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Precise determination of cadmium and lead isotopic compositions in river sediments

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ABSTRACT

A method for the accurate determination of Cd and Pb isotope compositions in sediment samples is presented. Separation of Cd and Pb was designed by using an anionic exchange chromatographic procedure. Measurements of Cd isotopic compositions were carried out by multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS), by using standard-sample bracketing technology for mass bias correction and Pb isotopic ratios were determined by thermal ionization mass spectrometry (TIMS). The factors that affect the accurate and precise Cd isotope compositions analysis, such as instrumental mass fractionation and isobaric interferences, were carefully evaluated and corrected. The Cd isotopic results were reported relative to an internal Cd solution and expressed as the $\delta^{114/110}$Cd. Five Cd reference solutions and one Pb standard were repeatedly measured in order to assess the accuracy of the measurements. Uncertainties obtained were estimated to be lesser than 0.11‰ (2s) for the $\delta^{114/110}$Cd value. Analytical uncertainties in 2s for Pb isotopic ratios were better than 0.5‰. The method has been successfully applied to the investigation of Cd and Pb isotope compositions in sediment samples collected from North River in south China.

1. Introduction

Cadmium (Cd) is a trace element that occurs at the concentration levels of ppb in most terrestrial materials. It has eight stable isotopes that span 10 amu from mass number 106 to 116 (Table 1). Cd concentrations were measured on meteorites and terrestrial samples in order to survey the Cd level in the environment [1–4]. Since the advent of a technique for Cd separation and isotopic analysis, the application of this system has increased over the last decade and has proven useful in a wide variety of measurements in meteorites and other extraterrestrial samples to study the mass-dependent fractionation for cosmochemical applications [5–8]. During the last few years, new instruments and analytical developments have made possible precise isotopic measurements for Cd in the environment. Multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) permits stable isotope ratio measurements of heavy and transitional elements at a level of precision that is sufficient to resolve isotopic variations of a few tenths of a per mill [9]. Cd isotopic compositions of

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Table 1 – MC-ICPMS collector configurations and isotope abundances of interferences on Cd

Mass	106	108	110	111	112	113	114	116	117	118
Collector configuration	–	–	Ax	H1	H2	H3	H4	–	H5	H6
Isotope abundances (%)										
Pd	27.3	26.5	11.7							
Cd	1.25	0.89	12.5	12.8	24.1	12.2	28.7	7.49		
Sn					0.97		0.65	14.5	7.68	24.23
In						4.3				

terrestrial and extraterrestrial materials were measured precisely by MC-ICPMS [10–13]. Other studies measured the Cd isotopic fractionation in seawater and ocean [14,15]. Although large variations in Cd isotopic compositions were observed for chondritic meteorites and lunar soils [5,7,10,13], a restricted variation of about ±0.20‰ amu^{-1} has so far been reported for terrestrial rocks and minerals [11,12]. Recently, large Cd isotopic fractionations were reported for industrially partly evaporated Cd metal [11,12,16,17], suggesting that anthropogenic processes may lead to considerable variations of Cd isotopic composition. Therefore, Cd isotope ratios can give useful information about the source of the Cd in the environment, and are important to study its geochemical behavior. Up to now, there were a large number of studies on accurate and precise measurements of Pb isotopic ratios [18]. Most exclusively Pb isotopes were used to effectively trace metal pollution sources in the environment [19–30]. The first application of both Cd and Pb isotopic compositions to environmental geochemistry provided evidence that the anthropogenic activities could result in the Cd isotopic variation in soils and Cd isotopes might be used to document mixing process industrial inputs in polluted environment [25]. The use of Cd and Pb isotopic compositions together can give a better understanding of metal pollution and their geochemical behavior. Pb isotopes will directly trace the sources of pollution and Cd isotopes can trace the anthropogenic fractionations.

For the accurate determination of Cd and Pb isotopic compositions in sediment samples, it is important to have a sufficiently clean sample because sediment samples have a complicated matrix that makes it difficult to obtain accurate Cd and Pb isotope measurements. Different kinds of chromatographic methods were applied to separate Cd from environmental samples for stable Cd isotope measurements in previous studies [11,12]. However, nearly all of these methods can only provide separation for individual Cd or Pb from the matrix, but cannot separate both Cd and Pb simultaneously in one-stage procedure.

In our work, we presented a method for the accurate determination of Cd and Pb isotope compositions in sediment samples. After the sample was digested in mixture of different acids, we subsequently employed a one-stage anionic exchange procedure that both Cd and Pb can be separated from any other elements with a high recovery, resulting in a very "clean" final solution for accurate determination of Cd and Pb isotopic composition with MC-ICPMS and thermal ionization mass spectrometry (TIMS), respectively. The factors that affect the accurate and precise Cd isotope compositions analysis, such as instrumental mass fractionation and isobaric interferences were carefully evaluated and corrected. In order to assess the accuracy, five Cd standard solutions and one Pb standard were repeatedly measured and yielded accurate and reproducible Cd and Pb isotopic results, which were identical to most previously published methods. As a potential tool for source identification of Cd and Pb in the environment, this method has been applied to the investigation of Cd and Pb isotope compositions of sediments collected in the North River in south China.

2. Experimental

2.1. *Reagents and materials*

All critical sample preparation work was carried out in a class 100 clean room facility. All acids used in this study were purified by subboiling distillation and the water was 18.2 MΩ grade purified from Milli-Q water purification system (Millipore, Bedford, MA, USA). HNO_3 and HCl that were required for the experiment were purchased from Beijing Institution of Chemical Reagents (Beijing, China) and were prepared freshly on the day of use.

In this study, five different Cd solutions were used: (1) A 1003 mg L^{-1} Cd solution (Lot No: CL3-82CD) was purchased from SPEX (Metuchen, NJ, USA), and this solution was termed "SPEX Cd" and used as a "zero delta" Cd standard. (2) Another 1000 mg L^{-1} SPEX Cd solution (Lot No: 7-29 Cd), was provided by Cloquet et al. [12]. (3) A commercial ICP standard solution (Lot No: 502552A) was purchased from Alfa Aesar (Karlsruhe, Germany) and termed "JMC Cd". (4) A fractionated Cd isotope reference material termed "Münster Cd" was provided by Wombacher et al. [16]. (5) A solution was issued by the German Bundesanstalt für Materialwissenschaften und-prüfung (BAM), a member of the Joint European Project for Primary Isotopic Measurements. This solution termed "BAM-1020 Cd" was as suggested in the literatures [16,31]. Cd isotopic compositions of SPEX-1 Cd, JMC Cd, Münster Cd and BAM-1020 Cd were already reported in the previous literatures and used in this study to access the accuracy of Cd isotopic measurement. However, SPEX Cd used in this study was a new Cd standard solution and was not reported before. Moreover, A GSS-1 soil reference sample and GSD-12 sediment reference sample were used in this study. These two reference samples were obtained from the Institute of Geophysical and Geochemical Prospecting (Langfang, China).

Seven sediment samples used in this study were collected at a depth of 0–10 cm from North River. North River is the important branch of the Pearl River, which was polluted by