Supporting Information

Selective Diffusive Gradients in Thin Films (DGT) for the Simultaneous Assessment of Labile Sr and Pb Concentrations and Isotope Ratios in Soils

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# Contents

| Section                                                                 | Page |
|------------------------------------------------------------------------|------|
| **Experimental Section**                                               |      |
| Laboratory procedures and materials                                    | S-3  |
| Table S1. Instrumental setups and parameters for Sr and Pb isotope ratio measurements | S-4  |
| Figure S1. Uptake efficiency of TK100 resin and gels for Sr            | S-5  |
| Uncertainty estimation                                                 | S-6  |
| Diffusion cell experiment                                              | S-7  |
| Solution preparation in pH and ionic strength experiments              | S-8  |
| Solution preparation and analysis in time-dependent accumulation and isotopic fractionation experiments | S-9  |
| Table S2. Composition of synthetic soil solutions                      | S-10 |
| DGT deployment, soil solution sampling, and NH$_4$NO$_3$ extraction     | S-11 |
| **Results and Discussion**                                            |      |
| Table S3. Applied elution schemes and elution recoveries               | S-12 |
| Table S4. Diffusion coefficients of Sr and Pb in APA diffusive gel     | S-13 |
| Table S5. DGT-measured solution concentrations ($c_{\text{DGT}}$), bulk solution concentrations ($c_{\text{soln}}$), and ratios of $c_{\text{DGT}}$ to $c_{\text{soln}}$ values of Pb in synthetic soil solutions | S-14 |
| Table S6. Efficiency of TK100 DGT for separation of Sr and Pb from different potentially interfering matrix cations | S-15 |
| Table S7. Elemental mass concentrations in soil solutions of the experimental soils | S-16 |
| Table S8. Isotope ratios of Sr and Pb in NH$_4$NO$_3$ ($c = 1 \text{ mol L}^{-1}$) extracts of the experimental soils | S-17 |
Experimental Section

To comply with notation conventions used in DGT literature, the symbol $c$ is used throughout this work for both molar and mass concentrations in solution instead of the designated symbols $c$ and $\gamma$ recommended by the International Union of Pure and Applied Chemistry (IUPAC).

Laboratory procedures and materials

Polyethylene (PE) vials, containers, test tubes, and pipette tips, as well as piston-type acrylonitrile butadiene styrene (ABS) DGT moldings (R-SDU; DGT Research Ltd., UK) were pre-cleaned in a two-stage washing procedure with dilute HNO$_3$ ($w = 10\%$ and $w = 1\%$, respectively; p.a., Merck, DE), rinsed with laboratory water type 1 (0.055 $\mu$S cm$^{-1}$; TKAGenPure, Thermo Electron LED GmbH, DE) and dried in a metal-free class 100 laminar flow cabinet. Laboratory water type 1 was used for preparing all experimental solutions. Laboratory water type 1, as well as concentrated HCl ($w = 37\%$; trace metals basis, PanReac AppliChem, DE) and HNO$_3$ ($w = 65\%$; p.a., Merck, DE) were further purified by sub-boiling distillation (DST-100, Savillex, USA) and used for pre-cleaning, conditioning, rinsing, storage, and elution of TK100 membranes as well as all ICP-MS analyses. Wherever possible, handling and preparation of DGT components and samples was performed in a laminar flow cabinet (Clean Air, EuroFlow EF/S, Telstar Laboratory Equipment B.V., NL). Chemical reagents of analytical grade or higher were used in all experiments. Single element stock solutions were prepared by dissolving Sr(NO$_3$)$_2$ (Merck), Pb(NO$_3$)$_2$ (Merck), NaNO$_3$ (Merck), Mg(NO$_3$)$_2$ (Merck), KNO$_3$ (VWR, AT), Ca(NO$_3$)$_2 \times 4$ H$_2$O (Merck), RbCl (Fluka, CH), HgCl$_2$ (Alfa Aesar, USA), and NH$_4$NO$_3$ (VWR). These stocks were used for preparing the experimental single- or multielement solutions. Certified isotopic reference standards were obtained from the National Institute of Standards and Technology, USA (NIST SRM 987, SrCO$_3$; NIST SRM 981, $\geq 99.9\%$ purity lead metal).
Table S1. Instrumental setups and parameters for Sr and Pb isotope ratio measurements

| Parameter                  | Sr                                          | Pb                                          |
|----------------------------|---------------------------------------------|---------------------------------------------|
| RF power                   | 1300 W                                      | 1300 W                                      |
| Coolant flow               | 13 L/min                                    | 13 L/min                                    |
| Auxiliary flow             | 0.9 L/min                                   | 0.9 L/min                                   |
| Nebulizer pressure         | 30 psi                                      | 26-31 psi                                   |
| Interface cones            | Nickel, dry                                 | Nickel, dry                                 |
| Sample introduction system | Apex Omega with MicroFlow PFA-ST nebulizer (both ESI) | Aridus II (Teledyne CETAC) with MicroFlow PFA-ST nebulizer (ESI) |
| Measurement mode           | Static batch analysis (6 blocks with 10 measurement cycles with 10 s integration time) | Static batch analysis (6 blocks with 10 measurement cycles with 10 s integration time) |
| Resolution mode            | \( \frac{m}{\Delta m} \approx 300 \)        | \( \frac{m}{\Delta m} \approx 300 \)        |
| Cup configuration          | H10: \(^{91}\)Zr; H8: \(^{90}\)Zr; H6: \(^{86}\)Sr; H4: \(^{84}\)Sr; H2: \(^{86}\)Sr; Ax: \(^{85}\)Rb; L2: \(^{84}\)Sr; L4: \(^{83}\)Kr; L6: \(^{82}\)Kr | H3: \(^{208}\)Pb; H2: \(^{207}\)Pb; H1: \(^{206}\)Pb; Ax: \(^{205}\)Tl; L1: \(^{204}\)Pb; L2: \(^{207}\)Tl; L3: \(^{202}\)Hg |
| Axial mass / mass separation | 85 / 0.5                                    | 205 / 1                                     |
| Typical sensitivity        | 900 V/(µg g\(^{-1}\))                       | 1300 V/(µg g\(^{-1}\))                     |

| Parameter                  | MC ICP-MS Nu Plasma HR (NP048, Nu Instruments) b | MC ICP-MS Nu Plasma HR (NP048, Nu Instruments) b |
|----------------------------|-----------------------------------------------|-----------------------------------------------|
| RF power                   | 1300 W                                        | 1300 W                                        |
| Coolant flow               | 13 L/min                                      | 13 L/min                                      |
| Auxiliary flow             | 0.9 L/min                                      | 0.9 L/min                                     |
| Nebulizer pressure         | 26-31 psi                                     | 26-31 psi                                     |
| Interface cones            | Nickel, dry                                   | Nickel, dry                                   |
| Sample introduction system | Aridus II (Teledyne CETAC) with MicroFlow PFA-ST nebulizer (ESI) | Aridus II (Teledyne CETAC) with MicroFlow PFA-ST nebulizer (ESI) |
| Measurement mode           | Static batch analysis (6 blocks with 10 measurement cycles with 10 s integration time) | Static batch analysis (6 blocks with 10 measurement cycles with 10 s integration time) |
| Resolution mode            | \( \frac{m}{\Delta m} \approx 300 \)        | \( \frac{m}{\Delta m} \approx 300 \)        |
| Cup configuration          | H6: \(^{91}\)Zr; H5: \(^{90}\)Zr; H2: \(^{88}\)Sr; Ax: \(^{87}\)Sr; L2: \(^{86}\)Sr; L3: \(^{85}\)Rb; L4: \(^{84}\)Sr | H4: \(^{208}\)Pb; H3: \(^{207}\)Pb; H2: \(^{206}\)Pb; H1: \(^{205}\)Tl; Ax: \(^{204}\)Pb; L1: \(^{207}\)Tl; L2: \(^{202}\)Hg |
| Axial mass / mass separation | 87 / 0.5                                     | 204 / 1                                      |
| Typical sensitivity        | 130 V/(µg g\(^{-1}\))                        | 385 V/(µg g\(^{-1}\))                       |

\( \text{a Used for the following isotope ratio measurements: Sr in synthetic soil solutions; Sr in natural soil samples; Pb in synthetic soil solutions; Pb in natural soil samples} \)

\( \text{b Used for the following isotope ratio measurements: Investigation of time-dependent Sr isotopic fractionation; Sr in separated NH}_4\text{NO}_3 \text{ soil extracts; Pb in separated NH}_4\text{NO}_3 \text{ soil extracts} \)
Figure S1. Uptake efficiency of TK100 resin and gels for Sr. Error bars show 1SD ($n = 4$). Experimental conditions: $V = 10$ mL, $c$(Sr) = 500 µg L$^{-1}$, pH = 5.5, $c$(NaCl) = 0.01 mol L$^{-1}$, $t = 24$ h.
Uncertainty estimation

Combined uncertainties ($u_c$) of the Sr and Pb uptake and elution factors were calculated as the square root of the sum of the squared standard deviations of the measurement repeatability ($n = 3$ for single-step elution; $n = 4$ for three-step elution) and reproducibility ($n = 2$). $u_c$ of DGT-measured concentrations were calculated according to Kreuzeder et al.\textsuperscript{1} and $u_c$ of the DGT-measured isotope ratios were calculated according to Horsky et al.,\textsuperscript{2} both including the DGT application repeatability ($n = 3$). Uncertainties provided on $c_{\text{DGT}}/c_{\text{soln}}$ values were calculated based on the uncertainties of both $c_{\text{DGT}}$ and $c_{\text{soln}}$. Uncertainties provided on $\Delta_{\text{std}}(\delta/\epsilon)_{\text{DGT/Ref}}$ values were calculated based on the uncertainties of both $\delta_{\text{std}}(\delta/\epsilon)_{\text{DGT}}$ and $\delta_{\text{std}}(\delta/\epsilon)_{\text{Ref}}$. The expanded uncertainty $U$ was obtained by multiplying $u_c$ with a coverage factor ($k$) of two.
Diffusion cell experiment

The diffusion cell was made of two 150 mL poly(methyl 2-methylpropenoate) compartments, each equipped with a circular 1.6 cm diameter opening. A 2.5 cm diameter APA diffusive gel with 0.8 mm thickness was placed between the openings and the compartments were clamped together. The compartments were filled with 100 mL of NaNO$_3$ solution ($c = 0.01$ mol L$^{-1}$) either with Sr ($c = 5$ mg L$^{-1}$; source solution) or without Sr (receptor solution). The source and receptor solutions were stirred continuously using magnetic stirrers. After 10 min of equilibration, 200 µL aliquots were taken from both reservoirs every 10 min for 2.5 h, acidified to give a dilute HCl ($w = 2\%$) matrix and analyzed by ICP-MS. $D$(Sr) was calculated from the slope (ng s$^{-1}$) of the regression line and the mass concentration of Sr in the source solution as described previously.$^{3, 4}$ The diffusion cell experiment was repeated three times over the course of three different days to assess the within-lab reproducibility. The pH and temperature of both solutions was measured at the start and end of each experiment and remained constant (pH 5.3 ± 0.1; $T = 22.3 \, ^{\circ}C \pm 0.4 \, ^{\circ}C$).
Solution preparation and analysis in pH and ionic strength experiments

To test the effect of pH on TK100 DGT performance for simultaneous sampling of Sr and Pb, TK100 DGT devices were deployed in solutions with pH 3.9, 4.8, 6.5, 7.5, and 8.2 at a constant NaNO₃ ($c = 0.01 \text{ mol L}^{-1}$) background. The pH was adjusted using dilute HNO₃ or NaOH (both $c = 1 \text{ mol L}^{-1}$). Solutions with pH 6.5, 7.5, and 8.2 were buffered with 2-morpholin-4-ylethanesulfonic acid (MES), 3-(Morpholin-4-yl)propane-1-sulfonic acid (MOPS), and 2-[4-(2-Hydroxyethyl)piperazin-1-yl]ethane-1-sulfonic acid (HEPES), respectively (all $c = 0.05 \text{ mol L}^{-1}$), to ensure a stable pH during the deployment period. These solutions were further prepared with an ionic background of NaNO₃ ($c = 0.001 \text{ mol L}^{-1}$) and Mg(NO₃)₂ ($c = 0.004 \text{ mol L}^{-1}$) to reduce sorption of Pb to the container walls at elevated pH. To test the effect of ionic strength, TK100 DGTs were deployed in solutions containing NaNO₃ at $c = 0.001$, 0.01, 0.1, and 0.75 mol L⁻¹. The pH of these (non-buffered) solutions decreased over the deployment time from pH ~5 to ~4 due to H⁺ release from HDEHP following ion exchange with Sr²⁺ and Pb²⁺. In both pH and ionic strength experiments, the Sr and Pb spikes were added 24 h before DGT deployment, the solution temperature (24.9 °C ± 0.9 °C) was monitored over the deployment period, and grab samples ($n = 3$) were analyzed by ICP-MS.
Solution preparation and analysis in time-dependent accumulation and isotopic fractionation experiments

To investigate the time-dependent analyte accumulation and possible isotopic fractionation, TK100 DGT devices were deployed for 2, 4, 6, 8, 10, 16, and 24 h in the deployment solution \([c(\text{Sr}) = 50 \text{ mg L}^{-1}; \delta_{\text{SRM 987}}(^{87}\text{Sr}/^{86}\text{Sr}) = -3.74 \pm 0.30 \% \text{‰}; \text{c(NaNO}_3\text{)} = 0.01 \text{ mol L}^{-1}]\). The pH of the deployment solution was adjusted and buffered to 6.6 ± 0.1 using NaOH \((c = 1 \text{ mol L}^{-1})\) and MES \((c = 0.05 \text{ mol L}^{-1})\), respectively. Grab samples were taken at each time point and analyzed for Sr concentrations by ICP-MS as well as for changes in Sr isotope ratios by MC ICP-MS. Eluates were measured by ICP-MS to determine the mass of Sr adsorbed on TK100 membranes. Moreover, \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in DGT eluates, \(\delta_{\text{SRM 987}}(^{87}\text{Sr}/^{86}\text{Sr})_{\text{DGT}}\), were measured by MC ICP-MS and compared to those in grab samples to evaluate possible isotopic fractionation effects. The solution temperature was monitored over the deployment period and remained stable at 23.1 °C ± 0.4 °C.
Table S2. Composition of synthetic soil solutions

| Parameter | Unit     | Mean value(s) in synthetic soil solutions | Typical values in natural soil solutions | Reference |
|-----------|----------|------------------------------------------|------------------------------------------|-----------|
| pH        |          | 6.0 \(^a\)                             | 3 - 8                                    | 6         |
| \(I\)     | mol L\(^{-1}\) | 0.013                                   | 0.004 - 0.016 \(^b\)                     | 6         |
| \(c(Mg)\) | mg L\(^{-1}\) | 11.9                                    | 0.1 - 25                                 | 6         |
| \(c(K)\)  | mg L\(^{-1}\) | 13.1                                    | 1 - 30                                   | 6         |
| \(c(Ca)\) | mg L\(^{-1}\) | 51; 112; 159                            | 1 - 160                                  | 6         |
| \(c(Rb)\) | µg L\(^{-1}\) | 208                                     | 1 - 1000                                 | 7, 8      |
| \(c(Sr)\) | µg L\(^{-1}\) | 275                                     | 1 - 1000                                 | 9, 10, 11 |
| \(c(Pb)\) | µg L\(^{-1}\) | 15                                      | <1 - 1000                                | 6, 12     |

\(^a\) pH was buffered using MES (\(c = 0.05\) mol L\(^{-1}\)). \(^b\) \(I\) was calculated from literature values of the electrical conductivity according to Alva et al.\(^{13}\)
DGT deployment, soil solution sampling, and NH$_4$NO$_3$ extraction

For DGT deployment, ~150 g of each soil sample was mixed with laboratory water type 1 to reach 100% of their maximum water holding capacity. The saturated soil pastes were incubated at 24 °C for 24 h and then applied as a ~2 mm-thick layer on the DGT devices ($n = 3$). The DGTs were then gently tapped a few times to ensure a complete contact between the filter surface of the sampler and the soil. DGT sampling was conducted in closed plastic boxes for 24 h at 24 °C in an incubator. After deployment, DGTs were washed to remove the adhering soil paste and disassembled. The TK100 discs were retrieved and subjected to three-step elution. Sub-samples ($V = \sim 20$ mL) of the incubated soil pastes were used to collect soil solution by centrifugation at 5000 × g for 15 min. The supernatants were passed through a 0.45 µm-pore size PES syringe filter, immediately acidified to give a dilute HCl (w = 2%) matrix, and then analyzed by ICP-MS. In parallel, NH$_4$NO$_3$ ($c = 1$ mol L$^{-1}$) extraction of soil samples was performed according to DIN ISO 19730. The NH$_4$NO$_3$ extracts were diluted 20-fold and subjected to matrix separation using an automated, low-pressure chromatographic system (prepFAST-MC, ESI). Simultaneous separation of Sr and Pb was achieved using self-packed columns with 3 mL bed volume of DGA resin (TrisKem). Recoveries over all samples were ≥98% for Sr and ≥71% for Pb. A detailed description of the procedure can be found elsewhere.
Results and Discussion

Table S3. Applied elution schemes and elution recoveries (expressed as elution factors $f_e$) determined in mass balance experiments

| Elution scheme | Analyte | $\text{HNO}_3$ ($c = 8 \text{ mol L}^{-1}$) | HCl ($c = 0.01 \text{ mol L}^{-1}$) | HCl ($c = 2 \text{ mol L}^{-1}$) | HCl ($c = 6 \text{ mol L}^{-1}$) | total |
|----------------|---------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-------|
| (1) single-step | Sr      | -                               | -                               | -                               | -                               | 0.95 ± 0.02 | 0.95 ± 0.02 |
|                | Pb      | -                               | -                               | 0.82 ± 0.04                     | 0.82 ± 0.04                     |       |
| (2) three-step (not further used) | Sr | 0.42 ± 0.01 | - | 0.56 ± 0.01 | 0.02 ± <0.01 | 1.00 ± 0.01 |
|                | Pb | 0.27 ± 0.01 | - | 0.17 ± 0.02 | 0.47 ± 0.02 | 0.91 ± 0.01 |
| (3) three-step | Sr | 0.23 ± 0.03 | 0.75 ± 0.03 | 0.01 ± <0.01 | 0.99 ± 0.01 |
|                | Pb | 0.04 ± 0.01 | 0.31 ± 0.01 | 0.56 ± 0.02 | 0.90 ± 0.01 |
|                | Ca | - | 0.73 ± 0.01 | 0.30 ± 0.03 | 0.02 ± 0.01 | 1.05 ± 0.03 |
|                | Rb | - | 0.90 ± 0.02 | 0.09 ± <0.01 | <LOD | 0.99 ± 0.02 |
|                | Hg | - | 0.02 ± <0.01 | 0.58 ± 0.01 | 0.21 ± <0.01 | 0.81 ± 0.01 |

a Errors are combined uncertainties ($u_c$) for Sr and Pb in elution schemes (1) and (3), all others are 1SD ($n = 4$).
Table S4. Diffusion coefficients ($D; \times 10^{-6}$ cm$^2$ s$^{-1}$) of Sr and Pb in APA diffusive gel. $D$(Sr) was measured in a diffusion cell experiment and calculated for different temperatures between 1 °C and 35 °C. $D$(Pb) values were taken from DGT Research Ltd.\textsuperscript{17}

| Temperature (°C) | $D$(Sr) | $D$(Pb) |
|-----------------|---------|---------|
| 1               | 2.88    | 3.75    |
| 2               | 2.99    | 3.89    |
| 3               | 3.10    | 4.04    |
| 4               | 3.21    | 4.18    |
| 5               | 3.33    | 4.34    |
| 6               | 3.45    | 4.49    |
| 7               | 3.57    | 4.65    |
| 8               | 3.70    | 4.81    |
| 9               | 3.82    | 4.97    |
| 10              | 3.95    | 5.14    |
| 11              | 4.08    | 5.31    |
| 12              | 4.22    | 5.49    |
| 13              | 4.35    | 5.66    |
| 14              | 4.49    | 5.84    |
| 15              | 4.63    | 6.03    |
| 16              | 4.77    | 6.21    |
| 17              | 4.92    | 6.40    |
| 18              | 5.07    | 6.59    |
| 19              | 5.22    | 6.79    |
| 20              | 5.37    | 6.99    |
| 21              | 5.53    | 7.19    |
| 22              | 5.68    | 7.40    |
| 23              | 5.84    | 7.60    |
| 24              | 6.01    | 7.82    |
| 25              | 6.17    | 8.03    |
| 26              | 6.34    | 8.25    |
| 27              | 6.51    | 8.47    |
| 28              | 6.68    | 8.69    |
| 29              | 6.85    | 8.92    |
| 30              | 7.03    | 9.15    |
| 31              | 7.21    | 9.38    |
| 32              | 7.39    | 9.62    |
| 33              | 7.57    | 9.86    |
| 34              | 7.76    | 10.1    |
| 35              | 7.95    | 10.3    |
Table S5. DGT-measured solution concentrations ($c_{\text{DGT}}$), bulk solution concentrations ($c_{\text{soln}}$), and $c_{\text{DGT}}/c_{\text{soln}}$ ratios of Pb in synthetic soil solutions a

| Solution | $c(\text{Ca})$ / mg L$^{-1}$ | $c_{\text{DGT}}$ / µg L$^{-1}$ | $c_{\text{soln}}$ / µg L$^{-1}$ | $c_{\text{DGT}}/c_{\text{soln}}$ |
|----------|-----------------|------------------|-----------------|------------------|
| A        | 51.4 ± 1.6      | 13.3 ± 1.6       | 13.7 ± 0.3      | 0.97 ± 0.12      |
| B        | 112 ± 10        | 16.5 ± 2.0       | 15.9 ± 0.7      | 1.04 ± 0.13      |
| C        | 159 ± 6         | 15.6 ± 3.6       | 15.2 ± 0.9      | 0.93 ± 0.24      |

a Errors are expanded uncertainties ($U, k = 2$)
Table S6. Efficiency of TK100 DGT for separation of Sr and Pb from different potentially interfering matrix cations

| Matrix cation | Sr      | Pb      |
|--------------|---------|---------|
| Mg$^{2+}$    | 99 ± 1 %| 100 ± <1 % |
| K$^+$        | 93 ± <1 %| 100 ± <1 % |
| Ca$^{2+}$    | 94 ± 2 %| 100 ± <1 % |
| Rb$^+$       | 99 ± <1 %| 100 ± <1 % |

*Matrix separation is expressed as average relative difference between the elemental mass concentration ratio in the synthetic soil solutions and in the DGT eluates. Errors are 1SD ($n = 3$).*
**Table S7.** Elemental mass concentrations in soil solutions of the experimental soils obtained by centrifugation of incubated soil pastes\(^a\)

| Soil sample | \(c(\text{Mg})\) (mg L\(^{-1}\)) | \(c(\text{K})\) (mg L\(^{-1}\)) | \(c(\text{Ca})\) (mg L\(^{-1}\)) | \(c(\text{Rb})\) (µg L\(^{-1}\)) | \(c(\text{Sr})\) (µg L\(^{-1}\)) | \(c(\text{Pb})\) (µg L\(^{-1}\)) |
|-------------|----------------------------------|----------------------------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|
| SL          | 9.02 ± 1.70                      | 6.90 ± 0.80                      | 53.4 ± 9.41                      | 13.3 ± 1.6                      | 183 ± 36                        | 0.95 ± 0.12                     |
| AC          | 17.7 ± 4.8                       | 20.1 ± 3.0                       | 59.6 ± 17.9                     | 26.4 ± 3.0                      | 218 ± 63                        | 362 ± 23                       |
| MC          | 63.5 ± 2.6                       | 5.43 ± 0.38                      | 488 ± 23                        | 13.9 ± 0.7                      | 865 ± 30                        | 108 ± 5                        |

\(^a\) Errors are expanded uncertainties \((U, k = 2)\).
Table S8. Isotope ratios of Sr and Pb in NH$_4$NO$_3$ ($c = 1$ mol L$^{-1}$) extracts of the experimental soils $^a$

| Soil sample | $\delta^{\text{SRM 987}}_{\text{NH}_4\text{NO}_3}/(^{87}\text{Sr}/^{86}\text{Sr})$ | $\delta^{\text{SRM 981}}_{\text{NH}_4\text{NO}_3}/(^{207}\text{Pb}/^{206}\text{Pb})$ |
|-------------|---------------------------------|---------------------------------|
| SL          | 12.8 ± 0.3                      | n.m.                            |
| AC          | 0.33 ± 0.28                     | -67.2 ± 0.4                     |
| MC          | -1.24 ± 0.29                    | -67.4 ± 0.3                     |

$^a$ Errors are expanded uncertainties ($U, k = 2$). n.m. = not measured.
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