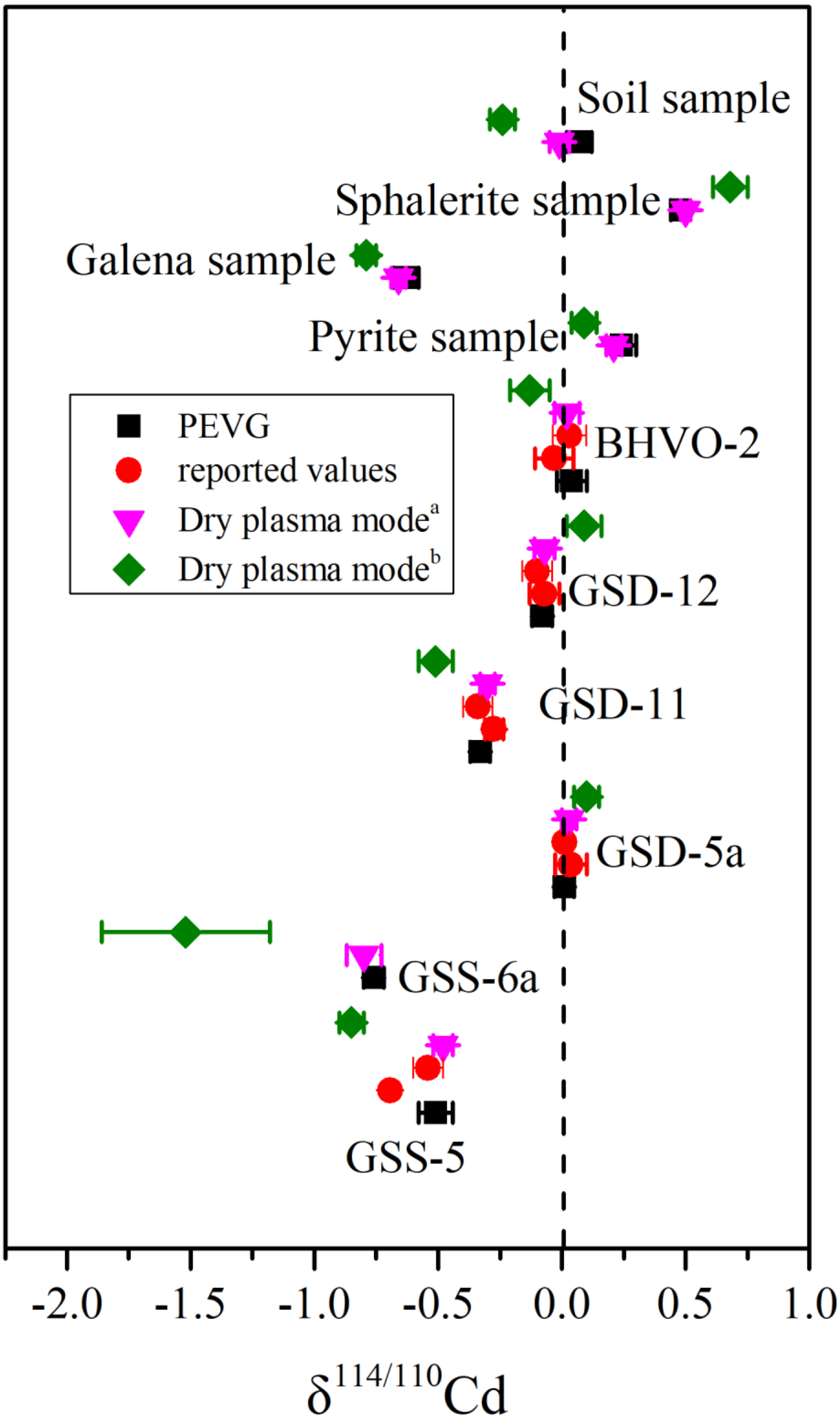

Figure 6. Cd isotopic compositions of geological reference materials and 4 real samples measured in this study and the reported data. [a]Dry-plasma mode with two-step purification; [b]Dry-plasma mode with one-step simplified purification.

Table 1. Sample Purification Time for the conventional “Dry” and PEVG Methods

	First-step purification	Evaporation and redissolution	Second-step purification	Digestion of resin residual	Evaporation and redissolution	Total time
Dry	~4 hours	~20 hours	~4 hours	~20 hours	~24 hours	~72 hours
PEVG	~3 hours	0 hours	0 hours	0 hours	0 hours	~3 hours