- 1 Multi-elemental isotopic analysis for trace metals in geochemical samples, Part 2: nickel, copper, zinc, cadmium,
- 2 and lead in sediments, atmospheric particles, and plankton
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#### 8 Abstract

9 The isotope ratios of Ni, Cu, Zn, Cd, and Pb are utilized to trace the origins and investigate the various 10 processes affecting these elements. In Part 1, we presented a method for the simultaneous analysis of isotope 11 ratios of dissolved trace metals in seawater using NOBIAS PA1 chelate extraction and AG MP-1M anion 12 exchange. In Part 2, we extend the applicability of this method to sediments, atmospheric particles, and plankton. 13 In the NOBIAS PA1 chelate extraction, NH<sub>4</sub>F solution was used to separate Ni, Cu, Zn, Cd, and Pb from Al, Ti, 14 Cr, Mn, Fe, Zr, and Sn, which are abundant in sediment and atmospheric particles. Then, Ni, Cu, Zn, Cd, and 15 Pb were separated using anion exchange. The accuracy and precision were evaluated by the repeated analysis 16 of reference materials of marine sediments (PACS-3), atmospheric particles (NIES-28), and river plankton 17 (BCR-414). This method has the following advantages over conventional methods: 1) simultaneous analysis of 18 isotope ratios of multiple elements from a single sample in only two chemical separation steps, allowing for 19 high-throughput analysis; 2) clean and excellent chemical separation providing highly precise data; and 3) high 20 applicability to a wide range of samples including marine sediments, plankton, and atmospheric particles. The 21 methods presented in Parts 1 and 2 are expected to accelerate the multi-elemental isotope research of trace 22 metals in the ocean, atmosphere, and sediments.

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#### 24 **1. Introduction**

25 Ni, Cu, Zn, Cd, and Pb are essential or toxic to phytoplankton. In Part 1, we present a method for the 26 determination of isotope ratios of trace metals, Fe, Ni, Cu, Zn, Cd, and Pb, in seawater. To understand the 27 biogeochemical cycles of these metals in the ocean, analysis of particulate trace metals in plankton, atmospheric 28 particles, and sediments is required. Plankton play a crucial role in absorbing dissolved trace metals from 29 seawater, while biogenic particles facilitate the transport of these metals to the deep ocean. Atmospheric 30 particles, originating from natural sources like windblown fine sand and human activities such as fossil fuel 31 combustion, contribute to the input of trace metals into the ocean. Marine sediments act as both sinks and 32 sources of trace metals in seawater, as dissolved trace metals undergo distribution to the particle phase through 33 biological uptake and particle adsorption before being ultimately buried in sediments. Conversely, diagenesis 34 of marine sediments releases dissolved trace metals back into seawater, completing the dynamic cycle of trace 35 metal distribution in marine environments.<sup>1</sup>

Multi-elemental isotope ratio analysis shows promise in identifying the sources of trace metals. For instance, Araújo et al.<sup>2</sup> utilized multi-elemental isotope ratios to identify trace metal sources in Mediterranean coastal sediments, revealing the impact of various anthropogenic contributions to the coastal ocean. SoutoOliveira et al.<sup>3</sup> investigated the concentrations and isotope ratios of Cu, Zn, and Pb in atmospheric particles in São Paulo, London, and Barcelona, concluding that these elements likely originated from car wear-off, car exhaust, industrial emissions, and cement. Pontér et al.<sup>4</sup> investigated the isotope ratios of Cu, Zn, Cd, and Pn in products and ores from the Rönnskär Cu–Pb–Zn smelter in Sweden and nearby brackish water and sediments. They assessed the extent of heavy metal contamination associated with the smelter and the behavior of these heavy metals in brackish water and sediments.

- 7 In Part 1, we described a method for the simultaneous determination of Fe, Ni, Cu, Zn, Cd, and Pb 8 isotope ratios in seawater by two-step chemical separation using solid-phase chelate extraction and anion 9 exchange. This process effectively extracts dissolved Fe, Ni, Cu, Zn, Cd, and Pb from seawater while 10 eliminating alkali and alkaline earth metals. In this paper, we report a method to determine Ni, Cu, Zn, Cd, and 11 Pb isotope ratios in particulate samples, such as marine sediments and atmospheric particles. Compared with 12 seawater, particulate samples contain significant amounts of Al, Ti, Mn, Fe, Zr, and Sn. These elements generate atomic and molecular ions in MC-ICP-MS, leading to spectral interferences of <sup>58</sup>Fe<sup>+</sup>, <sup>27</sup>Al<sup>40</sup>Ar<sup>+</sup>, <sup>48</sup>Ti<sup>16</sup>O<sup>+</sup>, 13 <sup>55</sup>Mn<sup>16</sup>O<sup>+</sup>, <sup>94</sup>Zr<sup>16</sup>O<sup>+</sup>, and <sup>114</sup>Sn<sup>+</sup> during the isotopic measurements of Ni, Cu, Zn, Cd, and Pb. Hence, the chemical 14 15 separation procedure for seawater described in Part 1 is modified to remove these interfering elements, allowing 16 for isotopic analysis of Ni, Cu, Zn, Cd, and Pb in atmospheric particles, sediments, and plankton samples, which 17 play crucial roles as sources, transporters, and sinks for biogeochemical cycles of trace metals in the ocean.
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#### 19 **2. Experimental Section**

## 20 **2.1. Expression of isotope ratios**

21 The isotope ratios for Ni, Cu, Zn, and Cd are expressed using the  $\delta$ -notation (Eq. 1).

22  $\delta^{m/n} \mathbf{E} = \left[ ({}^{m} \mathbf{E} / {}^{n} \mathbf{E})_{\text{Sample}} / ({}^{m} \mathbf{E} / {}^{n} \mathbf{E})_{\text{Reference}} - 1 \right] \times 1000, \quad (1)$ 

where *m* and *n* represent the mass numbers of the isotopes for element E. In this study, all δ values are expressed relative to NIST-986 Ni (National Institute of Standards and Technology), NIST-976 Cu (National Institute of Standards and Technology), JMC-Lyon Zn,<sup>5</sup> and NIST-3108 Cd (National Institute of Standards and Technology). Wako Ni, Wako Cu, and AA-ETH Zn were used as working standards.<sup>5-6</sup> Isotope ratios of Pb are represented as <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>207</sup>Pb, and <sup>206</sup>Pb/<sup>207</sup>Pb. NMIJ-3681 Pb (National Institute of Advanced Industrial Science and Technology) was used as the reference material for Pb isotopes.

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#### 30 **2.2. Materials and chemicals**

31 The chemical separation in this study utilizes the same ultrapure water and reagents (HCl, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, 32 HBr, CH<sub>3</sub>COOH, and NH<sub>4</sub>OH) as in Part 1. An ultrapure regent of HF (Ultrapur) was obtained from Kanto 33 Chemicals. A 2.5 M NH<sub>4</sub>F solution was prepared by mixing HF and NH<sub>4</sub>OH. The perfluoroalkoxy alkane (PFA) 34 vials (Savillex) and low-density polyethylene (LDPE) bottles (Thermo Scientific Nalgene) used for storing 35 reagents and conducting the chemical separation were subjected to the same cleaning procedure as described in 36 Part 1. To conduct recovery tests, multi-elemental sample solutions, denoted as samples CE and AE, were 37 prepared from 10 ppm XSTC-622 multi-elemental standard (SPEX CertiPrep) and 1000 ppm Bi standard 38 solutions (Wako Chemicals). The elemental compositions of samples CE and AE are shown in Supplementary 1 Table S1.

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## 3 2.3. Sample digestion

Certified reference materials for marine sediments (PACS-3) were obtained from the National Research Council Canada, riverine plankton (BCR-414) from the Joint Research Centre, and urban atmospheric particles (NIES-28) from the National Institute for Environmental Studies. For analysis, 22.8 mg of PACS-3, 53.2 mg of BCR-414, and 24.7 mg of NIES-28 were weighed into separate PFA vials. Subsequently, the samples were digested using a mixture of 0.5 mL of 28 M HF, 1.5 mL of 12 M HCl, and 3 mL of 14 M HNO<sub>3</sub> on a hotplate at 150°C for more than 12 h.

After the initial digestion, the acid was evaporated, and the residue was subjected to a second digestion using a mixture of 1 mL of 12 M HCl and 3 mL of 14 M HNO<sub>3</sub> on a hotplate at 150°C for more than 12 h. Following this step, the acid was evaporated, and the remaining residue was redissolved in 0.3 M HNO<sub>3</sub>, with 10 mL used for PACS-3 and BCR-414 and 18 mL for NIES-28.

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# 15 2.4. NOBIAS PA1 chelate extraction

16 Chemical separation was performed in a clean room. A NOBIAS Chelate PA-1F column (Hitachi 17 High-Technologies) containing 250 mg of NOBIAS Chelate PA1 resin in a syringe-type polypropylene column 18 was used to extract Ni, Cu, Zn, Cd, and Pb in the digested particulate samples. Chelate extraction was performed 19 following the procedure outlined in Table 1a. All solutions were passed through the NOBIAS Chelate PA-1F column by gravity. The flow rate was ~3 mL/min. At least one day before chemical separation, double-spike 20 solutions of <sup>61</sup>Ni-<sup>62</sup>Ni, <sup>67</sup>Zn-<sup>70</sup>Zn, and <sup>110</sup>Cd-<sup>111</sup>Cd (the compositions are shown in Part 1) were added to the 21 22 digested sample. The double-spike solutions were added to the digested samples, with the amounts of Ni, Zn, 23 and Cd from the spike solutions being 1-4, 0.5-2, and 1-2 times, respectively, the amount of each element 24 originally present in the digested sample. Prior to chemical separation, a CH<sub>3</sub>COOH-CH<sub>3</sub>COONH<sub>4</sub> buffer was 25 added to the digested sample to a concentration of 1 mol/L, and the pH of the sample was adjusted to 4.6-4.8. 26 The sample was processed through the column after cleaning and conditioning. Then, 8 mL of ultrapure water 27 was passed through to remove alkali and alkaline earth metals, and 0.5 mL of 2.5 M NH<sub>4</sub>F was passed four 28 times at 5 min intervals to remove hard-acid metal ions (i.e., Al<sup>3+</sup>, V<sup>5+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, and Ga<sup>3+</sup>). Then, 38 mL of 29 ultrapure water was passed to remove NH4F. Finally, 2 mL of 1 M HNO3 was passed three times every 5 min to 30 elute Ni, Cu, Zn, Cd, and Pb. The eluate was then completely evaporated on a hotplate (160°C), and the 31 remaining residue was redissolved in 0.2 mL of 9 M CH<sub>3</sub>COOH-3 M HCl.

Table 1 Procedure of NOBIAS PA1 chelate extraction (a) and AG MP-1M anion exchange (b)

(a)			
	Solution	Volume mL	
Cleaning	1 M HNO <sub>3</sub>	10	
Conditioning	1 M CH <sub>3</sub> COOH-CH <sub>3</sub> COONH <sub>4</sub>	2	
Sample loading	Sample	1–5	
Removing salts	Ultrapure water	8	
Removing hard-acid ions	2.5 M NH <sub>4</sub> F	2	
Removing NH <sub>4</sub> F	Ultrapure water	38	
Elution	1 M HNO <sub>3</sub>	6	

(b)

	Solution	Volume mL
Cleaning	1 M HNO <sub>3</sub>	0.40
Conditioning	9 M CH <sub>3</sub> COOH - 3 M HCl	0.20
Sample loading	Sample	0.20
Elution of Ni	9 M CH <sub>3</sub> COOH - 3 M HCl	0.24
Elution of Pb	12 M HCl	0.28
Elution of Cu	0.5 M HCl	1.20
Elution of Zn	3 M HNO <sub>3</sub> - 0.1 M HBr	1.20
Elution of Cd	3 M HNO <sub>3</sub>	0.90

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#### 2.5. Anion exchange

After solid-phase chelate extraction, Ni, Cu, Zn, Cd, and Pb were separated using an anion-exchange column. The anion-exchange column was the same as that described in Part 1. The procedure of anion exchange is shown in Table 1b. All solutions were added using a micropipette and passed through the column by gravity. After cleaning and conditioning, the sample was introduced to the column. 9 M CH<sub>3</sub>COOH–3 M HCl, 12 M HCl, 0.5 M HCl, 3 M HNO<sub>3</sub>–0.1 M HBr, and 3 M HNO<sub>3</sub> solutions were passed sequentially to elute Ni, Pb, Cu, Zn, and Cd, respectively. The eluates from each step were completely evaporated on the hotplate, and the residue was redissolved in 0.3–2 mL of 0.3 M HNO<sub>3</sub> for isotopic measurements.

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#### 11 **2.6.** Measurements of isotope ratios and concentrations

12 The isotope ratios of Ni, Cu, Zn, Cd, and Pb were measured using a Neptune Plus multi-collector 13 inductively coupled plasma mass spectrometry (MC-ICP-MS) instrument at the Research Institute for Humanity 14 and Nature, Kyoto, Japan. The measurement conditions were consistent with those described in Part 1. For Cu, 15 samples were introduced using a PFA nebulizer (at a flow rate of 50 µL/min) and a glass spray chamber. Isotope 16 fractionations during chemical separation and MC-ICP-MS measurements were corrected using the double-17 spike technique.<sup>7</sup> Isotope fractionations for Cu and Pb in measurements were corrected using Ga-doping external 18 correction for Cu and the standard bracketing method for Pb. Isotope ratios for Ni, Cu, Zn, and Cd were 19 expressed using the  $\delta$ -notation (Eq. 1).

The concentrations of Ni, Zn, and Cd were determined by an isotope dilution method at the same time as the isotopic measurement. The concentration of Cu was determined by an internal standard method with Gadoping at the same time as the isotopic measurement. The concentration of Pb was determined by a calibration curve method using an Element II high-resolution ICP-MS instrument at the Institute for Chemical Research,

- 1 Kyoto University.
- 2
- 3 **3. Results and Discussion**

#### 4 **3.1. NOBIAS PA1 chelate extraction**

5 Particulate samples, including sediments and atmospheric particles, often contain significant amounts of Al, Ti,

6 Mn, Cr, Fe, Zr, and Sn, which can interfere in the isotopic measurements of Ni, Cu, Zn, and Cd.<sup>8-11</sup> In this study,

7 2 mL of 2.5 M NH<sub>4</sub>F solution was passed through a NOBIAS Chelate PA1F column after sample loading. To

8 determine the recoveries of Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Mo, Cd, Sn, Ba, Pb, and

9 Bi, 1 mL of sample CE (Supplementary Table S1) was processed using chelate extraction with and without

- 10 NH<sub>4</sub>F solution (Fig. 1). The recoveries of various elements in the fraction of 1 M HNO<sub>3</sub> of the chelate extraction
- 11 were as follows:
- Without NH<sub>4</sub>F solution: Al: 16%, Ti: 90%, V: 75%, Cr: 17%, Mn: 72%, Fe: 106%, Ga: 88%, Sn: 76%
  With NH<sub>4</sub>F solution: Al: 2%, Ti: 0.6%, V: 15%, Cr: 1%, Mn: 0.5%, Fe: 0.2%, Ga: 15%, Sn: 0.2%

The recoveries of Ni, Cu, Zn, Cd, and Pb were consistently high, more than 96%, both with and without NH<sub>4</sub>F
solution.



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# 18 **3.2. Anion exchange**

19 After chelate extraction, Ni, Cu, Zn, Cd, and Pb were separated. To determine the recoveries of the 20 Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Mo, Cd, Sn, Ba, Pb, and Bi in the Ni, Cu, Zn, Cd, 21 and Pb fractions, 0.2 mL of sample AE (Supplementary Table S1) was processed by anion exchange (Fig. 2). 22 Ni, Cu, Zn, Cd, and Pb were successfully separated. Na, Mg, Al, Ca, Ti, V, Cr, Zr, and Ba were eluted in the Ni 23 fraction, Mn was eluted in the Pb fraction, Fe, Co, Ga, and Mo were eluted in the Cu fraction, and Mo and Sn 24 were eluted in the Zn fraction. Because NOBIAS PA1 chelate extraction effectively removes these elements, or 25 they naturally occur in low abundance in sediments, atmospheric particles, and plankton samples, their contents 26 in the final fraction of Ni, Cu, Zn, Cd, or Pb is low.



Fig. 2 Recoveries of 21 elements in anion exchange (n = 3). The sample AE was processed with the anion exchange procedure. The elemental composition of sample AE is shown in Table S1. The error bars represent 2-standard deviations.

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#### 3.3. Procedure blank

To determine the procedure blanks, digestion and solid-phase chelate extraction were performed without a particulate sample (Table 2). For anion exchange, which involves the subsequent digestion of organic matter, 0.2 mL of 9 M CH<sub>3</sub>COOH–3 M HCl was used as a sample (Table 2). The total procedure blanks for Ni, Cu, Zn, Cd, and Pb were less than 0.03%, 0.02%, 0.02%, 0.07%, and 0.9% of the concentrations in the samples analyzed in this study, respectively.

Ni Cu Zn Cd Pb п Sample digestion and chelate extraction  $0.4 \pm 0.1$  $0.5 \pm 0.2$  $2.6 \pm 0.7$  $0.03 \pm 0.03$  $1.9 \pm 0.6$ 6  $0.01 \pm 0.03$ Anion exchange 6  $0.2\ \pm\ 0.1$  $0.6\,\pm\,0.3$  $1 \pm 2$  $0.02 \pm 0.04$  $0.6 \pm 0.2$  $1.0 \pm 0.3$  $4 \pm 2$  $0.05 \pm 0.04$  $1.9\,\pm\,0.6$ Total

Table 2 Procedure blanks (pmol, mean  $\pm$  standard deviation)

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#### 3.4. Interferences of coexisting elements in the isotopic measurements of Ni, Cu, Zn, Cd, and Pb

The reference materials, PACS-3 marine sediment, NIES-28 urban atmospheric particles, and BCR-414 plankton, were subjected to the solid-phase chelate extraction and anion exchange procedures, and the concentrations of 21 elements were determined in the Ni, Cu, Zn, Cd, and Pb fractions (Tables S2–4).

In the Ni isotopic measurement, Ca, Ti, and Fe cause spectral interference, as described in Part 1. In the Ni fractions that were separated from PACS-3, NIES-28, and BCR-414, the maximum Ca/Ni and Ti/Ni molar ratios were 0.03 and 0.2, respectively. These ratios are lower than the levels at which significant interference occurs, as discussed in Part 1. The Fe/Ni molar ratio in the Ni fraction was 0.003. Considering the natural abundance of  ${}^{58}$ Fe (0.28%) and  ${}^{58}$ Ni (68%), the contribution of  ${}^{58}$ Fe to the  ${}^{58}$ Ni signal intensity is only 0.01‰, and the  ${}^{58}$ Fe isobaric interference can be appropriately corrected, as described in Part 1.

3 Isotopic measurements of Cu are susceptible to interference from Na, Mg, Cr, Mn, Ti, and Ba. 4 However, in the Cu fractions separated from PACS-3, NIES-28, and BCR-414, the maximum molar ratios to 5 Cu were 0.1 for Na, 0.01 for Mg, 0.002 for Cr, and 0.0004 for Mn, and Ti and Ba were not detected (Tables S2-6 4). These ratios were found to be lower than the levels at which significant interference occurs, ensuring reliable 7 isotopic measurements of Cu.9 Unlike the anion exchange procedure described in Part 1, Cu was eluted with 0.5 8 M HCl to save regents and time. Therefore, Fe, Ga, and Mo were also eluted with Cu. However, no Fe or Mo 9 molecular ions cause spectral interference on Cu and Ga isotopes. The original contents of Ga in phytoplankton, 10 sediments, and atmospheric aerosols are low, and >80% of Ga was removed by the rinse with NH<sub>4</sub>F solution 11 during chelate extraction. The Ga contents in the Cu fractions from BCR-414, PACS-3, and NIES-28 were less 12 than 1% of the Ga that was added to the Cu fractions for the external correction of isotopic fractionation in the isotopic measurements. For samples with high Ga contents (e.g., coal),<sup>12</sup> the anion exchange procedure in Part 13 14 1 should be applied.

Isotopic measurements of Zn are subject to interferences of Mg, Al, Ca, Ti, V, Cr, and Ba. Tables S2–
4 show that Mg, Ca, Ti, V, and Ba were not detected in the Zn fractions. Additionally, the contents of Al and Cr
were less than 0.1% of Zn and well below the levels that could cause interference.<sup>9</sup>

- 18 Isotopic Cd measurements are subject to Zr, Mo, and Sn interferences. In the Cd fractions, Zr and Mo 19 were present at levels less than 0.7% and 13%, respectively (Tables S2-4). The interference of MoO for 20  $\delta^{114/110}$ Cd was found to be negligible, with only a minor effect of  $-0.07 \pm 0.08\%$  (mean  $\pm$  standard deviation, SD, n = 8) observed in measurements of a sample containing 2.3 times more Mo than Cd (Part 1). The Zr content 21 22 in the Cd fraction was found to be low compared to the Mo content, with Zr levels up to 0.7% of Cd, indicating 23 that interferences of ZrO were also negligible. Additionally, the Sn content in the Cd fraction was up to 0.7% of Cd, and the isobaric interferences of <sup>112</sup>Sn and <sup>114</sup>Sn were only 0.3‰ of <sup>112</sup>Cd and 0.2‰ of <sup>114</sup>Cd, respectively, 24 both of which were appropriately corrected by the isobaric correction (Part 1). Furthermore, the isobaric 25 interference of <sup>204</sup>Hg was found to be less than 0.001% of <sup>204</sup>Pb, confirming that this interference was also 26 27 negligible in the isotopic measurements of Pb.
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# 29 **3.5. Accuracy and precision**

30 PACS-3 (23 mg) was digested and divided equally into ten aliquots, and four out of ten samples were doped with 1.5 nmol of Ni (Wako Ni,  $\delta^{60/58}$ Ni = -0.28‰), 11 nmol of Cu (Wako Cu,  $\delta^{65/63}$ Cu = +0.28‰), <sup>6</sup> 12 31 nmol of Zn (NIST-682,  $\delta^{66/64}$ Zn = -2.45‰),<sup>13</sup> 0.043 nmol of Cd (BAM-I012 Cd,  $\delta^{114/110}$ Cd = -1.33‰),<sup>14</sup> and 32 33 1.9 nmol of Pb (NMIJ-3681 Pb, <sup>206</sup>Pb/<sup>204</sup>Pb = 18.0900, <sup>208</sup>Pb/<sup>207</sup>Pb = 2.43577, and <sup>206</sup>Pb/<sup>204</sup>Pb = 1.15756, 34 https://unit.aist.go.jp/mcml/rg-inorg/rm.html). Then, the ten samples were individually processed using chelate 35 extraction and anion exchange to determine the concentrations and isotope ratios of Ni, Cu, Zn, Cd, and Pb (Table 3). The recoveries of Ni, Cu, Zn, Cd, and Pb ranged from 97% to 105%. The 2-SDs of  $\delta^{60/58}$ Ni,  $\delta^{65/63}$ Cu, 36  $\delta^{66/64}$ Zn, and  $\delta^{114/110}$ Cd in PACS-3 were all less than 0.05. The 2-SDs of  ${}^{206}$ Pb/ ${}^{204}$ Pb,  ${}^{208}$ Pb/ ${}^{207}$ Pb, and  ${}^{206}$ Pb/ ${}^{207}$ Pb 37 38 were 0.06–0.16‰. This precision is sufficient to detect variations of a few permille in isotopic values for Ni,

1 Cu, Zn, and Cd, as well as several percent for Pb in the environment. The isotope ratios were plotted against the 2 reciprocal concentrations for each element (Fig. 3). Notably, the isotope ratios of the added standard materials 3 fell within the 95% prediction range at the intercept, providing evidence of minimal systematic errors in the 4 analysis.



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6 The concentrations and isotope ratios of Ni, Cu, Zn, Cd, and Pb in reference materials of marine 7 sediments (PACS-3), atmospheric particles (NIES-28), and river plankton (BCR-414) were determined and are 8 presented in Tables 4 and 5. NIES-28 and BCR-414 were digested, divided into five aliquots, and analyzed 9 individually. The concentrations of Ni, Cu, Zn, Cd, and Pb in the reference materials were within 11% of the 10 certified or consensus values. The isotope ratios determined using this method were compared with those reported in previous studies. For BCR-414,  $\delta^{60/58}$ Ni,  $\delta^{65/63}$ Cu, and  $\delta^{66/64}$ Zn in this study were consistent with 11 those reported by Takano et al.,<sup>15</sup> Jeong et al.,<sup>16</sup> Yang et al.,<sup>17</sup> and Druce et al.<sup>18</sup> within 0.1‰. For PACS-3, 12  $\delta^{65/63}$ Cu and  $\delta^{66/64}$ Zn were consistent with those reported by Jeong et al.<sup>16</sup> within 0.1‰, and <sup>206</sup>Pb/<sup>207</sup>Pb was 13 consistent with that reported by Jeong et al.<sup>16</sup> within 2‰. For NIES-28,  $\delta^{66/64}$ Zn was the same as that reported 14 by Liao et al.,<sup>19</sup> and the isotope ratios of Pb were consistent with those reported by Yamakawa et al.<sup>20</sup> within 15 16 2‰.

Table 3 Concentrations and isotope ratios of Ni, Cu, Zn, Cd, and Pb in PACS-3

	Ni				Cu		Zn		
	Concentraion	Recovery% <sup>a</sup>	$\delta^{60/58} Ni^a$	Concentraion	Recovery% <sup>a</sup>	$\delta^{65/63}Cu^a$	Concentraion	Recovery% <sup>a</sup>	$\delta^{66/64}Zn^a$
PACS ( <i>n</i> =6)	1000000000000000000000000000000000000		$0.26 \pm 0.02$	$5.0 \pm 0.1$		0.03 ± 0.03	$5.45 \pm 0.2$		0.20 ± 0.01
doped PACS (n=4)	$1.3367\ \pm\ 0.040$	$107\pm3$	$-0.01 \pm 0.01$	$10.4\pm0.3$	$101\pm5$	$0.18\pm0.04$	$11.1\pm0.3$	$98\pm 6$	$\textbf{-1.13}\pm0.02$

		Cd		РЬ					
	Concentraion mmol/g <sup>b</sup>	Recovery% <sup>a</sup>	$\delta^{114/110}Cd^a$	Concentraion mmol/g <sup>b</sup>	Recovery% <sup>a</sup>	<sup>206</sup> Pb/ <sup>204</sup> Pb <sup>a</sup>	<sup>208</sup> Pb/ <sup>207</sup> Pb <sup>a</sup>	<sup>206</sup> Pb/ <sup>207</sup> Pb <sup>a</sup>	
PACS $(n=6)$	$0.019\ \pm\ 0.001$		$\textbf{-0.17} \pm 0.05$	$0.80\pm0.02$		$17.701 \pm 0.002$	$2.4102 \pm 0.0001$	$1.1355 \pm 0.0002$	
doped PACS (n=4)	$0.038\ \pm\ 0.001$	$103\pm5$	$\textbf{-0.7} \pm \textbf{0.1}$	$1.74\pm0.05$	$99 \pm 4$	$17.908 \pm 0.001$	$2.4240 \pm 0.0001$	$1.14720 \pm 0.00003$	

<sup>a</sup>Mean  $\pm$  2-standard deviation from repeated analyses

<sup>b</sup> The uncertainty is assumed to be 3% of the mean concentration, which corresponds to uncertainties of pipetting and weighing. The 2-standard deviation of concentrations determined from repeated analyses is smaller than 3%.

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Table 4 Concentrations for geochemical reference materials

		Ni	Cu	Zn	Cd	Pb		
BCR-414 (river plankton)	This study, $n = 5^{a}$	$0.319\pm0.010$	$0.427\pm0.003$	$1.61\pm0.05$	$0.00318 \pm 0.00010$	$0.0198 \pm 0.0023$		
unit: µmol/g	Certified values <sup>b</sup>	$0.320\pm0.028$	$0.464\pm0.041$	$1.71\pm0.08$	$0.00341 \pm 0.00025$	$0.0192 \pm 0.0018$		
PACS-3 (marine sediment) unit: µmol/g	This study, $n = 6^{a}$	$0.713\pm0.021$	$5.01 \pm 0.12$	$5.78 \pm 0.01$	$0.0197 \pm 0.0006$	$\textbf{0.805} \pm \textbf{0.019}$		
	Certified values <sup>b</sup>	$0.673\pm0.037$	$5.13 \pm 0.16$	$5.75\pm0.18$	$0.0198 \pm 0.0014$	$0.907\pm0.036$		
NIES-28 (atmospheric particle unit: µmol/g	This study, $n = 5^{a}$	$1.09\pm0.03$	$1.65\pm0.14$	$17.3\pm0.5$	$0.0464 \pm 0.0014$	$1.77\pm0.12$		
	Certified values <sup>b</sup>	$1.09\pm0.06$	$1.64\pm0.19$	$17.4\pm1.5$	$0.0498 \pm 0.0038$	$1.94\pm0.15$		

<sup>a</sup> The n indicates the number of fractions divided from one digested reference material. The fractions were individually processed by NOBIAS PA1 chelate extraction and AG MP-1M anion exchange for measurements. The uncertainty is assumed to be 3% of the mean concentration, which

corresponds to uncertainties of pipetting and weighing., <sup>b</sup> The uncertainty is the 95% confidence interval.

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	Data source	$\delta^{60/58}$ Ni	$\delta^{65/63}Cu$	$\delta^{66/64}$ Zn	$\delta^{114/110}Cd$	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>207</sup> Pb
BCR-414	This study, $n = 5^{b}$	$0.12\pm0.04$	$-0.30 \pm 0.05$	$0.30\pm0.02$	$0.26\pm0.05$	$18.382 \pm 0.003$	$2.4544 \pm 0.0003$	$1.1730 \pm 0.0002$
	Takano et al.(2020), <i>n</i> =5	$0.11\pm0.06$	$-0.27 \pm 0.05$	$0.31\pm0.03$				
	Druce et al.(2020), n=14			$0.32\pm0.03$				
	Jeong et al.(2021), <i>n</i> =4		$-0.19\pm0.04$	$0.29\pm0.04$				
	Yang et al.(2020), <i>n</i> =3	$0.07\pm0.06$	$-0.3 \pm 0.1$					
PACS-3	This study, $n = 6^{b}$	$0.26\pm0.02$	$0.03\pm0.03$	$0.20\pm0.01$	$-0.17 \pm 0.05$	$17.701 \pm 0.002$	$2.4102 \pm 0.0001$	$1.1355 \pm 0.0002$
	Jeong et al.(2021), <i>n</i> =4		$0.13\pm0.04$	$0.17\pm0.08$				$1.134{\pm}\ 0.002$
	Sullivan et al.(2020), <i>n</i> =15		$-0.10 \pm 0.09$					
NIES-28	This study, $n = 5^{b}$	$0.18\pm0.03$	$0.07\pm0.03$	$0.06\pm0.02$	$-0.101 \pm 0.06$	$17.890 \pm 0.001$	$2.4422 \pm 0.0002$	$1.1474 \pm 0.0001$
	Liao et al.(2021), <i>n</i> =3			$0.06\pm0.07$				
	Yamakawa et al.(2021), <i>n</i> =3					$17.859 \pm 0.008$	$2.4411 \pm 0.0003$	$1.1472 \pm 0.0002$

Table 5 Isotope ratios for geochemical reference materials (mean  $\pm$  2-standard deviation)<sup>a</sup>

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<sup>a</sup>  $\delta^{60/58}$ Ni,  $\delta^{65/63}$ Cu,  $\delta^{66/64}$ Zn, and  $\delta^{114/110}$ Cd are relative to NIST-986 Ni (National Institute of Standards and Technology), NIST-976 Cu (National Institute of Standards and Technology), JMC-Lyon Zn, <sup>14</sup> NIST-3108 Cd (National Institute of Standards and Technology), respectively. <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>207</sup>Pb, and <sup>206</sup>Pb/<sup>207</sup>Pb are based on the certified values of NMIJ-3681 Pb (National Institute of Advanced Industrial Science and Technology)., <sup>b</sup> The *n* indicates the number of fractions divided from one digested reference material. The fractions were individually

processed by NOBIAS PA1 chelate extraction and AG MP-1M anion exchange for measurements.

#### 1 4. Conclusions

2 In this study, we developed a novel method for analyzing the isotopic ratios of Ni, Cu, Zn, Cd, and Pb 3 in sediments, atmospheric particles, and plankton samples based on the method for seawater presented in Part 1. Prior to conducting isotopic measurements using MC-ICP-MS, we separated Ni, Cu, Zn, Cd, and Pb in the 4 5 samples using NOBIAS PA1 chelate extraction and AG MP-1M anion exchange. NOBIAS PA1 chelate 6 extraction using NH<sub>4</sub>F solution effectively separated Ni, Cu, Zn, Cd, and Pb from Al, Ti, V, Cr, Mn, Fe, Ga, Zr, 7 and Sn. AG MP-1M anion exchange effectively separated Ni, Cu, Zn, Cd, and Pb. The accuracy and precision 8 of the developed method are sufficient to measure isotopic ratio variations of Ni, Cu, Zn, Cd, and Pb in solid 9 earth, atmospheric, and microorganism samples. Using this method, the concentrations and isotopic ratios of Ni, 10 Cu, Zn, Cd, and Pb in reference materials of marine sediments (PACS-3), atmospheric particulates (NIES-28), 11 and river plankton (BCR-414) were elucidated. This method has the following advantages over conventional 12 methods: 1) simultaneous analysis of isotope ratios of multiple elements from a single sample in only two 13 chemical separation steps, allowing for high-throughput analysis; 2) clean and excellent chemical separation 14 providing highly precise data; and 3) high applicability to a wide range of samples including marine sediments, 15 plankton, and atmospheric particles.

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Supporting Information: Compositions of samples for recovery tests and concentrations of 21 elements in
 reference materials after chemical separation

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