

1           **Improvements in Cd stable isotope analysis achieved through use of liquid-liquid**  
2           **extraction to remove organic residues from Cd separates obtained by extraction**  
3           **chromatography**

4  
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12 Main text 5045 words, 2 tables, 3 figures

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16 ***Abstract***

17           Organic compounds released from resins that are commonly employed for trace element  
18 separations are known to have a detrimental impact on the quality of isotopic analyses by  
19 MC-ICP-MS. A recent study highlighted that such effects can be particularly problematic for  
20 Cd stable isotope measurements (M. Gault-Ringold and C. H. Stirling, *J. Anal. At. Spectrom.*,  
21 2012, **27**, 449-459). In this case, the final stage of sample purification commonly applies  
22 extraction chromatography with Eichrom TRU resin, which employs particles coated with  
23 octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl  
24 phosphate (TBP). During chromatography, it appears that some of these compounds are  
25 eluted alongside Cd and cannot be removed by evaporation due to their high boiling points.

26           When aliquots of the zero- $\epsilon$  reference material were processed through the purification  
27 procedure, refluxed in concentrated HNO<sub>3</sub> and analyzed at minimum dilution (in 1 ml 0.1 M  
28 HNO<sub>3</sub>), they yielded Cd isotopic compositions ( $\epsilon^{114/110}\text{Cd} = 4.6 \pm 3.4$ , 2 SD, n = 4) that  
29 differed significantly from the expected value, despite the use of a double spike technique to  
30 correct for instrumental mass fractionation. This result was accompanied by a 35% reduction  
31 in instrumental sensitivity for Cd. With increasing dilution of the organic resin residue, both  
32 of these effects are reduced and they are insignificant when the eluted Cd is dissolved in  $\geq 3$   
33 ml 0.1 M HNO<sub>3</sub>. Our results, furthermore, indicate that the isotopic artefacts are most likely  
34 related to anomalous mass bias behavior.

35 Previous studies have shown that perchloric acid can be effective at avoiding such effects  
36 (Gault-Ringold and Stirling, 2012; K. C. Crocket, M. Lambelet, T. van de Fliertd, M.  
37 Rehkämper and L. F. Robinson, *Chem. Geol.*, 2014, **374–375**, 128-140), presumably by  
38 oxidizing the resin-derived organics, but there are numerous disadvantages to its use. Here  
39 we show that liquid-liquid extraction with n-heptane removes the organic compounds,  
40 dramatically improving quality of the Cd isotope data for samples that are analyzed at or  
41 close to minimum dilution factors. This technique is quick, simple and may be of use prior to  
42 analysis of other isotope systems where similar resins are employed.

43

## 44 **1. Introduction**

45 Recently, interest in the measurement of Cd isotopes has grown due to advances in mass  
46 spectrometry and the realization that there are resolvable isotopic differences in seawater,  
47 meteorites and other samples of geological, biological and anthropogenic origin. As natural  
48 terrestrial samples display only small isotopic differences, Cd isotopic compositions are most  
49 commonly reported using an  $\epsilon$  notation as follows:

$$50 \quad \epsilon^{114/110}Cd = \left[ \frac{\left( \frac{^{114}Cd}{^{110}Cd} \right)_{Sample}}{\left( \frac{^{114}Cd}{^{110}Cd} \right)_{Standard}} - 1 \right] \times 10^4 \quad (1)$$

51 where the standard reference material most widely adopted (and used here) is NIST SRM  
52 3108 Cd<sup>1</sup>. Isotopic compositions with  $\epsilon^{114/110}Cd$  values of between +50 and -7 (for surface  
53 seawater from off north west Africa<sup>2</sup>, and for North Pacific surface water, respectively<sup>3</sup>) have  
54 been found in the natural terrestrial environment. Even larger fractionations can be produced  
55 by processes that involve partial evaporation and condensation of Cd, and the signatures of  
56 such reactions are found in, for example, materials from industrial processes ( $\epsilon^{114/110}Cd = -17$   
57 to +5<sup>4-6</sup>) and meteorites (-80 to +160<sup>7</sup>).

58 The dominant method for the determination of Cd isotope compositions applies multiple  
59 collector inductively coupled plasma mass spectrometry (MC-ICP-MS), with instrumental  
60 mass bias correction by the double spike technique<sup>8,9</sup>. Prior to the measurements, Cd is  
61 separated from the sample matrix by a first stage of anion exchange chromatography,  
62 followed by extraction chromatography with Eichrom TRU resin for the removal of Sn<sup>8-15</sup>.

63 Various Eichrom resins, as well as similar homemade resin materials, are commonly  
64 employed for extraction chromatography in geochemical laboratories for the purification of  
65 numerous trace metals. Amongst users, it is common knowledge that the organic extraction  
66 agent (present as a coating on the resin particles) to some extent always elutes alongside the

67 analyte element. This organic material can have a detrimental impact on isotopic analyses by  
68 TIMS (thermal ionization mass spectrometry) if it hinders the ionization process<sup>16</sup>. For MC-  
69 ICP-MS, the presence of the organic residue appears to be relatively unproblematic for many  
70 analyses. In such cases, any effects caused by the organic material are presumably  
71 sufficiently small to be of no concern and this is supported by minimizing the amount of  
72 residue present, through pre-leaching the coated particles by storage in water or dilute acids  
73 and/or cleaning of the resin within the columns by acid elution directly prior to use<sup>11, 17</sup>.

74 In some cases, however, problems can occur despite such precautions. In particular,  
75 Gault-Ringold et al.<sup>13</sup> reported that the Cd isotope data for selected samples displayed a  
76 reproducibility and accuracy that was poor compared to that achievable for unprocessed  
77 standard solutions and concluded that this was caused by the organic residue that eluted  
78 alongside Cd from the TRU resin that was used in their chromatographic procedure. They  
79 furthermore suggested that this problem can be avoided if sufficiently large samples are  
80 processed on a single column. In this case, the final Cd sample solutions for isotopic analysis  
81 are diluted to a relatively large volume such that the eluted organic material is not present in  
82 concentrated form<sup>13</sup>. In practice, however, this is often not possible. The concentration of Cd  
83 in seawater can be as low as 0.1 pg/g (or 1 pmol/l), whilst other samples, such as meteorites,  
84 mineral separates or ferromanganese crusts, may only be available in small quantities<sup>18</sup>.

85 In cases where resin pre-rinsing or sample dilution is unable to circumvent the analytical  
86 problems that can be caused by organic resin residues, the material must be separated from  
87 the target element *after* extraction chromatography. To improve the quality of Cd and Nd  
88 isotope analyses following use of Eichrom resins, it was suggested that the organic material is  
89 best removed by oxidation of the residue with reagents such as HNO<sub>3</sub>, HNO<sub>3</sub> with added  
90 H<sub>2</sub>O<sub>2</sub>, or HClO<sub>4</sub><sup>13, 19, 20</sup>. Of these, HClO<sub>4</sub> was found to be the most effective oxidant<sup>13, 20</sup>, but  
91 there are many disadvantages to its use, such as various safety considerations, a high boiling  
92 temperature, and the availability of sufficiently pure supplies. Oxidation with HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>,  
93 can also be successful but is more time consuming (24 hours)<sup>13</sup>. In the current study, we have  
94 developed an improved alternative method for the removal of organic resin residues from Cd  
95 sample solutions for subsequent isotopic analysis by MC-ICP-MS. The procedure avoids use  
96 of oxidising agents entirely, as the organic compounds are separated by liquid-liquid  
97 extraction with heptane, and may be applicable for improving the sample preparation  
98 procedures of other elements prior to isotopic measurements.

99

## 100 **2. Method**

## 101 *2.1 Materials and reagents*

102 All sample preparation work was carried out in class 10 (ISO 4) laminar flow hoods in  
103 the class 1000 (ISO 6) MAGIC clean room laboratory at the Department of Earth Science and  
104 Engineering, Imperial College London. Some acids were purified by subboiling distillation in  
105 either Teflon (12 M HCl) or quartz (6 M HCl, 16 M HNO<sub>3</sub>) stills, whilst Optima grade 9 M  
106 HBr was purchased from Fisher Scientific. The HBr-HNO<sub>3</sub> mixtures were prepared on the  
107 day of use and all water was of 18.2 MΩ quality from a Milli-Q Academic dispensing system.  
108 The <sup>111</sup>Cd-<sup>113</sup>Cd double spike, with <sup>113</sup>Cd/<sup>111</sup>Cd = 0.5829, in 2 M HCl was prepared from  
109 solutions of enriched single isotopes purchased from Oak Ridge National Laboratory (USA)  
110 and characterized by MC-ICP-MS using external normalization relative to admixed Ag<sup>8</sup>.

111 Heptane was pre-cleaned by carrying out a liquid-liquid extraction with 6 M HCl.  
112 Specifically, approximately 40 ml of Alfa Aesar 99% n-heptane was shaken by hand for 30  
113 seconds with approximately 20 ml 6 M HCl in a 90 ml Savillex beaker and then left to stand  
114 for approximately 3 minutes. Once phase separation had been verified, the beaker was shaken  
115 again and allowed to stand for a further three minutes. The heptane was then transferred to a  
116 clean 90 ml Savillex beaker, being careful not to take up any of the underlying acid. This  
117 process was repeated twice for further purification.

118

## 119 *2.2 Samples*

120 Two different samples were used. The first, a pure solution of NIST SRM 3108 Cd  
121 (hereafter also referred to as NIST Cd), was employed so that complications arising from  
122 matrix effects due to the presence of other elements were avoided. Direct comparison  
123 between processed samples and unprocessed NIST Cd was enabled by using NIST Cd as the  
124  $\epsilon^{114/110}\text{Cd} = 0$  reference material to bracket the sample analyses. A second sample, the  
125 powdered ferromanganese nodule reference material Nod-A-1 from the USGS, was chosen as  
126 a natural material that is readily available. The Cd isotope composition of this material has  
127 been characterized previously as  $\epsilon^{114/110}\text{Cd} = 2.3 \pm 0.6$  (2SE,  $n = 2^{11}$ ) and  $\epsilon^{114/110}\text{Cd} = 1.3 \pm$   
128  $0.2$  (2SE,  $n = 2^{21}$ ), possibly reflecting minor sample heterogeneity.

129

## 130 *2.3 Sample preparation*

131 Aliquots of Nod-A-1 were digested and purified following the procedure described by  
132 Horner et al.<sup>11</sup>. In brief, this involved digestion of the sample powder with 6 M HCl, addition  
133 of double spike to obtain an optimum ratio of spike Cd/natural Cd of S/N  $\approx 1^9$ , anion  
134 exchange chromatography with 200  $\mu\text{l}$  Bio-Rad AG1-X8 resin (200-400 mesh size; for

135 separation of Cd from the matrix) and then extraction chromatography with 200  $\mu$ l Eichrom  
136 TRU resin (100-150 mesh size; primarily to remove any remaining Sn). The Eichrom TRU  
137 resin was pre-cleaned by shaking with 18.2 M $\Omega$  water and removing the foam that was  
138 produced. This was repeated 5-10 times (until no more foam appeared) and then stored in  
139 18.2 M $\Omega$  water. Once settled in the columns the resin was cleaned with 9 ml 6M HCl<sup>11</sup>. As  
140 the NIST Cd solution is sufficiently pure to make the first stage of column chemistry  
141 redundant, samples using this solution were only processed through the second stage of the  
142 separation procedure before any attempts were made to remove the organic resin residue.

143

#### 144 *2.4 Organic resin residue removal*

145 At this point, the samples were further treated using one of four different protocols and  
146 therefore we differentiate between *untreated*, *refluxed*, and *extracted* samples, and samples  
147 that were both *extracted and refluxed* or *refluxed and extracted* (note the different order).  
148 Unless otherwise specified, each individual sample processed separately through the column  
149 chemistry contained approximately 30 ng of natural Cd plus 30 ng Cd from the double spike  
150 for a total of 60 ng Cd. Following the treatments described in Table 1, most samples were  
151 dissolved in 1 ml 0.1 M HNO<sub>3</sub> to produce a 60 ng/ml solution for analysis by MC-ICP-MS.  
152 This approach highlights the problem caused by organic compounds eluted from the TRU  
153 resin, as it simulates the scenario where the Cd content of a sample suffices only for a single  
154 analysis (a ‘one shot’ sample), so that dilution of the organics is not possible.

155

#### 156 *2.5 Mass spectrometry*

157 All samples were analyzed on a Nu Plasma HR MC-ICP-MS (Nu Instruments Ltd,  
158 Wrexam, UK) at the MAGIC Laboratories. For sample introduction, either an Aridus I or  
159 Aridus II desolvating nebulizer system was used, fitted with a PFA nebulizer (CETAC  
160 Technologies) operating at a solution flow rate of about 120  $\mu$ l/min. The data acquisition  
161 procedures were similar to those outlined by Xue et al.<sup>9</sup>.

162 Solutions of spiked NIST Cd with S/N  $\approx$  1 and Cd concentrations similar to those of  
163 samples were repeatedly analyzed as bracketing standards throughout each measurement  
164 session, with between three and eight standards run between each sample. This allowed the  
165 stability of the instrument to be monitored, and any change in mass bias to be observed. Each  
166 analysis typically consumed about 30 ng natural Cd and 30 ng spike Cd, and a sensitivity of  
167 between 200 and 300 V/( $\mu$ g/ml) was normally achieved during the course of the study. All  
168 runs were bracketed by approximately four minutes of rinsing with 0.1 M HNO<sub>3</sub>.

169 The  $\varepsilon^{114/110}\text{Cd}$  values of the samples were determined offline, by using the online  
 170 collected raw ion beam intensities and electronic baselines as input to an Excel spreadsheet.  
 171 The spreadsheet applies previously outlined iterative methods to correct the measured  
 172  $^{112}\text{Cd}/^{111}\text{Cd}$ ,  $^{113}\text{Cd}/^{111}\text{Cd}$ , and  $^{114}\text{Cd}/^{111}\text{Cd}$  isotope ratios for isobaric interferences and solve  
 173 the double spike equations<sup>8,9,22</sup>. The general power law is applied using a mass dependence  
 174 of  $n = -0.1$  to correct for instrumental mass fractionation<sup>23</sup>.

175 Calculations analogous to Equation (1) were performed to obtain the  $\varepsilon^{114/113}\text{Cd}$  values of  
 176 samples, relative to the results that were obtained for bracketing analyses of spiked solutions  
 177 of NIST SRM 3108 Cd. In the majority of cases, the three or four analyses of the standard  
 178 solution on either side of the sample were chosen. On occasions where the instrument was  
 179 particularly stable, many more (up to 68) analyses of the standard solution were included.

180 Finally, the  $\varepsilon^{114/113}\text{Cd}$  data were translated into  $\varepsilon^{114/110}\text{Cd}$  using the relationship

$$181 \quad \varepsilon^{114/110}\text{Cd} = \left( \left( \frac{\varepsilon^{114/113}\text{Cd}}{10000} + 1 \right)^\beta - 1 \right) \times 10000 \quad (2)$$

182 The exponent,  $\beta$ , was determined assuming the kinetic law

$$183 \quad \beta = \frac{\ln\left(\frac{m_{114}}{m_{110}}\right)}{\ln\left(\frac{m_{114}}{m_{113}}\right)} \quad (3)$$

184 where  $m_i$  is the atomic mass of isotope  $i$ .

185 Samples were excluded from the data set where either the internal (within-run) 2SE or  
 186 the external (bracketing standards) 2SD uncertainties exceeded  $\pm 1 \varepsilon^{114/110}\text{Cd}$ , except for  
 187 occasional cases where the internal 2SE (typically better than  $\pm 0.8 \varepsilon$ ) was not unusually high  
 188 for the measurement session. As unstable instrument behavior is problematic, Table 2 also  
 189 highlights the number of sample measurements that were discarded relative to the total  
 190 number of attempted analyses for the different sample treatments that were investigated. Such  
 191 data selection was necessary to enable a reasonable evaluation of the results, as is further  
 192 explained in the discussion below. The complete data set, including all discarded  
 193 measurements, is provided in the Supplementary Information.

194 Changes in the instrumental mass bias of Cd during measurements sessions were  
 195 determined by monitoring changes in the  $^{111}\text{Cd}/^{114}\text{Cd}$  ratio of the spike–sample mixtures and  
 196 quantified in terms of the fractionation coefficient (sometimes also called beta factor, mass  
 197 bias factor or fractionation factor),  $f_{Kin}$  which is applied in the exponential mass fractionation  
 198 law:

$$199 \quad f_{Kin} = \frac{\ln(R/r)}{\ln(m_2/m_1)} = \frac{\ln(R_{111/114}/r_{111/114})}{\ln(m_{111}/m_{114})} \quad (4)$$

200 where  $R$  is the unbiased or ‘assumed true’ isotope ratio corrected for instrumental mass bias,  
201  $r$  is the same isotope ratio but fractionated relative to the true value due to instrumental mass  
202 bias, and  $m_i$  is the atomic mass of isotope  $i$ <sup>23</sup>.

203 Typical procedural blanks contained <20 pg Cd. As the blank constitutes just 0.03% or  
204 less of the total Cd in a sample, no blank corrections were applied to the isotope compositions.  
205 Repeat measurements of the secondary Cd isotope standard BAM-I012 gave  $\epsilon^{114/110}\text{Cd} = -$   
206  $13.2 \pm 0.7$  (2 SD,  $n = 15$ ), which is in excellent agreement with the consensus literature value  
207 of  $-13.3 \pm 0.4$ <sup>1</sup>.

208 In the following discussion, the quoted uncertainties for mean values refer to twice the  
209 standard deviation (2SD) of the individual sample results included in this average. The  
210 uncertainty of individual results refers to twice the standard deviation (2SD) obtained for  
211 bracketing runs of the NIST Cd standard.

212

### 213 **3. Results and discussion**

#### 214 *3.1 Isotope ratios and sensitivity*

##### 215 3.1.1 Untreated samples

216 For all untreated samples, a drop of transparent residue of about 2.5 mm remained after  
217 drying down the collected column elution. The analyses of such samples were associated  
218 with variable mass bias behavior and variable results. This is one of the features of handling  
219 samples in this manner and is an indicator that something is disturbing the behavior of the  
220 machine.

221 Analyses of NIST Cd samples all gave the correct isotope composition and a good  
222 overall reproducibility ( $\epsilon^{114/110}\text{Cd} = -0.1 \pm 0.8$ ,  $n = 6$ ; Table 2). There was also no disruption  
223 to the isotope composition of following standards, but the observation of sudden shifts in  $f_{kin}$   
224 of up to 0.07 (Fig. 1) suggests that there are mass bias changes between samples and  
225 subsequent standard analyses.

226 The results for the Nod-A-1 samples also provide a mean that is in accord with reference  
227 data (Table 2) but the overall precision is unsatisfactory ( $\epsilon^{114/110}\text{Cd} = 2.5 \pm 3.4$ ,  $n = 2$ ).

228 Further details of these analyses can be found in the Supplementary Information.

229

##### 230 3.1.2 Refluxed samples

231 Samples that were refluxed in concentrated  $\text{HNO}_3$  following extraction chromatography  
232 displayed isotope compositions that were heavier and more variable than expected. In  
233 particular, the NIST Cd samples provide a mean  $\epsilon^{114/110}\text{Cd}$  of  $+4.6 \pm 3.4$  (Table 2), which

234 deviates significantly from the expected value (of  $\epsilon^{114/110}\text{Cd} = 0$ ) and that shows a very poor  
235 reproducibility. Similarly, the two refluxed Nod-A-1 samples also reproduce poorly with  
236  $\epsilon^{114/110}\text{Cd}$  values of  $+6.4 \pm 0.6$  and  $+2.2 \pm 0.7$ . Clearly, this method of breaking down the  
237 organic resin residue is ineffective, and may in fact amplify the problem.

238 We also observed that many runs of refluxed NIST Cd clearly disturbed the instrumental  
239 running conditions, so that subsequent measurements of the bracketing NIST Cd standard  
240 yielded isotope compositions that were substantially offset from the runs immediately  
241 preceding the sample analysis. Such effects are most likely due to the presence of organic  
242 resin residue in the refluxed NIST Cd samples. In detail, the isotopic offset between the  
243 bracketing standard measurements was large enough, such that they displayed 2SD precisions  
244 exceeding  $\pm 1 \epsilon$  for about 50% of the refluxed NIST Cd samples (Table 2). In these cases, it  
245 was not possible to robustly calculate the  $\epsilon^{114/110}\text{Cd}$  values of the samples relative to the  
246 bracketing standards, and these measurements were, therefore, not included in calculation of  
247 the mean given in Table 2. The rationale for this approach is that such analyses would also be  
248 recognized as problematic and discarded when ‘unknowns’ are analyzed.

249 Accompanying these unexpected Cd isotope compositions, we also observed that the  
250 fractionation coefficient  $f_{kin}$  for the refluxed NIST Cd samples frequently (for 5 out of 8  
251 sample analyses) differed substantially from the bracketing standards (Fig. 1). This was also  
252 the case for the refluxed sample of Nod-A-1 shown in Fig. 2, indicating that the mass bias  
253 behavior is different for refluxed samples and pure, unprocessed NIST Cd solutions.

254 The analyses of refluxed samples also revealed that erroneous Cd isotope compositions  
255 were consistently accompanied by a reduced instrumental sensitivity for Cd (Fig. 3).  
256 Refluxed NIST Cd samples with a total Cd content of 60 ng, had been processed by  
257 extraction chromatography (Table 2), refluxing with 16 M  $\text{HNO}_3$  and dilution with 0.1 M  
258  $\text{HNO}_3$  to a Cd concentration of about 60 ng/ml. Such samples produced an instrumental  
259 sensitivity for Cd that was up to almost 40% lower, compared to the Cd sensitivity recorded  
260 by the unprocessed bracketing standards (Fig. 3). When larger Cd samples were refluxed and  
261 diluted to larger volumes, thereby producing more favourable (larger) ratios of Cd to organic  
262 residue, the sensitivity improved and the measured isotope compositions were closer to the  
263 expected value of  $\epsilon^{114/110}\text{Cd} = 0$ . Results that were unbiased by the presence of organic resin  
264 residue were achieved when samples with at least 180 ng total Cd were processed and diluted  
265 to a Cd concentration of 60 ng/ml using at least 3 ml 0.1 M  $\text{HNO}_3$  (i.e. a dilution factor of  
266 three; Fig. 3).

267

### 268 3.1.3 Extracted samples

269 After drying down the Cd fraction following column chemistry and extraction, the  
270 remaining residue, typically a nearly transparent drop with a diameter of ~0.5 mm, was  
271 noticeably smaller compared to that left by untreated samples (where the diameter of the drop  
272 was about 2.5 mm). Furthermore, all analyses of extracted samples showed the expected  
273 isotope compositions within uncertainty and replicate measurements displayed excellent  
274 reproducibility. Analyses of extracted NIST Cd yielded a mean  $\epsilon^{114/110}\text{Cd} = 0.0 \pm 0.5$  (Table  
275 2), whereby the reproducibility is essentially identical to that achieved for multiple  
276 measurements of the untreated BAM I012 Cd reference material (Table 2) and replicate  
277 analyses of unprocessed NIST Cd standards within a single measurement session. The  
278 measurements of extracted Nod-A-1 samples were of similar quality, again yielding a precise  
279 mean of  $\epsilon^{114/110}\text{Cd} = 1.7 \pm 0.5$ , which is identical to reference results (Table 2). It is also  
280 encouraging that the fractionation coefficient  $f_{Kin}$  observed for analyses of extracted samples  
281 is substantially closer to that of bracketing standard measurements in comparison to untreated  
282 or refluxed samples (Figs. 1 and 2). This implies that extracted samples typically ‘behave’ in  
283 the mass spectrometer in a nearly identical fashion to completely unprocessed pure Cd  
284 standard solutions. Furthermore, none of the six extracted Nod-A-1 samples and just two of  
285 the eight extracted NIST Cd analyses were excluded from the calculations due to  
286 unfavourable internal or external uncertainties. The poor repeatabilities recorded by the two  
287 NIST Cd measurements most likely reflect disturbances in the mass bias behavior from  
288 previous analyses of untreated and refluxed samples that were carried out in the same  
289 measurement session (see Supplementary Information).

290 The total blank for the procedure including the extraction was only about 10 pg Cd, and  
291 as this was less than 0.02% of the total Cd for most samples, no correction was applied to  
292  $\epsilon^{114/110}\text{Cd}$  data. The low blank was not unexpected given that cleaned n-heptane was found to  
293 have undetectable levels of Cd.

294 Our results, therefore, indicate that the extraction method can provide near complete  
295 removal of the organic material from the aqueous phase. Our method is, furthermore, easy to  
296 implement, as no unusual reagents or instrumentation is required, and was found to be  
297 reliable on a routine basis. In addition, it is quick in its use, as a batch of 10 samples can be  
298 readily extracted in about 30 minutes.

299

### 300 3.1.4 Extracted and refluxed samples

301 The results for Cd samples that were extracted and then refluxed showed the expected  
302 isotope composition and good reproducibility (Table 2), both for NIST Cd (mean  $\epsilon^{114/110}\text{Cd} =$   
303  $0.0 \pm 0.7$ ,  $n = 9$ , one excluded analysis) and for two aliquots of Nod-A-1 ( $\epsilon^{114/110}\text{Cd} = 2.0 \pm$   
304  $1.2$  and  $2.4 \pm 0.9$ , no excluded analyses). In addition, the  $f_{kin}$  values obtained for these  
305 samples were similar to the bracketing standards. However, no significant improvement is  
306 seen compared to carrying out the extraction procedure only, suggesting that the additional  
307 refluxing step is unnecessary.

308

### 309 3.1.5 Refluxed and extracted samples

310 Analyses of refluxed and extracted samples show isotope compositions that are  
311 isotopically heavier than expected, with mean data of  $\epsilon^{114/110}\text{Cd} = 3.0 \pm 0.8$  ( $n = 3$ ) for NIST  
312 Cd and  $\epsilon^{114/110}\text{Cd} = 3.6 \pm 1.2$  ( $n = 2$ ) for Nod-A-1 (Table 2). These poor results most likely  
313 reflect partial oxidation of the organic resin residues to secondary compounds that are more  
314 soluble in water, and which are therefore not sufficiently removed from the aqueous phase by  
315 liquid-liquid extraction.

316

### 317 3.2 Causes of poor analytical results

318 Most analyses of untreated and refluxed samples yielded inaccurate data combined with  
319 poor reproducibility. These effects are inferred to result from contamination of the Cd sample  
320 solutions by organic compounds, which are released from the Eichrom TRU resin that is used  
321 for purification. Eichrom TRU resin applies octylphenyl-N,N-di-isobutyl  
322 carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP)<sup>24</sup> as active  
323 ingredients. These long chain organic compounds have boiling points of more than  $480^\circ\text{C}$ <sup>25</sup>  
324 and hence they are not removed by evaporation from Teflon beakers, and oxidation with  
325 concentrated nitric acid is insufficient.

326 Our findings are in general accord with the study of Gault-Ringold and Stirling<sup>13</sup>. These  
327 workers found large shifts in the Cd isotope composition of bracketing standards after  
328 samples containing organic resin residue had been analysed. Gault-Ringold and Stirling<sup>13</sup>  
329 also applied Cd purification by extraction chromatography with TRU resin and the mass  
330 spectrometric methods, including double spiking, were similar to those used here. To  
331 circumvent this problem, the authors suggested that samples should be oxidized with  
332  $\text{HClO}_4/\text{HNO}_3$  or  $\text{H}_2\text{O}_2/\text{HNO}_3$  mixtures and they show that samples treated in this manner  
333 yield accurate and precise results. This method appears to be successful because the treatment  
334 with such media likely oxidizes the majority of the organic material present, possibly largely

335 to CO<sub>2</sub> and H<sub>2</sub>O. Crocket et al.<sup>20</sup>, who use Eichrom RE (CMPO dissolved in TBP but at a  
336 different ratio to that of TRU resin) and Ln resins to separate neodymium in fossil corals,  
337 found that organic compounds from the RE resin had a detrimental effect on Nd yields and  
338 that oxidation of the sample aliquot after the RE chemistry using HClO<sub>4</sub> solved the problem.  
339 However, this approach can be further improved. Oxidation of the organic residue may be  
340 incomplete in some cases, and this is difficult to monitor. At the very least, even complete  
341 oxidation of CMPO and TBP will leave behind a small residue of H<sub>3</sub>PO<sub>4</sub>, which cannot be  
342 effectively removed from Teflon beakers by evaporation due to its high boiling point of  
343 213°C.

344 Gault-Ringold and Stirling<sup>13</sup> concluded that the analytical artefacts stemming from  
345 the use of TRU resins were caused either by polyatomic interferences (e.g.,  
346 organophosphorus compounds) or anomalous mass bias behavior, such as mass independent  
347 or non-exponential mass dependent isotope fractionation. The results of modelling that was  
348 carried out to study the impact of spectral interferences show (i) that differences in  $\epsilon^{114/110}\text{Cd}$   
349 of approximately 3 to 6  $\epsilon$ -units can be produced by a 100 to 200 ppm increase in ion beam  
350 intensity at either mass 111 or 114, and (ii) that changes in Cd isotope compositions will  
351 exhibit a linear correlation with the magnitude of the interferences (see Supplementary  
352 Information). Our data therefore indicate that the observed analytical artefacts are not due to  
353 spectral interferences, because the Cd isotope compositions of refluxed NIST Cd samples do  
354 not decrease linearly with dilution factor (Fig. 3).

355 The results obtained for such refluxed samples, however, cast further light on the  
356 processes responsible for the poor analytical results. The residual organic material, when only  
357 partially oxidised, has a clear impact on the instrumental sensitivity that is achieved for Cd  
358 (Fig. 3). A simple explanation of this would be that organic material alters the behaviour of  
359 the membrane of the desolvation unit that is used for sample introduction. However, as the  
360 reduction in sensitivity is accompanied by changes in the isotopic composition, we suggest  
361 that this is not the case and that a better explanation may be that the introduction of organic  
362 residue changes the conditions within the plasma and/or the plasma interface. Given that the  
363 organic matrix material has such a significant effect on sensitivity, it is conceivable that it can  
364 also impact the mass bias behavior to a sufficient extent to produce inaccurate results, despite  
365 use of the double spike technique. Indeed, unusual mass bias conditions (as quantified by  $f_{\text{kin}}$ )  
366 are observed for about half of the bracketing NIST Cd standards that were analyzed after  
367 refluxed samples. Hence, we speculate that the poor data quality is most likely related to  
368 anomalies in the absolute mass bias and mass bias behavior that are caused by the presence of

369 organic compounds. We demonstrate this to be feasible by modelling the effects of changing  
370 the mass dependence of the instrumental mass fractionation. To this end, we use the general  
371 power law (GPL)

$$372 \quad R_A = r_A \cdot f_{GPL}^{(m_2^n - m_1^n)} \quad (5)$$

373 where  $R_A$  is the mass bias corrected or assumed true isotope ratio corrected for instrumental  
374 mass bias,  $r_A$  is the same isotope ratio but fractionated relative to the true value due to  
375 instrumental mass fractionation,  $m_i$  is the atomic mass of isotope  $i$ , and  $n$  controls the type or  
376 extent of mass dependence ( $n = 1$  for the power law,  $n = -1$  for the equilibrium law, and  $n \rightarrow$   
377  $0$  for the exponential/kinetic law) that is applied to correct for the instrumental mass  
378 fractionation<sup>23</sup>.

379 Under normal circumstances, our data reduction applies  $n \approx -0.1$ <sup>23</sup>, but other values  
380 may be more appropriate for samples that are contaminated with particular organic  
381 compounds. To test this, we recalculated the instrumental mass fractionation-corrected (or  
382 assumed true) isotope compositions of refluxed NIST Cd samples using a range of  $n$  values,  
383 relative to analyses of the bracketing standard, which were corrected with  $n = -0.1$ . For all  
384 refluxed NIST Cd samples, there is a linear relationship with negative gradient between  $n$  and  
385  $\epsilon^{114/110}\text{Cd}$  (see Supplementary Information). This implies that the inaccurate  $\epsilon^{114/110}\text{Cd}$  data  
386 for refluxed NIST Cd samples can, in principle, be corrected to accurate results simply by  
387 adjusting the  $n$  to a more appropriate value. In detail, the modelling shows that  $n$  values of  
388 between 0.2 and 0.6 are needed for such a correction (see Supplementary Information). This  
389 finding has two main implications. Firstly, our results indicate that the presence of organic  
390 compounds generates a mass dependence of mass fractionation that is intermediate between  
391 the kinetic/exponential and power laws ( $n \approx 0.2$  to  $0.6$  for refluxed NIST Cd samples) whilst  
392 it is normally intermediate between the kinetic/exponential and equilibrium laws (e.g.,  $n \approx -$   
393  $0.1$  for unprocessed NIST Cd). This suggests that the organic material induces a significant  
394 change in the processes that are responsible for the instrumental mass bias. Secondly, the  
395 range of calculated  $n$  values implies that the induced changes in mass bias and mass  
396 dependence are either not constant, or that the samples differ in their matrix content. Neither  
397 of these explanations can be ruled out at present. As changes in the mass dependence of  
398 isotope fractionation can produce both positive or negative artefacts, this process may also  
399 explain the deviations towards lighter isotope compositions seen by Gault-Ringold and  
400 Stirling<sup>13</sup>.

401 The sources of instrumental mass bias in MC-ICP-MS are not well understood, but  
402 the majority of the relevant processes are generally thought to occur either in the plasma or  
403 the interface region of the instruments. In the plasma, the radial spread of ions is mass  
404 dependent so the portion of the sample that passes through the aperture in the sample cone  
405 has a heavier isotope composition than the original sample<sup>26, 27</sup>. In addition the ionisation  
406 environment of the plasma can be altered by the presence of matrix, so the distribution of  
407 isotopes in the plasma can also change. This has the potential to have an impact on both  
408 instrumental sensitivity and isotope ratios, as under normal running conditions the plasma  
409 sampling depth (i.e. distance between the load coil and sampler cone) is kept constant<sup>26</sup>.  
410 Between the sample and skimmer cones, ions gain kinetic energy by supersonic expansion.  
411 Lighter ions do not gain as much kinetic energy as heavier ions, and are therefore more likely  
412 to be deflected away from the beam axis when collisions with argon neutrals occur<sup>27</sup>.  
413 Specifically for Cd, Kivel et al.<sup>28</sup> showed that the Cd exiting the skimmer cone has a heavier  
414 isotope composition than the original sample, and that the outer part of the ion beam before  
415 the first lens features a lighter Cd isotope composition than the central region. Therefore, we  
416 speculate that the presence of organic compounds, which are produced by partial oxidation of  
417 organic material leached from Eichrom TRU resin, may change the distribution of isotopes in  
418 the plasma and thus alter both the extent and mass dependence of the instrumental mass bias.

419

## 420 **5. Conclusion**

421 This study provides further evidence that organic resin residues can have a significant  
422 detrimental impact on the reproducibility and accuracy of Cd isotope analyses by MC-ICP-  
423 MS. These organic residues are eluted from Eichrom TRU resin during Cd purification by  
424 extraction chromatography and do not evaporate, even when heated to high temperatures.  
425 When left untreated, the organic residue can cause the Cd isotope composition of samples to  
426 be isotopically heavier than expected, and this effect is even more severe (with analytical  
427 artefacts of up to  $\sim 6.6 \text{ } \epsilon^{114/110}\text{Cd}$ ) when samples are refluxed with concentrated nitric acid  
428 prior to analysis. In such cases, the instrumental sensitivity for Cd is also reduced by up to  
429  $\sim 40\%$ . Our results indicate that spectral interferences are unlikely to be the cause of these  
430 analytical artefacts. Rather, they are probably related to changes in the extent and mass  
431 dependence of the instrumental mass bias, which are induced by the presence of the resin-  
432 derived organic material. These analytical problems for Cd isotope measurements are  
433 circumvented by performing a quick and easy liquid-liquid extraction step using heptane,  
434 which removes resin-derived organic compounds from sample solutions. Given the efficiency

435 of this method it should be particularly appropriate for analyses of samples with low Cd  
436 contents.

437 It is common knowledge that traces of organic material are leached from the resins  
438 that are commonly used in isotope geochemistry for sample purification by ion exchange and  
439 extraction chromatography. In many cases, this leaching is not problematic and has no impact  
440 on data quality. However, as ever-more ambitious analytical targets are addressed, more  
441 analytical problems related to resin-derived organics may become apparent and knock-on  
442 effects may arise when the problematic resin is not used in the final purification stage.

443 Although not yet tested on organic compounds eluted from resins other than Eichrom TRU,  
444 the principles of our liquid-liquid extraction technique should be applicable to and may solve  
445 problems associated with other resin types and isotopic analyses of other elements.

446

## 447 **6. Acknowledgements**

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450 comments which helped improve the manuscript.

451

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500

501 **8. Tables**

502

503 **Table 1** Summary of organic residue removal methods.

504

Sample treatment protocol	Elution dried down	Dried with 1 drop 16 M HNO <sub>3</sub>	Refluxed <sup>a</sup>	Dried down	Dissolved in 1 ml 0.1 M HNO <sub>3</sub>	Extraction procedure <sup>b</sup>	Refluxed <sup>a</sup>	Dried down	Dissolved in enough 0.1 M HNO <sub>3</sub> to produce a 60 ng/ml solution
Untreated	✓	✓✓							✓ <sup>c</sup>
Refluxed	✓	✓	✓					✓	✓ <sup>d</sup>
Extracted						✓		✓	✓ <sup>c</sup>
Extracted and refluxed						✓	✓	✓	✓ <sup>c</sup>
Refluxed and extracted	✓	✓	✓	✓	✓	✓		✓	✓ <sup>c</sup>

505

506 <sup>a</sup> Refluxed in 0.5 ml 16 M HNO<sub>3</sub> at 140°C for 5 days. <sup>b</sup> Extraction procedure is as follows: 1.2 ml pre-cleaned n-heptane added to beaker. Shaken for 30  
507 seconds, stood for 3 minutes, repeated once. Organic upper layer carefully removed with a pipette. 1.2 ml pre-cleaned n-heptane added. Shaken for 30  
508 seconds, stood for 3 minutes, repeated once. Organic upper layer carefully removed with a pipette. Residual heptane allowed to evaporate at ambient  
509 temperature in a laminar flow hood for 30 - 60 minutes. <sup>c</sup> 1 ml 0.1 M HNO<sub>3</sub>. <sup>d</sup> Most refluxed samples contained 60 ng total Cd, but some had up to 240 ng. All  
510 samples, however, had S/N ≈ 1 and were dissolved in the appropriate amount of 0.1 M HNO<sub>3</sub> to produce solutions with a total Cd concentration of 60 ng/ml  
511 for analysis. In one exceptional case, two samples, each with 30 ng total Cd dissolved in 0.5 ml 0.1 M HNO<sub>3</sub>, were combined to produce a single 1 ml  
512 solution with 60 ng/ml Cd. This approach enabled us to generate Cd solutions that featured variable dilution factors for the eluted organic resin compounds.

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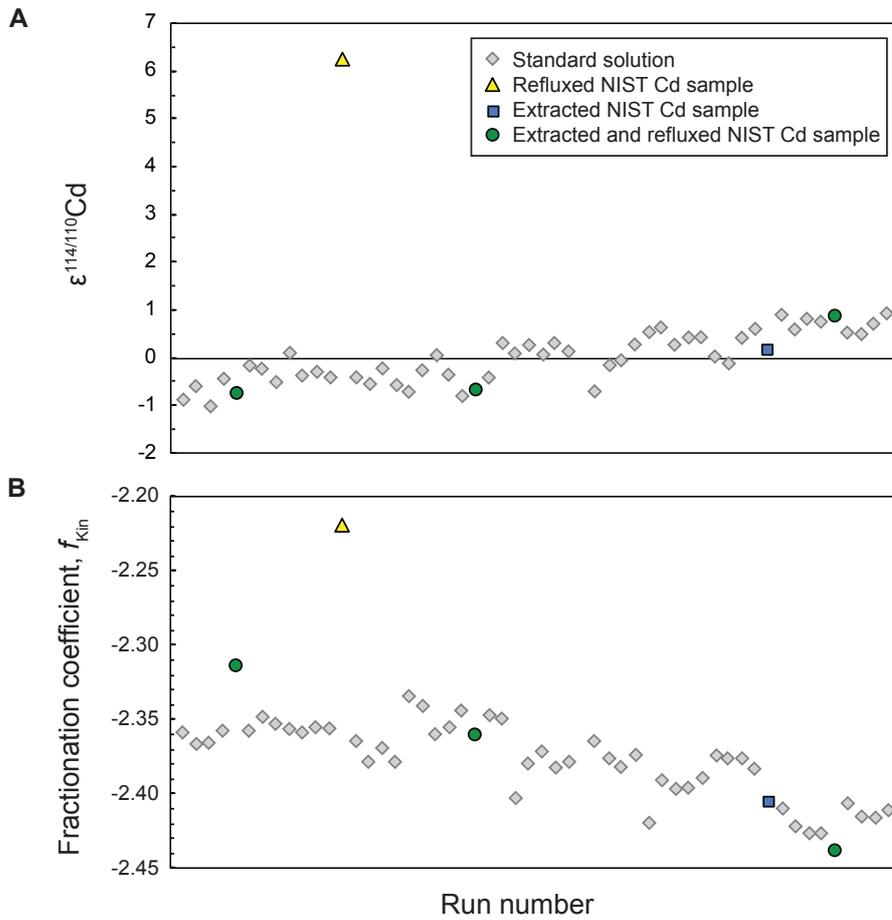
523 **Table 2** Mean Cd isotope composition of samples with approximately 60 ng total Cd and analyzed at 60 ng/ml Cd. All individual data are  
 524 provided in the Supplementary Information.  
 525

Sample	Source	Treatment after purification	Mean $\epsilon^{114/110}\text{Cd}$	2 SD	Number analyses included	Number analyses discarded <sup>a</sup>
NIST SRM 3108 Cd <sup>b</sup>	This study	None	-0.1	0.8	6	1
	This study	Refluxed	4.6	3.4	4	4
	This study	Extracted	0.0	0.5	6	2
	This study	Extracted and refluxed	0.0	0.7	9	1
	This study	Refluxed and extracted	3.0	0.8	3	0
USGS SRM Nod-A-1 <sup>c</sup>	This study	None	2.5	3.4	2	1
	This study	Refluxed	4.3	5.9	2	0
	This study	Extracted (preferred value)	1.7	0.5	6	0
	This study	Extracted and refluxed	2.1	0.7	2	0
	This study	Refluxed and extracted	3.6	1.2	2	0
	Horner et al. <sup>11</sup>	None	2.3	0.6 <sup>d</sup>	2	
	Schmitt et al. <sup>21</sup>	None <sup>e</sup>	1.3	0.2	2	
BAM-I012	This study	No purification procedure	-13.2	0.7	15	0
	Abouchami et al. <sup>1</sup>	No purification procedure	-13.3	0.4		

526 <sup>a</sup>Analyses were excluded when either the internal precision (2 SE) or the external precision (2 SD) exceeded  $\pm 1 \epsilon^{114/110}\text{Cd}$ , unless the internal 2 SE was not  
 527 unusual for that particular instrument session (see text for details). <sup>b</sup> NIST Cd samples underwent just the second stage of the separation chemistry. <sup>c</sup> Nod-A-1  
 528 samples underwent both stages of the separation chemistry. <sup>d</sup> Reported uncertainty is 2 SE, not 2 SD. <sup>e</sup> Analysed by thermal ionisation mass spectrometry  
 529 (TIMS).

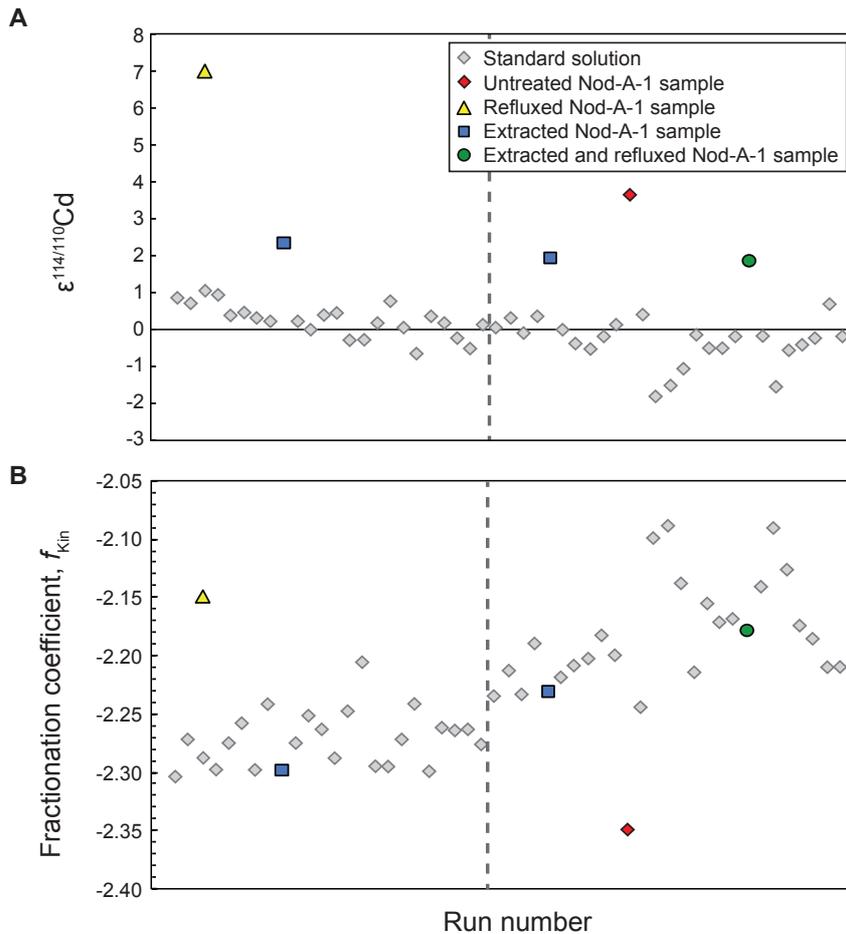
530 **9. Figures and figure captions**

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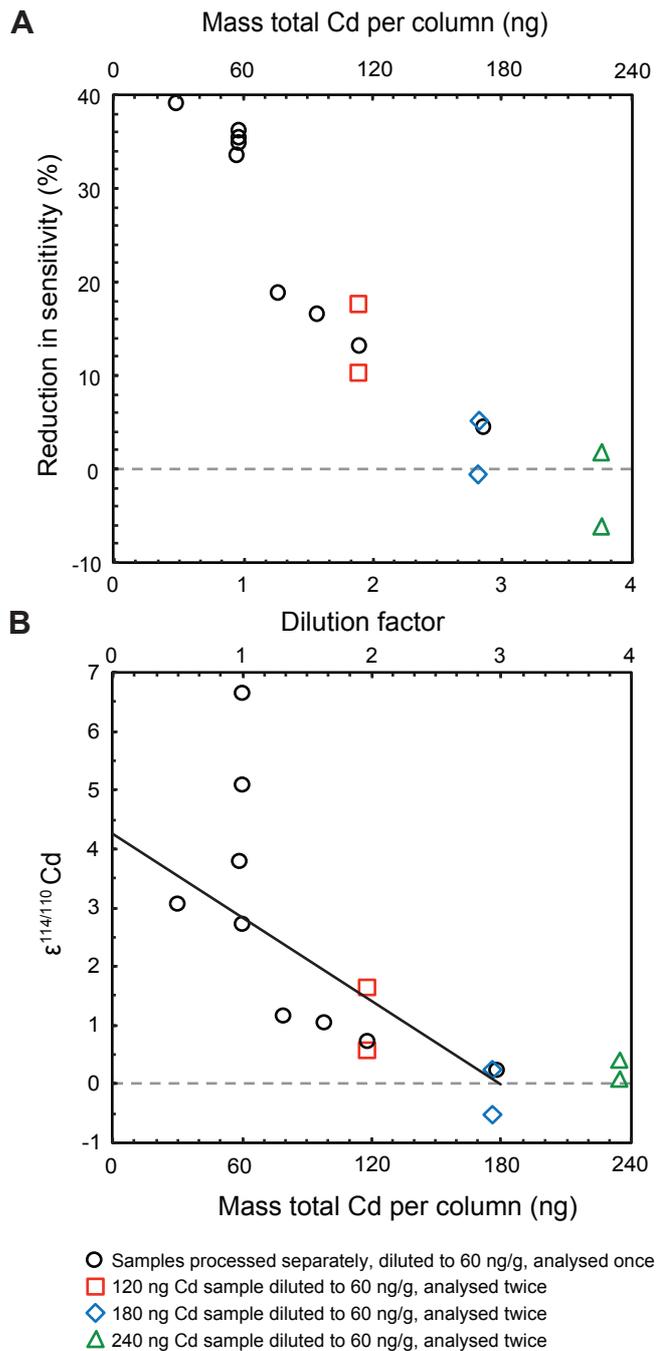
532

533 **Fig. 1** Typical analytical session of repeat measurements of the NIST SRM 3108 Cd standard  
534 solution doped with the Cd double spike (to  $S/N \approx 1$ ) together with interspersed  
535 measurements of aliquots of NIST SRM 3108 Cd that were passed through the extraction  
536 chromatography separation stage (Eichrom TRU resin) and subsequently extracted and/or  
537 refluxed to remove the organic residue. All solutions and standards should have identical  
538 isotope composition as they all contain only (spiked) NIST Cd, yet the refluxed sample is  
539 offset by  $6 \epsilon$  (A). Simultaneous shifts in the instrumental fractionation coefficient  $f_{Kin}$  are  
540 shown in (B).



541

542 **Fig. 2** Typical analytical session of repeat measurements of the NIST SRM 3108 Cd standard  
 543 solution doped with Cd double spike together with interspersed measurements of the  
 544 ferromanganese nodule Nod-A-1 that passed through both stages of column chemistry and  
 545 were subsequently extracted and/or refluxed to remove the organic residue, or left untreated.  
 546 The dashed grey line indicates when the sweep gas of the desolvating sample introduction  
 547 system was adjusted; this typically leads to a change in the instrumental mass bias. All  
 548 samples of Nod-A-1 should yield identical isotope compositions (A). For this particular  
 549 instrument session, samples that were cleaned by extraction or extraction and refluxing give  $\epsilon$   
 550  $^{114/110}\text{Cd} = 2.1 \pm 0.4$  (2SD), whilst the untreated and particularly the refluxed samples have  
 551 much higher  $\epsilon^{114/110}\text{Cd}$  values. Note the delayed 2  $\epsilon$  shift in the isotope data for the NIST Cd  
 552 standards that were analyzed following the untreated sample. The shift occurs only with the  
 553 second standard analyses after the sample and the instrumental fractionation coefficient  $f_{kin}$   
 554 does not display a simple step change after this analysis (B).



555

556 **Fig. 3** The presence of an organic residue reduces the sensitivity of the instrument (A) and  
 557 produces analyses that yield inaccurate  $\epsilon^{114/110}\text{Cd}$  data (B). All samples shown are aliquots of  
 558 the NIST SRM 3108 Cd standard solution doped with the Cd double spike. They were passed  
 559 through the second stage of the column chemistry that applies Eichrom TRU resin,  
 560 subsequently refluxed in concentrated nitric acid and then diluted to 60 ng/ml. The solid trend  
 561 line in panel (B) is shown to illustrate that the changes in  $\epsilon^{114/110}\text{Cd}$  with dilution factor are  
 562 not appropriately described by a simple linear trend.

563

**Supplementary Information to:**

**Improvements in Cd stable isotope analysis achieved through use of liquid-liquid extraction to remove organic residues from Cd separates obtained by extraction chromatography**

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**S1** Complete Cd isotope data set for NIST 3108 Cd and Nod-A-1 samples. See main text for description of sample treatment methods. The reduction in sensitivity was not calculated for all samples, but it is appropriate to assume that the reduction was negligible unless stated.

Sample	Type	Mass Cd (ng)	Treatment	$\epsilon^{114/110}\text{Cd}$	2SE (internal)	2SD (external)	Number of bracketing standards	Included in Table 2?	Reduction in sensitivity (%)	Comments
1	NIST Cd	60	Untreated	-0.14	1.35	0.83	3	No		
2	NIST Cd	60	Untreated	0.49	0.67	0.42	4	Yes		
3	NIST Cd	60	Untreated	0.06	0.77	0.65	5	Yes		
4	NIST Cd	60	Untreated	-0.44	0.80	1.00	9	Yes		
5	NIST Cd	60	Untreated	0.25	0.84	0.43	5	Yes		
6	NIST Cd	60	Untreated	-0.55	0.82	0.59	6	Yes		
7	NIST Cd	60	Untreated	-0.31	0.58	0.62	34	Yes		
8	NIST Cd	30 + 30	Refluxed	3.09	0.85	0.65	68	No	39	
9	NIST Cd	30	Refluxed	3.48	1.13	0.85	8	No	33	
10	NIST Cd	59	Refluxed	1.41	1.25	1.51	5	No	31	
11	NIST Cd	60	Refluxed	0.95	0.98	1.18	6	No	21	
12	NIST Cd	59	Refluxed	7.23	1.36	2.03	5	No	42	
13	NIST Cd	59	Refluxed	4.00	0.94	1.01	10	No	28	
14	NIST Cd	60	Refluxed	5.08	0.87	0.62	11	Yes	35	
15	NIST Cd	60	Refluxed	6.64	0.73	0.24	6	Yes	36	
16	NIST Cd	59	Refluxed	3.79	1.15	0.77	6	Yes	34	Internal precision not unusual for session
17	NIST Cd	60	Refluxed	2.73	0.65	0.62	34	Yes	36	
18	NIST Cd	79	Refluxed	1.17	0.98	0.78	6	No	19	
19	NIST Cd	98	Refluxed	1.05	0.98	0.67	6	No	17	
20	NIST Cd	118	Refluxed	1.65	0.70	0.94	8	No	10	

## S1 continued

Sample	Type	Mass Cd (ng)	Treatment	$\epsilon^{114/110}\text{Cd}$	2SE (internal)	2SD (external)	No. bracketing standards	Included in Table 2?	Reduction in sensitivity (%)	Comments
21	NIST Cd	118	Refluxed	0.57	1.00	0.75	8	No	18	
22	NIST Cd	118	Refluxed	0.73	1.18	0.59	6	No	13	
23	NIST Cd	176	Refluxed	-0.51	0.84	0.66	7	No	5	
24	NIST Cd	176	Refluxed	0.23	0.83	0.63	6	No	-1	
25	NIST Cd	178	Refluxed	0.25	0.90	0.45	8	No	5	
26	NIST Cd	235	Refluxed	0.41	0.89	0.59	9	No	-6	
27	NIST Cd	235	Refluxed	0.09	1.18	0.87	6	No	2	
28	NIST Cd	60	Refluxed (overnight only)	3.85	0.91	0.80	6	No		
29	NIST Cd	60	Extracted (once)	0.44	1.06	0.48	6	No		
30	NIST Cd	60	Extracted	1.12	0.77	1.86	10	No		Run after several refluxed samples, instrument possibly unstable
31	NIST Cd	60	Extracted	-0.31	1.10	0.69	6	No		
32	NIST Cd	60	Extracted	-0.21	1.17	0.54	7	Yes		Internal precision not unusual for session
33	NIST Cd	60	Extracted	0.33	0.95	0.51	8	Yes		
34	NIST Cd	60	Extracted	-0.34	0.88	0.74	8	Yes		
35	NIST Cd	60	Extracted	-0.19	0.46	0.62	34	Yes		
36	NIST Cd	60	Extracted	0.00	0.69	0.62	34	Yes		
37	NIST Cd	60	Extracted	0.21	0.42	0.62	7	Yes		
38	NIST Cd	60	Extracted (once), refluxed	-0.19	0.56	0.63	6	No		
39	NIST Cd	60	Extracted and refluxed	0.07	0.52	1.15	5	No		
40	NIST Cd	60	Extracted and refluxed	0.07	0.46	0.46	5	Yes		
41	NIST Cd	60	Extracted and refluxed	-0.51	0.59	0.74	7	Yes		
42	NIST Cd	60	Extracted and refluxed	0.14	0.70	0.43	6	Yes		
43	NIST Cd	60	Extracted and refluxed	0.19	0.63	0.34	8	Yes		
44	NIST Cd	60	Extracted and refluxed	-0.14	0.57	0.76	9	Yes		

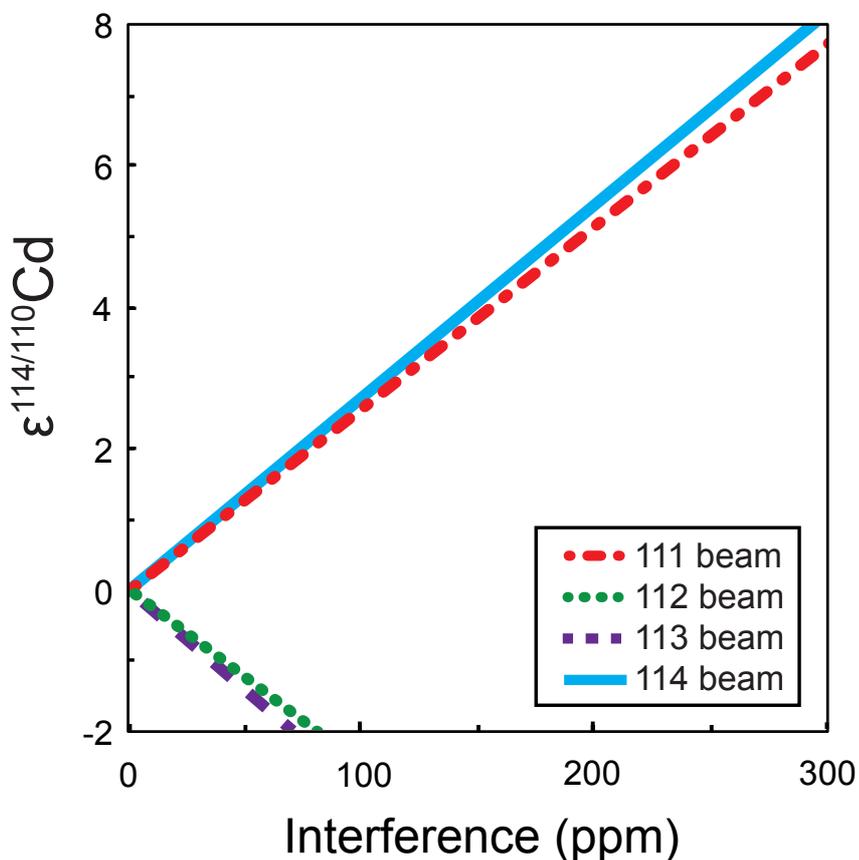
## S1 continued

Sample	Type	Mass Cd (ng)	Treatment	$\epsilon^{114/110}\text{Cd}$	2SE (internal)	2SD (external)	Number of bracketing standards	Included in Table 2?	Reduction in sensitivity (%)	Comments
45	NIST Cd	60	Extracted and refluxed	0.22	0.67	0.47	9	Yes		
46	NIST Cd	60	Extracted and refluxed	-0.47	0.53	0.81	6	Yes		
47	NIST Cd	60	Extracted and refluxed	0.48	0.44	0.60	7	Yes		
48	NIST Cd	60	Extracted and refluxed	0.32	0.57	0.67	7	Yes		
49	NIST Cd	60	Refluxed and extracted	2.69	0.62	0.37	6	Yes		
50	NIST Cd	60	Refluxed and extracted	2.85	0.62	0.62	34	Yes		
51	NIST Cd	60	Refluxed and extracted	3.42	0.60	0.62	34	Yes		
52	Nod-A-1	60	Untreated	3.73	0.69	0.66	6	Yes		
53	Nod-A-1	60	Untreated	1.34	0.71	0.76	9	Yes		
54	Nod-A-1	60	Untreated	3.01	1.57	0.96	7	No	87	Low beam intensity
55	Nod-A-1	120	Untreated	1.70	1.06	0.52	8	No		
56	Nod-A-1	60	Refluxed	6.36	0.86	0.62	8	Yes		
57	Nod-A-1	60	Refluxed	2.20	0.98	0.72	18	Yes		
58	Nod-A-1	120	Refluxed	1.80	0.83	0.52	6	No		
59	Nod-A-1	60	Extracted	1.98	0.55	0.56	9	Yes		
60	Nod-A-1	60	Extracted	1.36	0.62	0.87	6	Yes		
61	Nod-A-1	60	Extracted	1.51	0.90	0.76	8	Yes		
62	Nod-A-1	60	Extracted	1.90	0.69	0.70	28	Yes		
63	Nod-A-1	60	Extracted and refluxed	1.97	0.70	1.24	9	Yes		
64	Nod-A-1	60	Extracted and refluxed	2.37	0.81	0.87	8	Yes		
65	Nod-A-1	60	Refluxed and extracted	4.04	1.08	0.72	6	Yes	58	Low beam intensity
66	Nod-A-1	60	Refluxed and extracted	3.16	0.80	0.53	6	Yes		
67	Nod-A-1	120	Refluxed and extracted	2.24	0.74	0.52	8	No		

## S2 Further information on untreated Nod-A-1 analyses

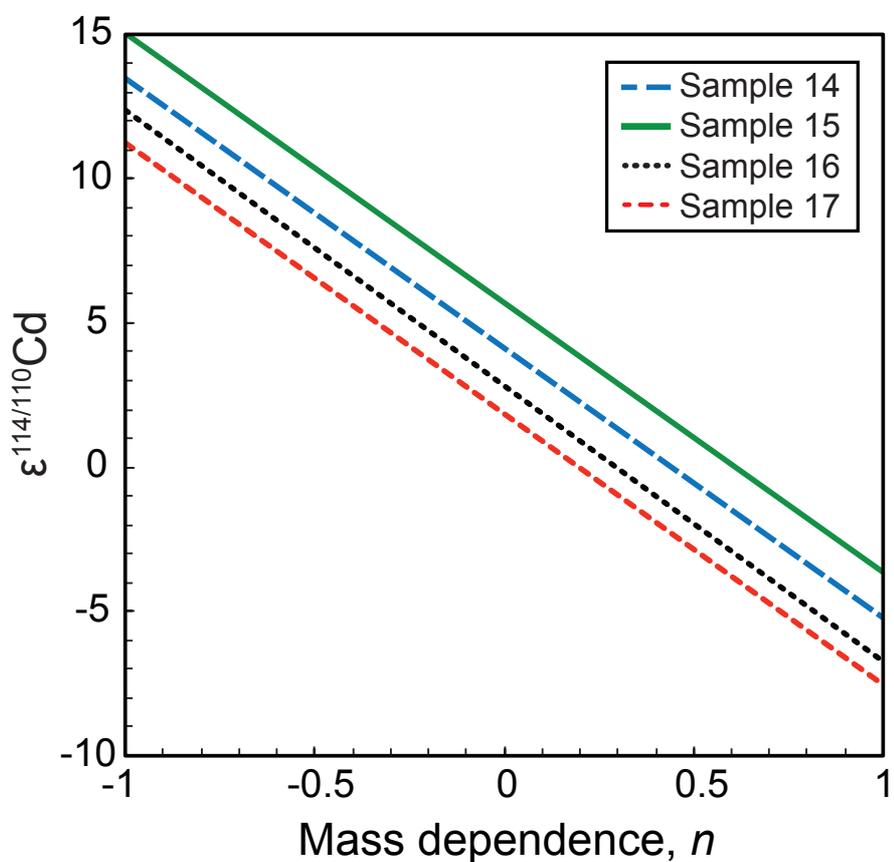
Of the three samples of untreated Nod-A-1 that were analyzed, only one produced a reasonable result, of  $\epsilon^{114/110}\text{Cd} = 1.3 \pm 0.8$ , which is in good agreement with literature values (Table 2). The second sample yielded an isotopic composition that was significantly heavier than literature values ( $\epsilon^{114/110}\text{Cd} = 3.7 \pm 0.7$ ). This analysis was also compromised by a 2.2  $\epsilon$  unit drop in the data obtained for subsequent measurements of the bracketing standard, so these analyses of the standard were excluded from the calculation of the sample isotope composition. This ‘drop’ occurred between the first and second analyses of the standard solution after the Nod-A-1 sample, and was accompanied by large changes in  $f_{kin}$  (Fig. 2). The instrumental sensitivity obtained during the analysis of the third untreated Nod-A-1 sample was just 14% of the expected level. Incomplete dissolution of the Cd fraction in 0.1 M  $\text{HNO}_3$  is unlikely to be responsible for this dramatic reduction in sensitivity. A more plausible explanation is that the organic resin residue disrupted the normal behavior of the instrument and/or sample introduction system.

### S3 Modeling of spectral interferences



The modeling shows that it is possible that a spectral interference on one ion beam can alter the mass bias corrected  $\epsilon^{114/110}\text{Cd}$  value. These experiments were conducted using the ion beam intensity data from a single measurement of a NIST SRM 3108 Cd standard solution (with  $\epsilon^{114/110}\text{Cd} = 0$ ) that was doped with the Cd double spike (to  $S/N \approx 1$ ) to obtain a total Cd concentration of 60 ng/ml. In the modeling, the ion beam intensity data were manipulated to simulate an interference on a single ion beam. This was repeated for a range of interference magnitudes, and on each ion beam. The Cd isotope compositions were subsequently calculated using the normal double spike data reduction spreadsheet, as an offset from the original (unaltered) Cd isotope composition.

**S4** Modeling the effects of changing the mass dependence ( $n$  factor) of the General Power Law that is used for correction of the instrumental mass fractionation



The mass bias corrected isotope composition of a sample was recalculated for values of  $n$  (which describes the mass dependence of the instrumental mass fractionation correction that is applied using the General Power Law) between -1 and 1 for four refluxed NIST Cd samples with 60 ng of total Cd. Using our normal value of  $n = -0.1$ , these samples yielded  $\epsilon^{114/110}\text{Cd}$  values of between +2.7 and +6.4. Notably, each sample can be corrected to the reference value of  $\epsilon^{114/110}\text{Cd} = 0$  using  $n$  values of 0.2 to 0.6. This is a reasonable range of values as they are intermediate between the kinetic/exponential and power laws. Sample numbers refer to the data presented in the Table of S1.