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GEOSTANDARDS and GEOANALYTICAL RESEARCH

Measurement of Mass-Independent Perturbations of Cadmium in Nuclear Debris Samples

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The isotopic composition of cadmium in nuclear debris was measured by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). Mass-independent perturbations due to fission product decay on the isotopes of Cd were observed. Relative fission yields for masses 111, 112, 114 and 116 were determined in each sample of nuclear debris and compared with reported values found in irradiated plutonium and uranium fuels. Mass spectrometry measurements of the valley fission product endpoints are extremely challenging due to the low cumulative fission yields and small amounts of each isotope that are produced. To overcome these challenges, a new purification method for Cd was developed and validated by examination of a number of geological reference materials.

Keywords: cadmium, isotopic ratios, nuclear debris, fission product, mass spectrometry.

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Fission product measurements are important signatures of nuclear fission processes. In nuclear physics experiments, measurements of fission products can provide information about the type of special nuclear material that underwent fission and the neutron energy spectrum. This is because the cumulative yields of many fission product isotopes vary depending on the fissioning isotope and neutron energy. The effect is particularly pronounced for isotopes in the valley region of the fission product distribution curve (masses 110–126), which have significantly lower cumulative fission yields than the peak region isotopes (Figure 1). The element cadmium spans a wide region of the valley (masses 110–116) and has cumulative yields that show a large variation with fuel type and neutron energy. Cadmium isotopes can also undergo neutron capture reactions. For instance, the stable isotope ^{113}Cd has a very high cross section for thermal neutron capture reactions and is used in physics experiments as a powerful absorber of thermal neutrons. Although most of the information about valley fission product distributions has been obtained from radiochemical measurements of short-lived isotopes, these can suffer from uncertainties associated with nuclear decay data.

Fewer studies have focused on mass spectrometry measurements of valley fission product stable end-members, due in part to the challenges posed by the low concentrations

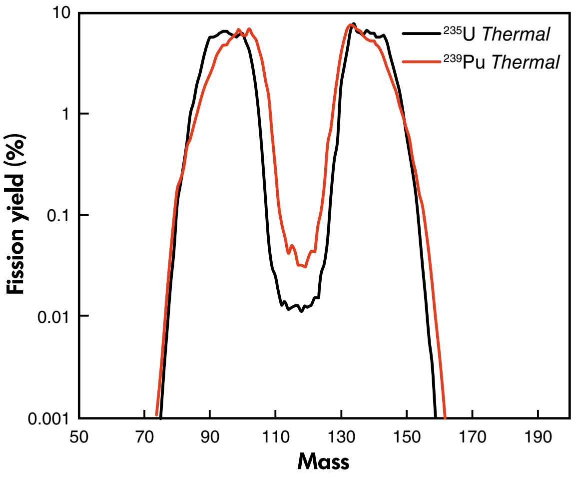

Figure 1. Fission product distribution curve for ^{235}U thermal fissions (black line) and ^{239}Pu thermal fissions (red line).

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of the isotopes formed in this region. The amounts of the elements available for analysis are small and typically accompanied by a high amount of radioactivity. Lisman *et al.* (1969) measured the stable Cd isotopic composition of a plutonium fuel rod irradiated in the fast neutron spectrum of the Experimental Breeder Reactor-1 (EBR-1), one of the first nuclear power reactors (Lisman *et al.* 1969). Although some contamination with natural Cd was observed, high quality measurements were obtained for Cd masses 110–116. Later work of de Laeter and Mathews involved similar isotopic measurements of Cd in ^{235}U thermal and ^{239}Pu thermal irradiation conditions (de Laeter and Thode 1975, Mathews 1977). These seminal studies clearly demonstrated that different cumulative yields of Cd isotopes were obtained for ^{235}U and ^{239}Pu in thermal and fast neutron spectra.

Cadmium isotope compositions have also been measured in geological material obtained from the Oklo natural nuclear reactor, a concentrated uranium ore deposit that underwent fission approximately two billion years ago (de Laeter and Rosman 1975, de Laeter *et al.* 1980, Loss *et al.* 1988, Curtis *et al.* 1989). Although some variability was observed depending on the sample location and extent of retention of the fission products in the geological repository, significant mass-independent perturbations were documented for Cd.

Although the concept had been demonstrated for the Oklo reactor and selected nuclear reactor fuels, comparable Cd isotopic measurements have never been performed for debris resulting from nuclear detonations. We hypothesised that this alternative type of nuclear sample would also exhibit mass independent perturbations arising from fission product decay.

This paper describes the development of a new method to measure Cd in nuclear debris using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). This work uses an established anion exchange procedure for initial Cd separation (Cloquet *et al.* 2005) followed by a newly developed second stage purification using Eichrom Ln resin. The method precision and accuracy was verified on a number of geological reference materials. The analysis of three nuclear debris samples reveals mass-independent perturbations that result from the radioactive decay of valley fission products. The results are compared with previous studies of nuclear reactor fuel and provide confirmation of prior studies demonstrating the Cd isotope distribution reflects the identity of the fissioning nucleus and neutron irradiation energy. This work applies an alternative method to radiometric analysis for cumulative yield measurements of short-lived fission products.

Experimental

Materials

All reagents were prepared using ultra-pure H_2O (resistivity: 18.2 MΩ cm). Fisher Optima™ grade acids and bases were used for all analytical procedures. Boric Acid (H_3BO_3) was obtained from Sigma Aldrich (Trace Metals Grade ≥ 99.99% purity). PFA jars obtained from Savillex and Biorad Poly-Prep columns (2 ml bed with 8 ml reservoir) were used for all separation procedures. AG-MP-1M anion exchange resin (100–200 mesh) was obtained from BioRad Laboratories and washed with concentrated HCl and H_2O before use. Ln resin (50–100 μm) was obtained from Eichrom Technologies and was used as received.

Cadmium reference material SRM 3108 (lot #130116) was obtained from the National Institute for Standards and Technologies (NIST). Münster Cd reference material (a mixture of Alfa JMC metal and strongly industrially fractionated Cd metal) was obtained from the CNRS-CRPG in Nancy, France. Spex CertiPrep Cd (Lot#AF14-143CDY), aka Spex Los Alamos (Spex-LA), was used as an in-house reference material. Spex CertiPrep Ag was used for mass bias corrections. The reference materials Montana I Soil SRM 2710a and Urban Particulate Matter SRM 1648a were obtained from NIST. BCR-176R, a fly ash collected in a city waste incineration plant, was obtained from the European Commission. Manganese Nodule NOD-A-1 and Basalt BHVO-2 were obtained from the U.S. Geological Survey (USGS).

Dissolution

For each reference material or nuclear debris, 2–3.5 g of solid material was dissolved. Prior to dissolution, the reference materials were heated at 110 °C for 2 h to drive off any residual moisture before weighing. NIST SRM 2710a was ashed at 550 °C to remove organics before dissolution. The samples were then placed into Savillex jars and treated with 1:1 HF and HNO_3 and heated to dryness at 100–150 °C. The samples were treated repeatedly with HF/HNO_3 (approximately three to five cycles). Saturated H_3BO_3 (3–5 ml) was added to dissolve the fluoride salts and the samples were transferred to PTFE bottles and stored in 3 mol l^{-1} HCl.

Cadmium purification

Cadmium purification involved using a combination of an anion exchange (AG-MP-1M) and extraction chromatography (Eichrom Ln resin, 50–100 µm). Dissolved materials were divided into test portions containing approximately 0.5 g of dissolved solid material, heated to dryness, and then dissolved in 2 mol l^{-1} HCl prior to loading onto the anion exchange column (2 ml of resin). The anion exchange column was adapted from a method developed by Cloquet *et al.* (2005). To remove Cd, Zn and Zr present on the resin itself, an extensive on-column resin cleaning procedure was developed (see Table 1). The test portions were loaded onto the column using 5–10 ml of 2 mol l^{-1} HCl. 1 ml of 3:1 HCl: HNO_3 was used to rinse the jar that contained the test portion to ensure any residual material was dissolved and then diluted with water before being added to the column. The columns steps were performed as indicated in Table 1 and Cd was eluted from the column using dilute HCl. After elution, the solutions were evaporated to dryness.

For the anion exchange column, a series of experiments determined that chemical yields diminished significantly at loading volumes above 0.5 g of solid, therefore larger test portions were divided across multiple columns and recombined after the first stage column. The impact of the total matrix mass was tested using solutions of NIST SRM 2710a (Montana Soil I). Although high Cd yields (> 90%) were observed for test portions having dissolved solid masses of 0.5 g or less, the yields decreased significantly for test portions of 0.75 g and 2.0 g, to 52% and 28%, respectively. Splitting larger test portions (> 0.5 g) across multiple columns allowed for these larger soil masses to be successfully analysed without modification to the column conditions.

Table 1.
Resin cleaning and Cd elution conditions for AG-MP-1M resin

Eluent		Volume (ml)
0.8 mol l^{-1} HNO_3		5
1 mol l^{-1} HCl + 1 mol l^{-1} HF		10
6 mol l^{-1} HNO_3		10
9 mol l^{-1} HCl		10
5% NH_4OH		10
6 mol l^{-1} HCl		10
H_2O		10
0.1 mol l^{-1} HCl		10
0.06 mol l^{-1} HCl		12
0.0012 mol l^{-1} HCl		30
2 mol l^{-1} HCl		10
2 mol l^{-1} HCl	Load	5–10
3:1 HCl:HNO_3 + H_2O	Rinse	1 + 3.5
2 mol l^{-1} HCl	Rinse	2
2 mol l^{-1} HCl		8
0.3 mol l^{-1} HCl		12
0.012 mol l^{-1} HCl		12
0.06 mol l^{-1} HCl		12
0.0012 mol l^{-1} HCl	Collect Cd	30

For the large soil masses examined in this study, the anion exchange column alone did not adequately remove Zr, Mo and Sn interferences. To provide improved decontamination against these elements, a secondary column utilising Eichrom Ln resin was developed. The details of the column are presented in Table 2. The 1 ml of resin column was washed extensively with 2 mol l^{-1} HF to remove Zr and Mo from the resin and then conditioned with 1 mol l^{-1} HCl. The test portion was loaded in 1 mol l^{-1} HCl, conditions under which the phosphoric acid functional group di-(2-ethyl-hexyl)phosphoric acid ligand (HDEHP) does not effectively bind Cd allowing it to pass through the column (≥ 99% Cd recovery) while retaining Zr, Mo and Sn. Following this column, the Cd eluent was evaporated and if necessary, the column was repeated a second time to ensure adequate decontamination of interfering species. The average decontamination factors for this column procedure based off of 1.5 µg loadings of each element are as follows: Zr ~ 3500, Mo ~ 2400, Sn ~ 1600.

After purification, the resulting residue was treated with 1 ml of HNO_3 and 1 ml of 30% H_2O_2 and heated to dryness to destroy any residual organic matrix. The test solutions were then made up in 2% HNO_3 for analysis by ICP-MS.

Mass spectrometry

Analysis was performed using a Thermo Scientific Neptune Plus MC-ICP-MS equipped with nine Faraday cups using a static configuration as shown in Table 3. The MC-ICP-MS was fitted with either a standard cyclonic spray chamber (SIS) or an Elemental Scientific Apex Ω desolvating nebuliser system (DSN). A static Faraday routine was used to measure the samples with 1×10^{11} ohm amplifiers assigned to each Faraday cup (Table 3).

For analyses using the SIS, a typical test solution concentration was ~ 200 µg l^{-1} Cd, with a sensitivity of

Table 2.
Secondary column procedure utilising Ln resin

Eluent		Volume (ml)	Eluted
2 mol l^{-1} HF		4	Zr, Mo
H_2O		2	
6 mol l^{-1} HCl		8	
H_2O		10	
1 mol l^{-1} HCl		10	
1 mol l^{-1} HCl	Load	0.5	Cd
1 mol l^{-1} HCl	Rinse	0.25	Cd
1 mol l^{-1} HCl		2	Cd
1 mol l^{-1} HCl		0.5	Cd

Table 3.
Faraday cup configuration used for cadmium isotope measurements

Detector	L4	L3	L2	L1	C	H1	H2	H3	H4
Isotope	^{107}Ag	^{108}Cd	^{109}Ag	^{110}Cd	^{111}Cd	^{112}Cd	^{114}Cd	^{116}Cd	^{117}Sn

~ 0.085 V per µg l^{-1} ^{238}U. For analyses using the DSN, a typical test solution concentration was ~ 15 µg l^{-1} Cd, with a sensitivity of 1.5–2 V per µg l^{-1} ^{238}U. To correct for instrumental mass fractionation, a Ag reference material was added to each purified Cd fraction prior to analysis; the ^{109}Ag/^{107}Ag ratio was normalised to a value of 0.92905 using the exponential fractionation law (Wombacher *et al.* 2003, Pallavicini *et al.* 2014, Shiel *et al.* 2010, Shiel *et al.* 2013).

During the analysis, each Cd test solution was bracketed by two solutions of the NIST SRM 3108, where the Cd concentrations were matched between the test solution and standard reference material solutions to within 10%. The Ag reference material was also added to each solution of the Cd NIST SRM 3108. Peak centres (mass calibration) and amplifier gains were updated daily and peak centring was performed at the start of each standard analysis bracket. Each measurement was followed by a rinse protocol involving forty cycles of 10% HNO_3-0.01 mol l^{-1} HF and a blank of twenty cycles of 2% HNO_3.

The isotopic measurement of Cd can be impacted by polyatomic and isobaric interferences. To monitor for potential polyatomic interferences, Zr and Mo levels were checked in each test solution prior to analysis. ^{117}Sn was monitored during analysis (H4) and Sn levels were typically < 0.005 V. Minor Sn contributions on masses 112, 114 and 116 were mathematically corrected from the ^{117}Sn signal using natural Sn isotopic abundances (Shiel *et al.* 2010). Process blanks averaged < 1 ng total of adventitious Cd therefore no blank subtraction was performed on the Cd isotopes measured in this study.

Results and discussion

A new method to purify Cd from nuclear debris was developed. It was expected that Cd mass fractions in nuclear debris would be low (~ 20–200 ng g^{-1}) so the method was optimised to handle large masses of geological material and effectively remove interfering elements. An anion exchange column was used to separate Cd from major matrix constituents and most isobaric interferences. Larger dissolved soil masses (up to 1 g) were split between two anion columns and then recombined. Subsequent purification using an Ln resin column provided improved decontamination against Sn, Zr and Mo. The development of this second stage column proved necessary since other published second stage columns in the literature did not provide the decontamination of isobaric interferences needed for the measurement of Cd in large masses of nuclear debris.

Although the isotopic composition of Cd in terrestrial materials typically varies by less than 1‰ per atomic mass unit (Yang *et al.* 2019, Zhang *et al.* 2016, Wiggenhauser *et al.* 2016, Cloquet *et al.* 2005, Wombacher *et al.* 2003, Weiss *et al.* 2008), mass-dependent Cd fractionation as a result of anthropogenic activities is well established. Previous studies have quantified mass-dependent Cd fractionation in a number of reference materials. To compare the accuracy and precision of our measurement method with these previous studies, the Cd isotopic ratios in the reference materials are expressed in per mil (δ) notation relative to NIST Cd 3108 (Tan *et al.* 2020, Abouchami *et al.* 2013) as follows in Equation (1):

$$\delta\frac{^{114}Cd}{^{110}Cd} = \left[\left(\frac{\left(\frac{^{114}Cd}{^{110}Cd}\right)_{sample}}{\left(\frac{^{114}Cd}{^{110}Cd}\right)_{NIST\ Cd\ 3108}}\right) - 1\right] \qquad (1)$$

Because the Cd concentrations were anticipated to be low in the nuclear debris examined in this study, mass spectrometry measurements were carried out using a DSN for enhanced sensitivity and lower oxide formation. To assess the precision and accuracy of these low-level measurements using a DSN, the Cd isotopes in a number of reference materials were measured initially at higher concentrations using a SIS followed by diluted measurements using the DSN. One well-documented Cd reference material is Münster Cd, a material that has been used by a number of groups as a Cd isotopic standard. Analysis of Münster Cd using the SIS provided a δ Cd/amu of 1.12(2) and a $\delta^{114}/^{110}$Cd of 4.46(11) that was identical to the value measured using the DSN (4.46(20), Table 4). Both of these values match the accepted value of 4.49(5) (Abouchami *et al.* 2013) as displayed in Figure 2.

Table 4.
Comparison of measured Cd isotopic compositions of various reference materials using the SIS and DSN

Material		δ111/110	2*s*	δ112/110	2*s*	δ114/110	2*s*	*N*
Münster	SIS	1.11	0.05	2.22	0.06	4.46	0.11	21
	DSN	1.12	0.06	2.24	0.10	4.46	0.20	22
BCR-176R	SIS	-0.20	0.05	-0.46	0.06	-0.87	0.07	6
	DSN	-0.17	0.01	-0.37	0.03	-0.74	0.09	5
2710a	SIS	-0.06	0.05	-0.13	0.06	-0.26	0.10	5
	DSN	-0.05	0.03	-0.14	0.05	-0.27	0.11	5
NOD-A-1	SIS	-0.01	0.05	-0.01	0.10	-0.03	0.07	3
	DSN	0.02	0.06	0.02	0.18	0.04	0.34	5
1648a	SIS	-0.06	0.03	-0.12	0.02	-0.20	0.05	5
	DSN	-0.01	0.04	-0.03	0.09	-0.06	0.19	5
SPEX LA	SIS	-0.30	0.05	-0.61	0.05	-1.24	0.11	5
	DSN	-0.30	0.06	-0.58	0.13	-1.16	0.27	10
NIST 3108	SIS	-0.01	0.04	-0.01	0.04	-0.02	0.09	17
	DSN	0.00	0.03	0.00	0.05	-0.01	0.09	15

SIS = Standard spray chamber
DSN = Desolvating nebuliser
N - Repeated measurements of the same test solution. 2*s* - two times the standard deviation of the repeated measurements.

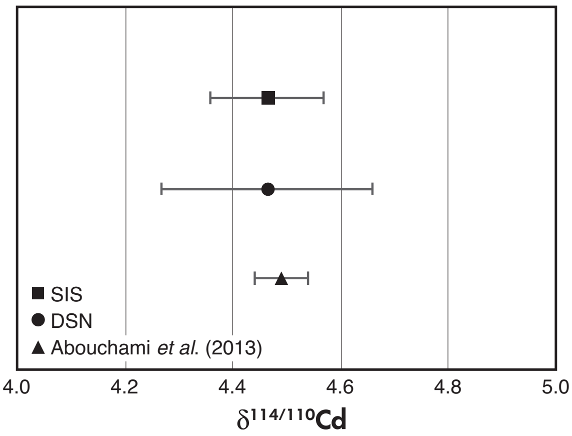

Figure 2. The results of the Münster Cd reference material measured by SIS and DSN compared with the accepted literature value.

The results of the analysis of several other reference materials, including BCR-176R, NIST SRM 2710a, NIST SRM 1648a, Spex LA and NOD-A-1, measured using both the SIS and DSN introduction systems are displayed in Table 4. The DSN afforded comparable results at low Cd concentrations, although the best available precision was achieved with the SIS at higher Cd concentrations.

The accuracy of the method can be assessed by comparing the results of the reference materials with previous studies where good agreement is noted. For the USGS geochemical reference material NOD-A-1, the measured Cd values agree with prior reported values ($\delta^{114/110}$Cd (-0.05-0.16)) and no extensive Cd isotopic fractionation was observed (Cloquet *et al.* 2005, Schmitt, Galer and Abouchami 2009, Pallavicini *et al.* 2014, Murphy *et al.* 2016, Li *et al.* 2018, Zhang *et al.* 2018, Tan *et al.* 2020, Borovička, Ackerman and Rejšek 2021). For NIST SRM 2710a, the measured $\delta^{114/110}$Cd (-0.26(10)) is also quite consistent with previous work (-0.20(5)) (Liu *et al.* 2020). Although the certified reference material BCR-176R has not been previously reported, prior measurements of its related predecessor material have been. BCR-176R replaced the exhausted certified reference material BCR-176 which was reported to have a $\delta^{114/110}$Cd of -0.3(1) (Cloquet *et al.* 2005). The $\delta^{114/110}$Cd value measured for BCR-176R (-0.87(7)) suggests this material is slightly more enriched in light isotopes relative to its predecessor.

Two other Cd reference materials were used to assess the intermediate precision of the measurement routine used in this study. In each measurement session, a bracketed NIST SRM 3108 Cd was analysed as a control for in-run stability; the results of which afforded a δ value close to 0 for all ratios measured. A Spex Certiprep Cd solution (Spex LA) was diluted and analysed as an in-house reference material along with each measurement session where a small degree of fractionation was observed (see Table 4). A similar fractionation was previously reported by Gao *et al.* (2008) for another Spex Cd reference material, referred to as Spex-1. The Spex LA reference material provided an additional monitor of the intermediate precision of the measurement routine.

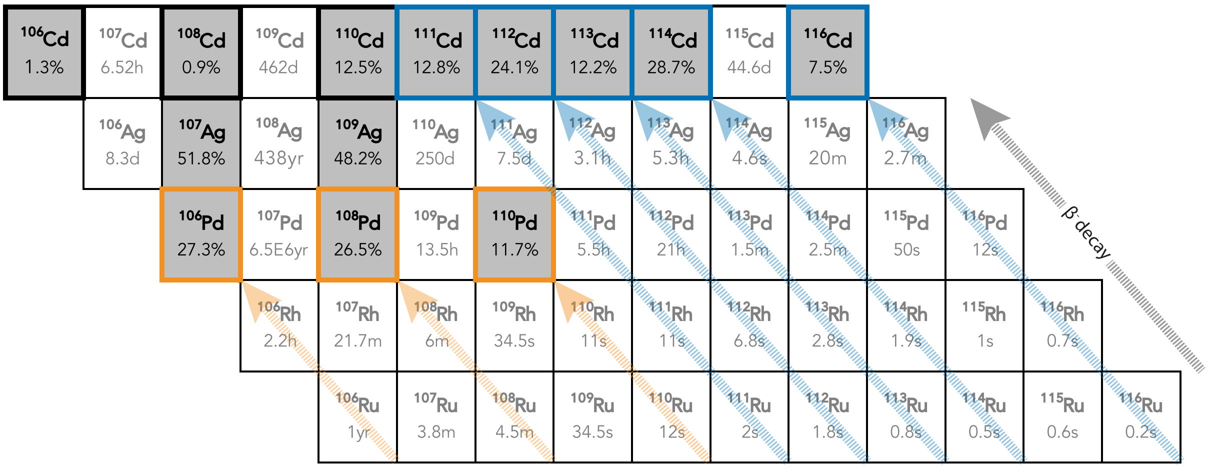

Figure 3. Beta decay scheme for fission products to form stable palladium and cadmium isotopes.

Three different nuclear debris collections were analysed which consisted of fused glassy material that was obtained from prompt fission experiments where plutonium was the dominant fissioning material. The masses ranged from 0.2–1.0 g. The test solutions were analysed by MC-ICP-MS using a DSN introduction system. The reference material Münster Cd and two 1 g samples of the geochemical reference material BHVO-2 were purified and analysed in parallel.

We hypothesised that the nuclear debris would exhibit mass-independent perturbations at isotopes 111, 112, 114 and 116 due to fission product decay. The beta decay scheme of the valley fission product isotopes is shown in Figure 3. Cadmium masses 106, 108 and 110 are not formed in any significant yield by fission and the beta decay chains terminate at the stable isotopes of ^{106}Pd, ^{108}Pd and ^{110}Pd. In contrast, Cd isotopes 111, 112, 113, 114 and 116 are formed from the cumulative beta decay of short-lived radioactive fission products. During the formation of the nuclear debris, fission products mix with natural rock in the surrounding environment. The Cd measured in these test solutions represents a mixture of terrestrial Cd with valley fission product end-members.

The results of the measured Cd isotopes in the nuclear debris along with the results of the reference materials are shown in Table 5. Münster Cd purified through column chemistry and BHVO-2 showed no measurable fractionation as a result of the column chemistry. The natural Cd isotopes observed in BHVO-2 from a two separate 1 g test portions highlight the ability of the second stage Ln resin column to

Table 5.
Results for the measured Cd isotopic compositions in the nuclear debris (ND), BHVO-2 and Münster Cd through chemistry

Material	δ111/110	δ112/110	δ114/110	δ116/110	*N*
ND-1	18.26	3.71	1.04	1.37	2
ND-2	3.56	0.90	0.23	0.62	2
ND-3	3.46	0.94	0.19	0.30	2
BHVO-2	-0.01	0.02	0.09	-0.31	2
BHVO-2	-0.02	0.00	0.05	-0.36	2
Münster	1.10	2.21	4.44	6.41	2
Münster	1.12	2.47	4.55	6.62	2
2*s*	0.06	0.10	0.19	0.33	

N - Repeated measurements of the same test solution. 2*s* - uncertainty is an estimate of the intermediate precision derived from the long-term running mean standard deviation of the Münster Cd reference material.

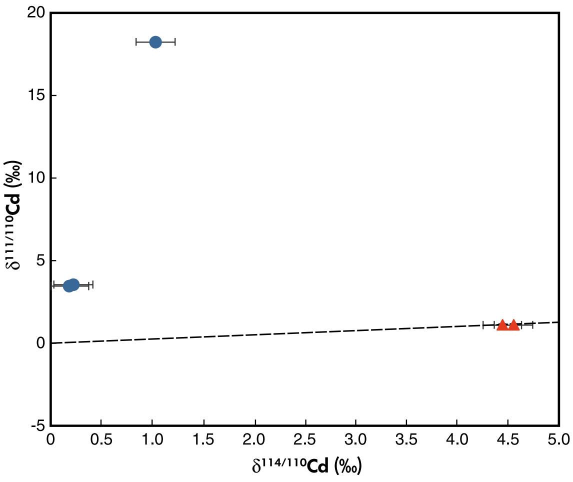

Figure 4. Three isotope plot of measured δ values for the three nuclear debris test solutions (blue dots) and Münster Cd purified through chemistry (red triangles). The theoretical mass dependent fractionation line is shown as a dashed black line. *Y*-axis 'error' bars are ±0.06 but not visible due to the scaling of the plot.

effectively remove isobaric interference from large soil masses containing lower mass fractions of Cd, ~ 152 ng g^{-1} according to the reference material information sheet.

For the three nuclear debris test portions analysed, elevations are observed in the $^{111/110}$Cd, $^{112/110}$Cd, $^{114/110}$Cd and $^{116/110}$Cd ratios. A three-isotope plot of the measured δ values reveals that the observed elevated ratios are not the result of mass-dependent fractionation (Figure 4). Rather, the nuclear debris displayed a mass-independent isotope pattern consistent with what would be expected for fission product decay inputs.

^{110}Cd is a blocked isotope (beta decay chain terminates at stable ^{110}Pd) and is not produced by nuclear fission. Therefore, it is possible to correct the nuclear debris values for the natural Cd contribution and estimate relative cumulative fission yields for each Cd isotope (Table 6). These yields were calculated by subtracting the natural isotopic ratios from those measured in the debris using ^{110}Cd as the common denominator, then dividing by the value obtained for mass 111 in each test solution. The highest cumulative fission yield for all three nuclear debris test solutions is observed for mass 111, with inputs decreasing somewhat with increasing mass (Table 6).

The measured relative cumulative fission yield values in the nuclear debris can be compared with end-point values previously determined by mass spectrometry in nuclear fuel (Table 6, Figure 5) (Lisman *et al.* 1969, de Laeter and Thode 1975, Mathews 1977). The measured values are quite similar to those reported by Lisman *et al.* (1969) for fast Pu fission observed in fuel rods from EBR-1. The measured

Table 6.
Calculated relative cumulative fission yields. Reported 114 values for ^{235}U*Thermal*, ^{238}U*Epithermal* and ^{239}Pu*Thermal* are combined 113 + 114 mass values due to the large cross section of 113 contributing to the increase in mass 114 preventing individual fission yield determination

Relative Cumulative Fission Yield

Material	**111**	±	**112**	±	**114**	±	**116**	±
ND-1	1	0.004	0.383	0.010	0.144	0.027	0.044	0.010
ND-2	1	0.023	0.476	0.054	0.143	0.124	0.101	0.054
ND-3	1	0.024	0.510	0.055	0.121	0.127	0.051	0.055
EBR-1	1	0.008	0.551	0.004	0.262	0.002	0.169	0.002
^{235}UThermal	1	0.105	0.876	0.099	0.744	0.055	0.826	0.829
^{238}UEpithermal	1	0.082	0.789	0.074	0.474	0.064	0.526	0.527
^{239}PuThermal	1	0.010	0.470	0.010	0.480	0.010	0.170	0.010

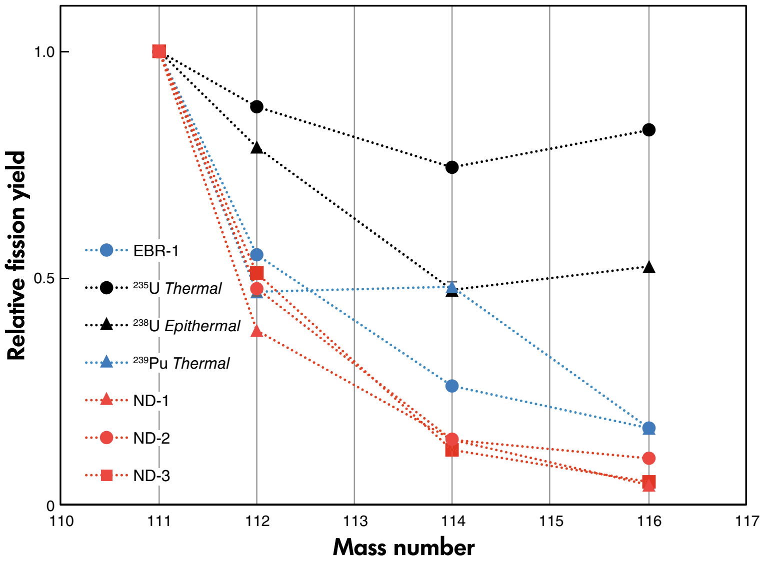

Figure 5. Relative cumulative fission yields calculated for the three nuclear debris test solutions and previously measured nuclear fuels. Error bars have been omitted for clarity.

values also closely resemble the endpoints for Pu fission reported by Mathews, consistent with Pu being the dominant fissioning fuel type for the debris examined in this study.

Similar mixtures of natural Cd and fissiogenic inputs were previously documented in material from the Oklo reservoir. These materials showed a range of mass independent fractionation and cumulative fission yields that more closely mirror the expected values for ^{235}U thermal, reflecting the dominant fissioning isotope in the natural nuclear reactor, which is clearly distinguishable from ^{239}Pu.

Conclusions

A new method has been developed for the measurement of Cd isotopic ratios in geological material containing low concentrations of Cd and has been applied to nuclear debris. This method allows for the purification and measurement of Cd in large test portions (~ 1 g of solid material) while ensuring thorough removal of interfering elements. This method has been validated through the measurement of a number of reference materials showing excellent agreement with previously published values.

The nuclear debris analysed exhibit large mass-independent isotopic perturbations consistent with the beta-decay of short-lived fission product isotopes at masses 111, 112, 114 and 116. From this data, relative cumulative fission yields for the different mass numbers were calculated. The cumulative yields determined for the nuclear debris is concordant with previous values measured for Pu reactor fuel, consistent with Pu being the dominant fissioning fuel type in the nuclear debris. This is the first time Cd isotopic perturbations have been measured in nuclear debris. The results demonstrate that mass spectrometry can be an alternative method to determine the total fission product inputs in the valley region of the fission product yield curve, as opposed to the more traditional approach involving radiometric measurements of short-lived isotopes.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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