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Non-exchangeable stable hydrogen isotope ratios in clay minerals and soil clay fractions: A method test

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Abstract

Stable hydrogen isotope ratios ($\delta^2 H$ values) in structural hydroxyl groups of pedogenic clay minerals are inherited from the surrounding water at the time of their formation. Only non-exchangeable H preserves the environmental forensic and paleoclimate information ($\delta^2 H_n$ value). To measure $\delta^2 H_n$ values in structural H of clay minerals and soil clay fractions, we adapted a steam equilibration method by accounting for high hygroscopicity. Our $\delta^2 H_n$ values for USGS57 biotite ($-95.3 \pm$ SD $0.9\permil$) and USGS58 muscovite ($30.7 \pm 1.4\permil$) differed slightly but significantly from the reported $\delta^2 H$ values ($-91.5 \pm 2.4\permil$ and $-28.4 \pm 1.6\permil$), because the minerals contained 1.1%–4.4% of exchangeable H. The low SD of replicate measurements ($n = 3$) confirmed a high precision. The clay separation method including destruction of Fe oxides, carbonates and soil organic matter, and dispersion did not significantly change the $\delta^2 H_n$ values of five different clay minerals. However, we were unable to remove all organic matter from the soil clay fractions resulting in an estimated bias of $1\permil$ in two samples and $15\permil$ in the carbon-richest sample. Our results demonstrate that $\delta^2 H_n$ values of structural H of clay minerals and soil clay fractions can be reliably measured without interference from atmospheric water and the method used to separate the soil clay fraction.

Highlights

- We tested steam equilibration to determine stable isotope ratios of structural H in clay.
- Gas-tight capsule sealing in Ar atmosphere was necessary to avoid remoistening.
- Our steam equilibration method showed a high accuracy and precision.
- The clay separation method did not change stable isotope ratios of structural H in clay.

1 | INTRODUCTION

The stable isotope ratios of structural H in clay minerals and soil clay fractions, which cannot easily be exchanged with water (δ^2H_n values), reflect that of ambient soil water at the time of mineral formation (Gilg & Sheppard, 1996; Lawrence & Taylor, 1972; Savin & Epstein, 1970a). The δ^2H_n values of structural H in minerals might bear geographic information similar to those of soil organic matter (SOM; Ruppenthal et al., 2015). This is attributed to the fact that the H-isotopic composition of soil water is related to that of local precipitation and is influenced by evapotranspiration in the soil–plant system, both of which vary with location (Bowen, 2021; Sprenger et al., 2016). Moreover, clay minerals could serve as paleoclimate indicators, because of the partly high geological age. Furthermore, clay minerals are more frequent than the authigenic carbonate minerals that are currently the most commonly used paleoclimate indicators in soils (Cerling, 1984; VanDeVelde & Bowen, 2013).

To reliably determine δ^2H_n values of structural H in clay minerals requires the removal of the influence of exchangeable H. The exchangeable H in clay minerals comprises adsorbed and interlayer water, which quickly equilibrates with ambient water and thus does not bear a stable isotopic signal (Bauer & Vennemann, 2014). The current state-of-the-art methods for continuous flow isotope ratio mass spectrometry (CF-IRMS) remove the exchangeable H at varying temperatures ranging between 100 and 250°C under vacuum (Bauer & Vennemann, 2014; Gilg et al., 2004; VanDeVelde & Bowen, 2013). Because different clay minerals require different temperatures for the removal of exchangeable H (Gilg et al., 2004), the currently applied methods cannot guarantee to always remove the entire exchangeable H pool in clay minerals or clay fractions. Another methodological challenge originates from the fact that after vacuum drying, a hygroscopic sample quickly attracts atmospheric water. This reintroduces exchangeable H, which must be prevented (Bauer & Vennemann, 2014; Bowen et al., 2005; VanDeVelde & Bowen, 2013).

An alternative to vacuum drying methods is provided by steam equilibration. A mass balance calculation after equilibrating the same clay mineral or fraction sample with several waters of different H-isotopic composition allows for the quantification of the contribution of exchangeable H to the total H pool and of the δ^2H_n values

(Schimmelmann, 1991). However, such methods have up to now mostly been applied to determine non-exchangeable H in organic matter (Bowen et al., 2005; Epstein et al., 1976; Hobson et al., 2012; Kelly et al., 2009; Qi & Coplen, 2011; Ruppenthal et al., 2013, 2015; Schimmelmann, 1991; Schimmelmann et al., 2020; Soto et al., 2017; Wassenaar & Hobson, 2000, 2003) and bulk soil (Ruppenthal et al., 2010). The only study we know of in which steam equilibration was applied to a clay mineral is that of Hsieh and Yapp (1999), who determined the δ^2H_n value of halloysite. However, steam equilibration was not further developed to a standard method for clay minerals (Gilg et al., 2004) or soil clay fractions.

To measure the δ^2H value of non-exchangeable H in soil clay fractions requires the separation of this fraction. To reach a full dispersion of the soil particles, Fe oxides, carbonates and SOM must be removed, using chemicals that might attack hydroxyl groups and thus have an effect on the δ^2H_n values of clay fractions. The removal of iron oxides by the dithionite-citrate-bicarbonate (DCB) method of Mehra and Jackson (1958) and carbonates by acetic acid was shown to not affect the δ^2H values of hydrous minerals (Gilg et al., 2004). The commonly used removal method for SOM by oxidation with hydrogen peroxide (H_2O_2) can change δ^2H values of some clay minerals, for example, montmorillonite (Hyeong & Capuano, 2000). Similarly, the alternative treatment with disodium peroxodisulphate ($Na_2O_8S_2$) showed a strong positive shift of the δ^2H values after the treatment of a montmorillonite sample (Menegatti et al., 1999). However, Hyeong and Capuano (2000) and Menegatti et al. (1999) did not test the possibility that the apparent change in δ^2H values after treatment with H_2O_2 or $Na_2O_8S_2$ was related to an unaccounted remoistening of the hygroscopic samples. We suggest that remoistening must be ruled out, before these two chemicals are defined as inappropriate for the purpose of determining δ^2H_n values of soil clay fractions. Moreover, both SOM oxidation methods may not remove organic matter exhaustively so that the measured δ^2H_n values of clay fractions need to be corrected for the δ^2H_n values of the remaining organic matter.

We hypothesised that (a) we can adapt a steam equilibration method, formerly applied to SOM and bulk soil (Ruppenthal et al., 2013) for clay minerals and clay fractions of soils and thereby strictly avoid remoistening of the hygroscopic samples via exchange with atmospheric

water. Moreover, we hypothesised that (b) the traditional treatment of soil samples (with the extraction of iron oxides, the removal of carbonates and SOM and the separation of the clay fraction) does not alter the isotopic composition of the non-exchangeable H pool of clay minerals.

2 | MATERIALS AND METHODS

2.1 | Samples

We used kaolinite (KGa-2), illite (IMt-2), Na-montmorillonite (SWy-3) and Mg-montmorillonite (SCa-3) distributed by the Clay Mineral Society (Chantilly, VA) and a vermiculite (contributed by Stefan Dultz, Hannover, Germany) as clay mineral reference materials (Table 1). SCa-3 and IMt-2 were delivered as brittle rock chips with a macroscopically visible heterogeneity in grain sizes and colours. SWy-3 and KGa-2 were delivered as fine-grained powders. The standards are described by the baseline studies of the Clay Minerals Society Source Clays (Borden & Giese, 2001; Chipera & Bish, 2001; A. U. Dogan et al., 2006; M. Dogan et al., 2007; Guggenheim & Van Groos, 2001; Kogel & Lewis, 2001; Mermut & Cano, 2001) and by Hower and Mowatt (1966) for IMt-2. The vermiculite was characterised by Dultz et al. (2005), Bors et al. (1997), Steudel (2008) and Steudel, Batenburg, et al. (2009).

Moreover, we used A horizons from the Osobita mountain in Slovakia (Oso, Lobe et al., 1998) and two sites near Karlsruhe (KA-1 and KA-2) in Germany (Table 2). We chose these samples because of their high concentrations of clay and SOM. High clay concentrations complicate the removal of SOM (Eusterhues et al., 2005; Kaiser et al., 2002; Mikutta et al., 2005; von Lützow et al., 2007) required for subsequent analysis of the isotope ratio of H in clay. Therefore, the treatment intensity and duration needed to be adjusted to constitute a worst-case test for methodological artefacts.

2.2 | Clay separation

We sieved the three air-dried A-horizon samples to <2 mm. The clay standards IMt-2 and SCa-3 were gently ground to this size with a hand mortar. Depending on the estimated clay content, 5–20 g of air-dry sample were weighed in a 250-mL wide mouth centrifuge bottle (PPCC, Nalgene, Thermo Fisher Scientific, Waltham, MA). To collect enough material for all analyses, we used 3–4 bottles per sample.

The following treatment steps and their sequence were chosen according to the recommendations of Gilg et al. (2004) and VanDeVelde and Bowen (2013). We treated the clay mineral standards and the topsoil samples during the clay separation process in the same manner, using the residual sediment of each step for the subsequent step, respectively (Figure 1).

To extract iron oxides, we used the DCB method of Mehra and Jackson (1958). We added 100 mL of 0.3 M Na-citrate and 15 mL of 1 M $NaHCO_3$ (both Carl Roth, Karlsruhe, Germany) solutions to the sample and the bottle was shaken for 1 h. Then, we added ∼7 g of Na-dithionite (Supelco, Merck, Darmstadt, Germany) to each beaker, while stirring at 60°C in a water bath under a fume hood, until the soil sediment lost the yellowish/brownish colour. After centrifugation (Heraeus Multifuge X3R with rotor TX-1000, Thermo Fisher Scientific) at a relative centrifugal force of 709 g for 5–60 min, we decanted the transparent supernatant into a separate beaker and added 100 mL of 0.3 M Na-citrate solution. This step was repeated once and the extracts were combined and made up to 1 L for Fe analysis with an atomic absorption spectrometer (Perkin-Elmer AAS 3100, Waltham, MA). If not noted otherwise, all chemicals used in this study were *pro analysis* quality, and the water was deionised.

Afterwards, we washed the samples three times by shaking the solution with 1 M NaCl solution (Carl Roth) for 1 h on an overhead shaker, centrifuged them for 10–30 min at 4122 g and decanted them. A fourth wash was done with 0.5 M NaCl solution.

To remove carbonates, soluble sulphates and salts without dissolving clay minerals, we made up the remaining sediment to 100 mL with deionised water and added 25 mL Na-acetate acetic acid buffer (164 g Na-acetate [water free] + 120 g 100% acetic acid L^{-1} [both Carl Roth]) adjusted to pH 4.8 (Lagaly et al., 2013). If, after stirring sporadically for 2 h in a water bath with 50°C, the pH was higher than 4.8, more buffer solution was added in 10-mL steps. After all samples had reached the pH value of 4.8, they were left to cool down to room temperature.

To remove organic matter, we added 30 mL of H_2O_2 (30%, Carl Roth). After stirring, we left the bottles overnight at room temperature. Following Hyeong and Capuano (2000), we used a water bath at 50°C with occasional stirring of the samples. We added 20 mL of H_2O_2 after 2.5–3 h and another 20 mL per beaker after further 2.5–3 h. We used the maximum duration and amount of H_2O_2 required by our soil samples for the clay minerals. When samples started to spill over, we sprayed a small amount of octane-2-ol (pro synthesis, Sigma–Aldrich, St. Louis, MO) into the foam. After washing once with 2 M NaCl solution, the whole H_2O_2 treatment was repeated.

In the following four-fold washing cycle with NaCl solution, we removed the supernatant with a peristaltic

TABLE 1 Selected properties of the used clay minerals

Sample	Origin	LOI[a] (Mass-%)	CEC (mmol$_c$ kg^{-1})	Principal cations	Surface area (N$_2$) (m^2 g^{-1})	Chemical composition
Kaolinite (KGa-2)	Georgia, United States	12.6	33		23.50	(Ca$_{tr}$K$_{tr}$)[Al$_{3.66}$Fe(III)$_{.07}$Mn$_{tr}$Mg$_{tr}$Ti$_{.16}$][Si$_{4.00}$]O$_{10}$(OH)$_8$
Na-montmorillonite (SWy-3)	Wyoming, United States	10.3[b] 0.612[c]	764	Na$^+$, Ca^{2+}	31.82	(Ca$_{.12}$Na$_{.32}$K$_{.05}$)[Al$_{3.01}$Fe(III)$_{.41}$Mn$_{.01}$Mg$_{.54}$Ti$_{.02}$][Si$_{7.98}$Al$_{.02}$]O$_{20}$(OH)$_4$
Mg-montmorillonite (SCa-3)	California, United States	21.2	~1170[d] 1140[e]	Mg^{2+e}	43.2–65.3	(Mg$_{.45}$Ca$_{.15}$Na$_{.26}$K$_{.01}$)[Al$_{2.55}$Fe(III)$_{.12}$Mn$_{tr}$Mg$_{1.31}$Ti$_{.02}$][Si$_{7.81}$Al$_{.19}$]O$_{20}$(OH)$_4$
Illite (IMt-2)	Montana, United States	8.02	120–150[f]	K^{+f}	17.5[g]	(Mg$_{.09}$Ca$_{.06}$K$_{1.37}$)[Al$_{2.69}$Fe(III)$_{.76}$Fe(II)$_{.06}$Mn$_{tr}$Mg$_{.43}$Ti$_{.06}$][Si$_{6.77}$Al$_{1.23}$]O$_{20}$(OH)$_4$
Vermiculite	Russia	20.2[b]	1620[h]	~85% Mg^{2+} 15% Ca^{2+h}	36[g]	Me$^+_{0.70}$(Si$_{3.04}$Al$^{3+}_{0.96}$)(Mg$^{2+}_{2.65}$Fe$^{3+}_{0.31}$Al$^{3+}_{0.01}$)[O$_{10}$(OH)$_2$][i]

Note: If not noted otherwise, the data are from the Clay Mineral Society (2021).

[a]Mass loss on ignition at 550°C.
[b]Steudel, Batenburg, et al. (2009).
[c]Mermut and Cano (2001).
[d]Komadel (2003).
[e]Grim and Kulbicki (1961).
[f]Hower and Mowatt (1966).
[g]M. Dogan et al. (2007).
[h]Bors et al. (1997).
[i]Grain-size fraction <2 μm (Steudel, 2008).
Abberiation: tr, traces.

pump (ISMATEC MCP Process, Cole-Parmer, Vernon Hills, IL with Tygon® LMT-55 hoses, ID: 8 mm, Tygon®, Saint-Gobain, La Défense, France) to avoid re-suspension. We continued the washing of the samples with deionised water until all beakers had an electrical conductivity <400 μS cm^{-1} in the decantate (DIN ISO 11277, 2002). We filled all beakers with deionised water with a pH of ~7.5 (adjusted with NaOH) and shook them overhead for 18 h. Then, we separated the remaining sediments of all clay mineral and soil samples into grain-size fractions starting with wet sieving (63 μm) the sand fraction. The grain-size distribution was determined by pipet analysis according to DIN ISO 11277 (2002), except that we did not use a dispersing agent following the suggestions of Dietrich et al. (1998) and Müller (1964). For kaolinite, we had to add a few millilitres of 0.01 M NaOH (Titripur, Merck) into the suspension and shortly shake it manually to reach full dispersion. Manual shaking for 2 min and letting the sample settle 20 cm in 2-L glass cylinders separated the clay fractions (<2 μm). We calculated the sedimentation time following Stokes' law considering the current temperature (Gee & Or, 2002). Then, we transferred the supernatant into 10-L buckets with the peristaltic pump and filled the glass cylinder with more deionised water (pH ~ 7.5). We repeated the separation via sedimentation three times to separate >50% of the

clay (Müller, 1964), using always water with a pH of ~7.5. This comparatively fast separation leaves residues of the clay in the silt separates, which we named therefore '≤silt'.

We added 15–25 g MgCl$_2$ (solid, ≥98.5%, Carl Roth) to the bucket to start sedimentation. The next day, we pumped out the clear supernatant and transferred the residual into a 1-L centrifugation beaker (PP, 75007300, Thermo Fisher Scientific). We washed the samples first with 1 M NaCl solution and then once with deionised water.

We treated the clay suspension of the clay minerals and the soils once again with H$_2$O$_2$ to further reduce their SOM concentrations. We made the 1-L centrifuge beaker up to 200 mL with deionised water and added 70 mL of 30% H$_2$O$_2$ and twice further 45 mL.

The final washing started with 1 M NaCl solution, followed by twice 0.5 M and deionised water until the conductivity of the supernatant was <100 μS cm^{-1}. Some samples needed centrifugation times of up to 4 h at 4122 g. The clay suspension was transferred into 250-mL PE wide-mouth beakers (Kautex Textron, Bonn, Germany) and dried at 60°C. We manually pulverised the '≤silt' and clay fractions to <200 μm in an agate mortar.

The entire clay separation procedure took 10–12 weeks and up to 12 samples could be simultaneously

TABLE 2 Soil type, selected topographical properties of the study sites and selected properties of the topsoil samples used for the clay separation method

Sample	Soil type[a]	Substrate	Slope	Land use	Sampling depth (cm)	Latitude longitude (WGS84)	Elevation (m above sea level)	Annual mean $\delta^2H_{modeledprecipitation} \pm$ SD (‰)[b]	pH in H_2O
KA-1	Gleyic Luvisol	Alluvial sediments	None	Agricultural	7–13	48.9311° 8.3567°	115	−58 ± 1	5.9
KA-2	Haplic Luvisol	Dilluvial sand dunes	None	Deciduous forest	0–12	48.9623° 8.357°	120	−58 ± 1	6.1
Oso	Dystric Cambisol[c]	Loess on limestone[c]	Upper slope[c]	Coniferous forest	0–10	49.26° 19.71°	1400	−76 ± 1	3.3

[a]IUSS Working Group WRB (2015).
[b]Data from OIPC version 3.1 (Bowen, 2021; Bowen & Revenaugh, 2003).
[c]Data from Lobe et al. (1998).

processed (Figure 1). The procedure was conducted three times for all samples in separate batches to yield three independent replicates of all clay fractions. After the treatment, the interlayers of all swellable clay minerals should be mostly Na saturated.

2.3 | Chemical sample properties

The carbon (C) concentrations were measured with an Elemental Analyser (EA) (Flash 2000 HTC, Thermo Fisher Scientific and EuroVector 3000, EuroVector, Pavia, Italy).

The pH was determined with a glass electrode (SenTix® 81 on pH 3310, WTW, Weilheim, Germany) in a deionised water suspension at a soil:water ratio of 1:2.5 (v/v).

The potential cation-exchange capacity (CEC_{pot}) was determined with the Cu(II)-triethylentetramine method (Ammann et al., 2005; Meier & Kahr, 1999). To avoid any pH dependency of the result (Stanjek & Künkel, 2016), we mixed 9.5 mL of the sample with 0.5 mL phosphate buffer (pH = 7.0; 1.814 g KH_2PO_4 [Carl Roth], 3.564 g $Na_2HPO_4*2H_2O$ [Emsure, Merck] in 0.5 L ultrapure water) and shook the suspension for 24 h (Steudel, Weidler, et al., 2009). The removal of the Cu complex by adsorption to the cation-exchange sites was photometrically determined at 577 nm. The potential CEC was referred to oven-dry soil (24 h at 105°C).

2.4 | Steam equilibration

We modified the equilibration device of Ruppenthal et al. (2013) (Figure 2). We replaced the liquid nitrogen trap with a diaphragm pump (VP 220, VWR, Radnor, PA) to remove water vapour, which could corrode the rotary vane pump (RZ 2.5, Vacuubrand, Wertheim, Germany), and we added a glove bag (Captair Pyramid, Erlab, Val de Reuil, France), which was filled with Ar to allow for a fast gas-tight sealing of the tin capsules without contact to ambient air.

The optimum equilibration time was determined experimentally for two soil samples (the sample KA-2 was not used, Table 2) and the clay reference materials following a suggestion of Wassenaar and Hobson (2000). After evacuating the stainless steel vessel (~10 L; Rovak, Grumbach, Germany; with steel tubing, fittings and valves from Swagelok, Solon, OH) for 2 h inside a fan-assisted heating oven at 120°C, we injected 4 mL of equilibration water with a δ^2H value of 335‰ using a syringe (needle: Sterican® G26, B.Braun, Melsungen, Germany) through a high-temperature septum (Trajan 041845,
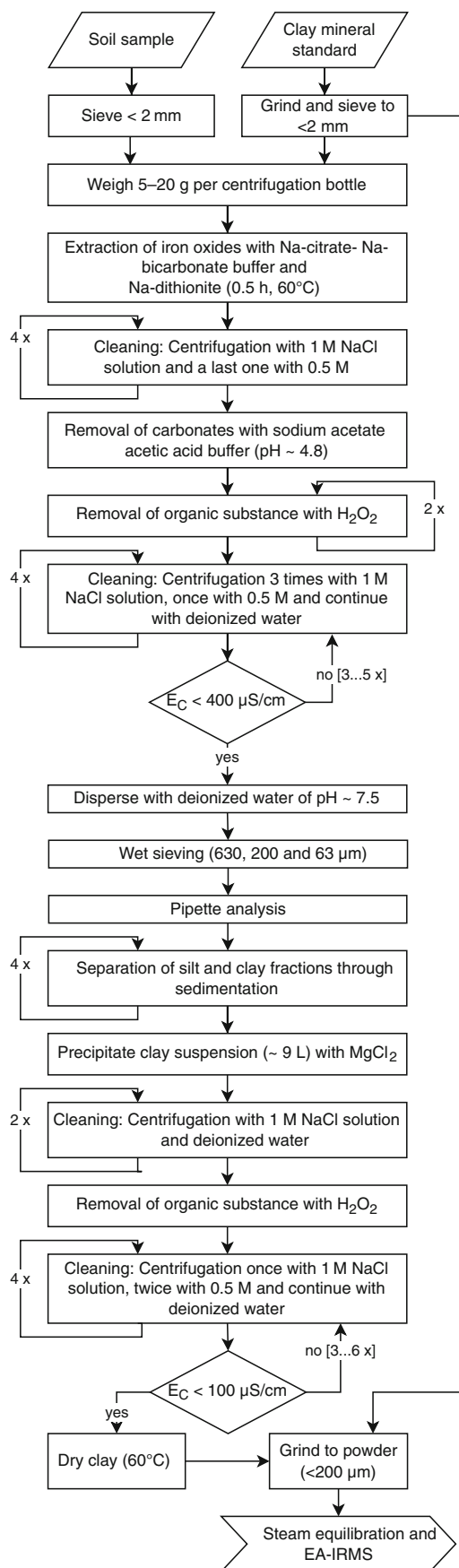
FIGURE 1 Workflow diagram of the clay separation method. EA-IRMS, Elemental Analyser Isotope Ratio Mass Spectrometry

Victoria, Australia or Restek 27088, Bellefonte, PA). After 0.25, 1, 4, 16 and 64 h, the vessel was reconnected to the vacuum line and evacuated for 1 h in the oven at 120°C using the diaphragm pump during the first 15 min. Then, the samples were evacuated for another 2 h at room temperature to cool down, reaching a vacuum ≤1 Pa. Afterwards, we placed the vessel in the glove bag that we evacuated and flushed with Ar (purity grade 4.8) twice. To depressurize the vessel to ambient air pressure, we flooded the vessel with Ar at ∼1.3 bar, dried with Sicapent (with indicator, Supelco, Merck). While the Ar continuously flowed into the vessel, we opened the vessel and directly closed the capsules with a filed and extended concretor's nippler (plier No. 99 10 250, Knipex, Wuppertal, Germany) inside the vessel. This was done in a way that the tin of the capsules was not cut off but compressed to a gas-tight seal (Qi et al., 2010), applying the same force to all capsules. This procedure was necessary to avoid even the slightest contact of the sample with ambient air moisture, which is a prerequisite for the correct determination of the H concentrations and $\delta^2 H$ values.

For further equilibrations, we chose an equilibration time of 16 h (Figure 3). We placed a maximum of 80 samples with an analyte mass of 1–2 mg, each, in the equilibration vessel, corresponding to a ratio of equilibration water-H to exchangeable sample-H >2000:1. We included triplicates of SCa-3 at the beginning and end of each equilibration batch to test for a potential shift in $\delta^2 H$ values because of diffusing moisture during the sealing process of the samples at the end of the equilibration. For quality control, we included KGa-2 and blanks in triplicates.

We used two to four waters with known $\delta^2 H$ values (AWI-TD1: $-266.4 \pm 0.8‰$, SD for $n = 4$ repeated measurements; laboratory water: $-57.5 \pm 0.8‰$, $n = 3$; medium deuterium-enriched water: $136.8 \pm 0.6‰$, $n = 3$; highly deuterium-enriched water: $334.6 \pm 1.8‰$, $n = 4$) to replace all exchangeable H in the sample with the H of the equilibration water and to calculate the contribution of exchangeable H and the $\delta^2 H_n$ value. We produced the two deuterium-enriched waters by mixing ^2H_2O (HN81.4, Carl Roth) and ultrapure water (Faghihi et al., 2015). The treatment batches one and two were equilibrated with two isotopically different waters and the third batch with four waters.

2.5 | Hydrogen isotope ratio measurement

The concentrations of H and $\delta^2 H$ values were determined with an EA-Isotope Ratio Mass Spectrometer (IRMS) (Flash 2000 HTC-Delta V Advantage, Thermo Fisher Scientific). The samples were pyrolyzed in the chromium-

FIGURE 2 Sketch of the modified steam equilibration apparatus of Ruppenthal et al. (2013)
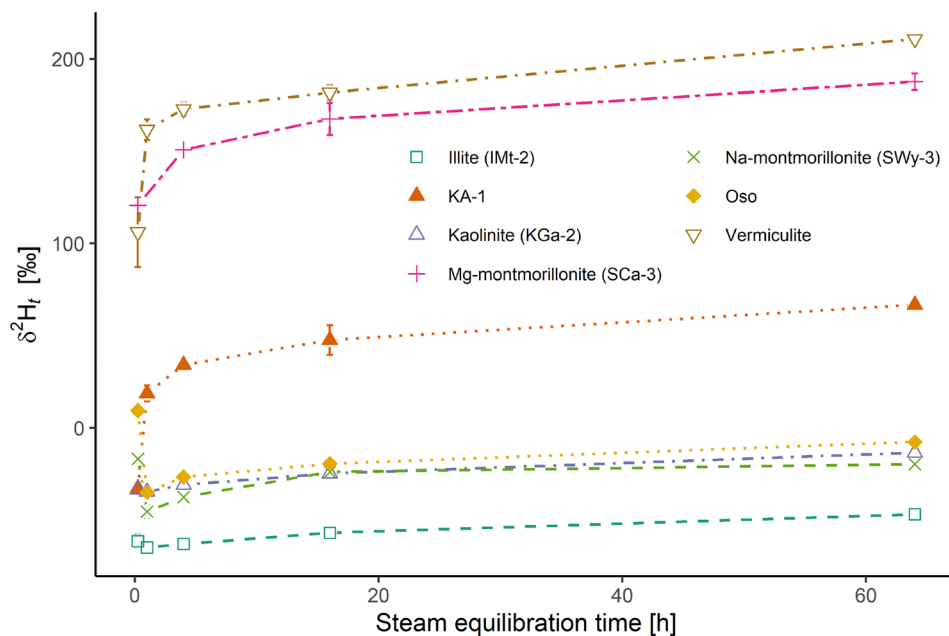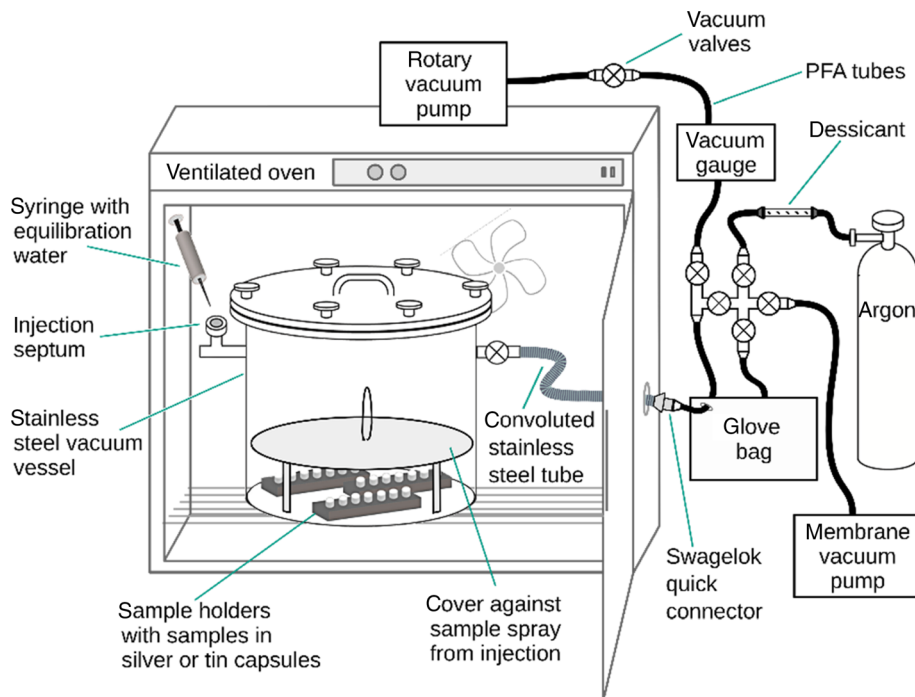

FIGURE 3 Relationship between steam equilibration time and δ^2H_t values of clay minerals and two clay separates (filled symbols) equilibrated with water with a δ^2H_W value of 335‰. Error bars show SD and might be smaller than the symbol size.

filled Al_2O_3 reactor (Alsint 99.7, IVA, Meerbusch, Germany) at 1250°C. We used the set-up 'A1' described in Gehre et al. (2017), but adapted it for a smaller inner diameter (7 mm) of the inner tube (DEGUSSIT AL23, Friatec, Mannheim, Germany) with a 40 mm octagonal graphite crucible (G52109.001E, OEA Labs, Exeter, UK). In combination with 2×5 mm smooth wall tin capsules (IVA184990326, IVA), long sequences of up to 130–150 capsules were possible. We renewed the Cr granulate (1–3 mm, 99+%, ChemPur, Karlsruhe, Germany) after each sequence. The He carrier flow was 80 mL min^{-1} and the

GC oven temperature was 90°C. The integrated peak area of m/z 2 and 3, calibrated against benzoic acid (SA990747, IVA-Analysentechnik), was used to determine the H concentration. Tin capsules did not show a measurable H_2 blank. The correction factor for H_3^+ ions produced in the ion source was ascertained before and after each carousel run using the automated procedure of the IRMS software. For normalisation of the measured δ^2H values of each carousel run, we used three international laboratory standards (Vienna Standard Mean Ocean Water [VSMOW], SLAP and IAEA-604). Additionally, we used GISP to test for

correct normalisation and to rule out an influence of the halogen release from the Cr-filled reactor on the H isotope measurements (Gehre et al., 2017). We purchased all international laboratory standards from USGS (Reston Stable Isotope Lab, Reston, VA) packed in silver capsules (25 μl). We used polyethylene powder (PE; low density, ≤400 μm, 42607 Alfa Aesar, Ward Hill, MA) as an internal laboratory standard for sample bracketing and IAEA-CH7 (IAEA, Vienna, Austria) for quality control at the beginning and end of each sequence. We did not notice drift or residual non-linearity of the EA-IRMS system. We corrected small memory effects with the help of a pool-wise memory correction algorithm using one or two pools (Guidotti et al., 2013). Over the duration of the experimental period, the PE-powder was measured at a mean δ^2H value of $-69.9 \pm 1.4‰$ ($n = 490$), GISP at $-188.8 \pm 1.9‰$ ($n = 72$) and IAEA-CH7 at $-100.3 \pm 1.5‰$ ($n = 88$). The values were indistinguishable from the certified or recommended values.

2.6 | Data evaluation

We corrected isotope data and performed statistical analyses with R, version 4.1 (R Core Team, 2021; Wickham et al., 2019). We normalised all stable H isotope ratios to the VSMOW-SLAP scale (Paul et al., 2007) and expressed them in ‰ relative to VSMOW. When the δ^2H_w value was >0‰, we extended the scale with IAEA-604 to 799.9‰. All errors are given as one SD.

We assumed that there is no equilibrium fractionation between the exchangeable H and water-H of the vapour, that is, we assumed a fractionation factor $\alpha_{ex\text{-}w}$ of 1. The fractionation factor $\alpha_{ex\text{-}w}$ is a temperature-dependent material constant, which is difficult to determine. Therefore, it is common practice to use preliminary values for organic materials (Qi & Coplen, 2011; Ruppenthal et al., 2010, 2013, 2015; Sauer et al., 2009; Soto et al., 2017; Wassenaar & Hobson, 2000, 2003). While for some clay minerals, several fractionation factors are available for the equilibrium fractionation between clay mineral H and ambient water-H at the time of mineral formation (Gilg & Sheppard, 1996; Liu & Epstein, 1984; Méheut et al., 2010; O'Neil & Kharaka, 1976; Savin & Epstein, 1970b), we do not know of any reported fractionation factor between exchangeable H in clay minerals and steam-H at 120°C.

We used the regression equation of the known δ^2H_w values on the measured δ^2H_t values to determine δ^2H_n values and the contribution of the exchangeable to the total H concentration in the clay minerals and soil clay fractions (χ_e; Feng et al., 1993; Filot et al., 2006; Ruppenthal et al., 2010, 2013, 2015; Sauer et al., 2009; Equation (1)).

$$\delta^2H_t = \chi_e\, \alpha_{ex-w}\, \delta^2H_w + (1-\chi_e)\delta^2H_n + 1000\chi_e(\alpha_{ex-w} - 1)$$

$$(1)$$

The slope is the product of χ_e and $\alpha_{ex\text{-}w}$ and the intercept is $(1-\chi_e)\delta^2H_n + 1000\chi_e(\alpha_{ex-w} - 1)$. Assuming $\alpha_{ex\text{-}w} = 1$ and using δ^2H_t from the regression line for $\delta^2H_w = 0$, Equation (1) is rearranged to calculate δ^2H_n (Equation (2)).

$$\delta^2H_n = \frac{\text{intercept}}{1 - \text{slope}}$$

$$(2)$$

Using Gaussian error propagation for Equation (2), we estimated the SD of the δ^2H_n values with Equation (3), neglecting covariance of slope and intercept.

$$SD = \sqrt{\left(\frac{1}{1 - \text{slope}} * SD_{\text{intercept}}\right)^2 + \left(\frac{\text{intercept}}{(\text{slope} - 1)^2} * SD_{\text{slope}}\right)^2}$$
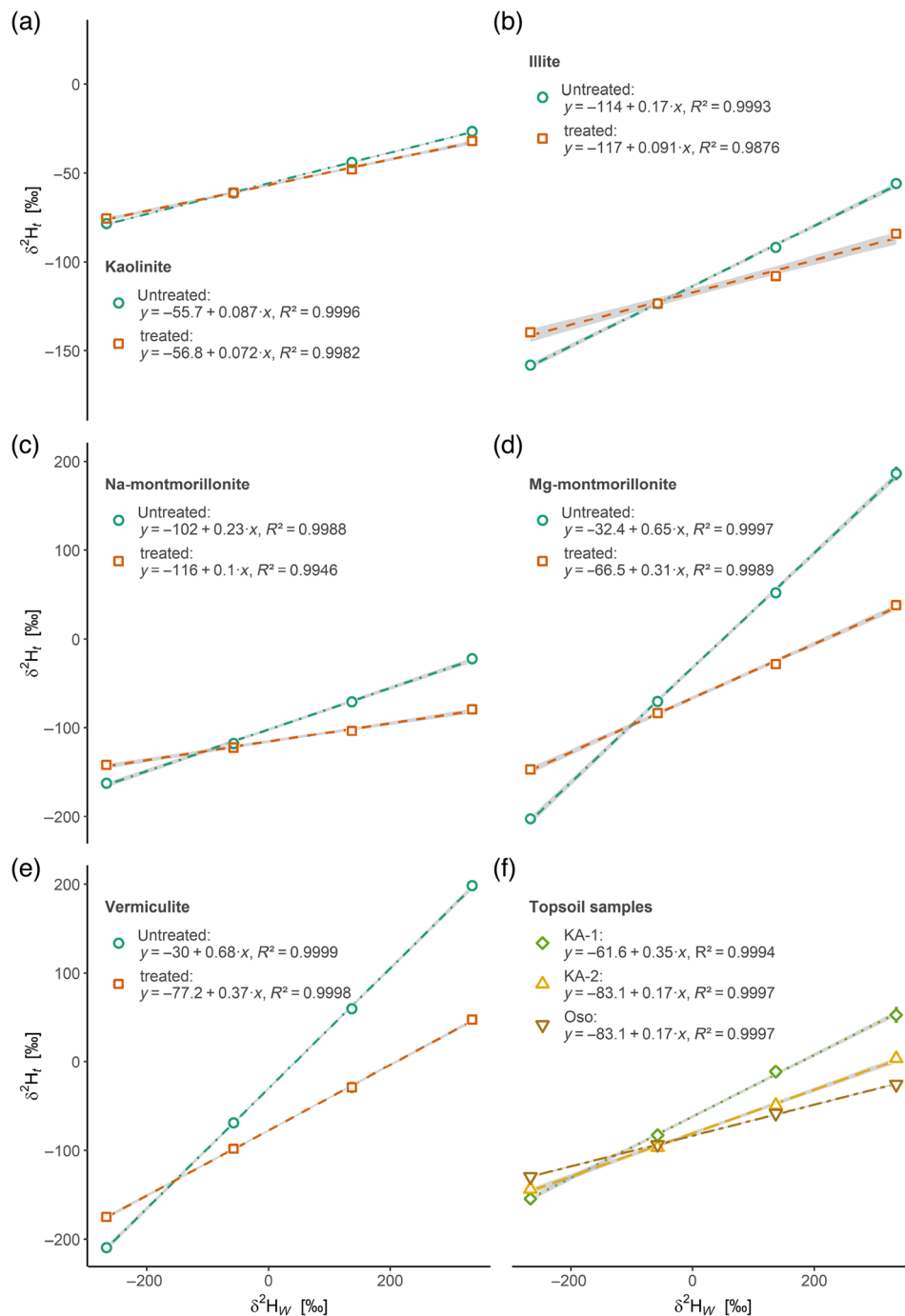
$$(3)$$

We removed samples that after the equilibration came into contact with atmospheric humidity. We detected such samples by (a) visual inspection for holes and (b) the absence of an Ar peak after the H_2 peak in the EA chromatogram. Steam equilibrations of the same sample with isotopically different waters need to result in the same contribution of exchangeable H to the total H concentration (same χ_e). Moreover, (c) we removed as outliers individual samples for which H concentrations and the residuals of the equilibration line fell 0.5 times outside the respective interquartile range of all other equilibrations of the same sample.

Because it was not possible to entirely remove all SOM from the clay fractions, we corrected the measured δ^2H values by mathematically removing the influence of the SOM on the δ^2H_n values of the clay minerals and soil clay fractions. Based on the known locations of the three study soils, we took the mean annual δ^2H value of the local precipitation (δ^2H_p) from Bowen and Revenaugh (2003) and Bowen (2021) (Table 2). Then, we used the regression function of Ruppenthal et al. (2015) to determine the δ^2H_n value of SOM and calculated the δ^2H_n value of the inorganic clay fraction ($\delta^2H_{n,\text{inorg.clay}}$) with Equation (4).

$$\delta^2H_{n,\text{inorg. clay}} = \frac{\delta^2H_{n,\text{clay}} - f_{n,\text{SOM}}\, \delta^2H_{n,\text{SOM}}}{1 - f_{n,\text{SOM}}}, \text{with}$$

$$\delta^2H_{n,\text{SOM}} = 1.25\, \delta^2H_p - 34 \qquad (4)$$

FIGURE 4 Regression lines of the $\delta^2 H_t$ values of equilibrated samples on the $\delta^2 H_W$ values of the equilibration waters for untreated, bulk samples (dot-dashed line) and treated clay separates (dashed line) of clay minerals (a–e) and three different soil clay separates (f). Shaded areas illustrate 68% CIs.

3 | RESULTS

3.1 | Adaptation of the steam equilibration method

In the first step, we determined the optimum equilibration time (Figure 3). In our experiment, the $\delta^2 H_t$ values of the

where $\delta^2 H_{n,clay}$ is the measured $\delta^2 H_n$ value of the clay fraction and $f_{n,SOM}$ is the mass fraction of SOM. In this approach, we assume that the clay separation procedure did not change the $\delta^2 H_n$ value of the SOM.

equilibrated samples did not fully reach a plateau after 64 h, but changed little beyond 16 h. The linear regression of the $\delta^2 H_t$ value of our samples on the $\delta^2 H$ values of the equilibration water consistently resulted in coefficients of determination >0.99 (Figure 4). Only USGS58 muscovite had an R^2 value of 0.82, which we consider a statistical artefact resulting from the small slope of only 0.009 (Figure 5). The accuracy of our $\delta^2 H$ measurement was tested with the USGS57 biotite and USGS58 muscovite standards (Table 3). Our $\delta^2 H$ values were statistically indistinguishable from the results of Qi et al. (2017), illustrating the high accuracy of our $\delta^2 H_t$ measurements. Our $\delta^2 H_n$ measurements show that the reference material USGS57 biotite after equilibration at
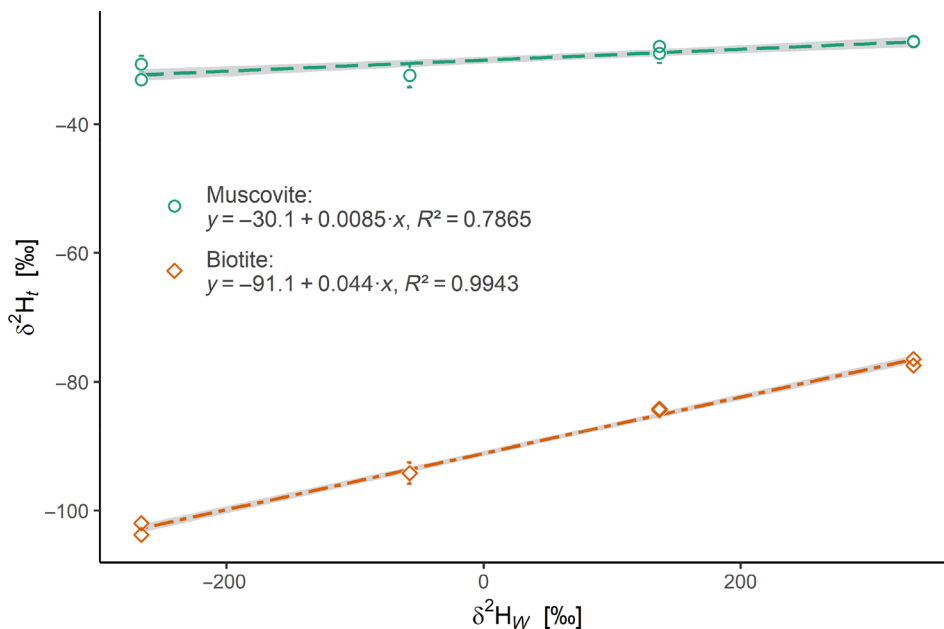
FIGURE 5 Regression lines of the δ^2H_t values of equilibrated samples on the δ^2H_W values of the equilibration waters for the standards USGS57 biotite and USGS58 muscovite. Each point originates from an independent equilibration batch, measured in a separate isotope ratio mass spectrometry sequence. Error bars show SD ($n = 2–3$) of samples measured in the same equilibration batch and might be smaller than symbol size. Shaded areas illustrate 68% CIs.

In the figure:

Muscovite: $y = -30.1 + 0.0085 \cdot x$, $R^2 = 0.7865$

Biotite: $y = -91.1 + 0.044 \cdot x$, $R^2 = 0.9943$

TABLE 3 Stable H isotope ratios of total (δ^2H) and non-exchangeable H (δ^2H_n), contribution of non-exchangeable H to total H concentrations and total H concentrations of the USGS mineral reference materials

Mineral	Treatment or origin	$\delta^2H \pm SD$ (‰)	$\delta^2H_n \pm SD$ (‰)	Exchangeable H ± SD (%)	n	Total H (mg g^{-1})	n
Biotite	Data from Qi et al. (2017)	-91.5 ± 2.4			24	4.16 ± 0.02	4
	Original sample, air dried	-93.8 ± 1.7			3	4.32 ± 0.09	2
	After steam equilibration		-95.3 ± 0.9	4.4 ± 0.2	3	4.13 ± 0.02	3
Muscovite	Data from Qi et al., 2017	-28.4 ± 1.6			24	4.48 ± 0.02	4
	Original sample, air-dried	-31.3 ± 0.9			3	4.68 ± 0.02	2
	After steam equilibration		-30.7 ± 1.4	1.1 ± 0.6	3	4.69 ± 0.02	3

Note: Errors are SD. Replicate measurements (n) refer to the preceding column.

120°C for 16 h has an exchangeable H pool size of 4.4% of the total H concentration.

The precision of the δ^2H_n measurements of the three soil clay fractions ranged from ±0.6‰ for Oso to ±6.9‰ for KA-1 (±1 SD); the precision of untreated bulk samples of clay minerals ranged from ±0.9‰ for kaolinite to ±7.5‰ for Mg-montmorillonite (all $n = 3$; Table 4). The kaolinite had the smallest exchangeable H fraction of all studied clay minerals and the Oso clay fraction of all studied soil samples. In contrast, the swellable vermiculites and montmorillonite contain less structural H and much more exchangeable H than kaolinite.

3.2 | Effect of the clay separation on the δ^2H_n values of clay minerals

The δ^2H_n values of the clay mineral samples, which we carried through the clay separation method, fell close to the 1:1 line, when plotted against the δ^2H_n values of the untreated samples, except for the vermiculite (Figure 6). With our treatment, we only collected 1% of the bulk sample in the clay fraction of the vermiculite (Table 4). As a consequence, the δ^2H_n value of the clay fraction of vermiculite was not representative of the bulk vermiculite. Therefore, we additionally measured the δ^2H_n values of the '≤silt' and sand fractions of the vermiculite and calculated a mass-weighted mean of the δ^2H_n values of the grain-size fractions. The resulting calculated δ^2H_n value of the bulk vermiculite was similar to that of the untreated sample, illustrating that the clay separation method did not influence the δ^2H_n value of the clay fraction (Figure 6). The δ^2H_n values of the soil clay fractions and bulk clay minerals of kaolinite, the two montmorillonites and the directly measured and from the grain-size fractions calculated bulk values of vermiculite were not significantly different between the untreated sample and the clay fraction (t-test, $p \geq 0.09$).

Because it was not possible to entirely remove SOM from the soil clay fractions, we had to consider the

TABLE 4 Mean stable isotope ratios of non-exchangeable H (δ^2H_n values) with propagated SD, total H concentrations, contribution of non-exchangeable H to total H concentrations and cumulative yield of the grain-size fractionation procedure

		Bulk				Yield		Clay fraction		
Name	Batch	$\delta^2H_{n,bulk} \pm$ SD (‰)	Total H conc. (mg g⁻¹)	Exchangeable H pool (%)	Grain-size fraction	(g)	(%)	$\delta^2H_{n,clay} \pm$ SD (‰)	Total H conc. (mg g⁻¹)	Exchangeable H pool (%)
Illite	1	−138.8 ± 2.4	5.5	17.0		2.4	16	−136.1 ± 1.4	6.3	10.1
	2	−140.3 ± 2.8	5.6	15.9	Clay	1.5	11	−128.8 ± 2.6	6.3	6.9
	3	−136.8 ± 3.3	5.3	17.0		2.4	13	−129.3 ± 3.6	6.2	9.2
Kaolinite	1	−62.4 ± 0.5	16.1	8.6		17.2	79	−63.5 ± 1.5	16.3	7.7
	2	−61.5 ± 1.3	16.4	7.9	Clay	11.2	84	−61.6 ± 0.8	16.4	6.1
	3	−61.0 ± 0.8	16.8	8.7		14.5	83	−61.2 ± 1.4	16.5	7.3
Mg-montmorillonite	1	−102.5 ± 3.3	7.7	65.4		9.2	92	−100.8 ± 6.2	7.2	34.1
	2	−107.4 ± 13.6	8.2	61.9	Clay	7.1	94	−103.3 ± 2.4	7.6	32.1
	3	−92.6 ± 14.4	8.0	64.5		8.1	93	−96.2 ± 6.3	7.3	30.6
Na-montmorillonite	1	−133.4 ± 1.4	6.1	23.4		7.2	78	−132.9 ± 3.6	6.6	9.3
	2	−140.2 ± 2.8	7.0	21.7	Clay	5.7	81	−132.3 ± 1.4	6.8	10.0
	3	−133.4 ± 6.2	6.8	22.8		6.4	79	−128.9 ± 3.2	6.5	10.4
Vermiculite	1					19.3	94	−105.0 ± 9.2	7.8	50.4
	2				Sand	23.5	95	−98.0 ± 5.1	7.8	44.4
	3					23.4	94	−99.5 ± 8.1	6.8	48.4
	1					1.1	5	−123.5 ± 14.6	8.9	45.3
	2				≤Silt	1.0	4	−120.9 ± 6.4	8.8	44.4
	3					1.3	5	−119.8 ± 11.9	8.9	43.9
	1	−101.8 ± 9.4	12.2	66.7		0.2	1	−125.3 ± 9.9	8.7	44.2
	2	−96.6 ± 12.4	11.9	67.1	Clay	0.2	1	−127.7 ± 6.6	8.7	39.0
	3	−92.8 ± 9.9	12.4	67.7		0.3	1	−122.3 ± 7.2	8.6	36.7
KA-1	1					13.1	51	−107.6 ± 4.2	11.5	36.0
	2				Clay	7.4	52	−101.3 ± 1.2	11.1	35.0
	3					10.5	54	−94.1 ± 6.9	11.3	34.7
KA-2	1					4.0	6	−111.9 ± 2.7	10.6	23.0
	2				Clay	0.9	5	−107.3 ± 4.4	9.7	23.0
	3					1.3	6	−106.7 ± 4.1	8.8	24.6
Oso	1					5.2	13	−99.4 ± 1.7	10.5	18.1
	2				Clay	4.6	12	−98.3 ± 1.3	10.7	18.7
	3					4.7	12	−99.2 ± 2.9	10.0	17.2

Note: The subscript 'bulk' refers to the bulk soil and 'clay' to clay fraction, '≤silt' indicates that our silt fraction still included some clay, because of imperfect separation.

influence of non-exchangeable H in the remaining SOM. The maximum residual organic C concentration in the clay fractions was 35.7 g kg^{-1} (Table 5). The organic C concentrations in three of the eight clay fractions including two of the three soil clay fractions were lower than in the bulk samples. This illustrates that the organic matter concentration had been reduced considerably in three samples but less so in the other five ones. To assess the influence of C-bonded H in organic matter on our δ^2H_n values of the three soil clay fractions, we assumed a conversion factor of 2 from organic C to SOM, a H concentration of 50 g kg^{-1} organic matter (Rice & MacCarthy, 1991; Ruppenthal et al., 2013) and a share of non-exchangeable H to total H of 80% (Ruppenthal et al., 2013; Schimmelmann, 1991; Wassenaar & Hobson, 2000). Based on these considerations, the non-exchangeable H from organic matter contributed 15%–34% to the total non-exchangeable H in our three soil clay fractions. This estimate is based on the assumption that the clay separation procedure did not change the δ^2H_n values of the organic matter. Moreover, we assumed that the linear relationship between the δ^2H_n values of SOM and the modelled δ^2H values of the precipitation found for Argentina by Ruppenthal et al. (2015) is also representative of our samples. Our correction of the δ^2H_n values of the soil clay fractions by the contribution of the non-removed SOM only affected the δ^2H_n value of one of our three soil samples, Oso, more than marginally. In the Oso sample, the corrected δ^2H_n value was shifted by 15‰ (Table 6).

4 | DISCUSSION

4.1 | Adaptation of the steam equilibration method

Our observation that the δ^2H_t values of the equilibrated samples did not fully reach a plateau after 64 h (Figure 3) is in contrast to the findings of Wassenaar and Hobson (2000) and Ruppenthal et al. (2010) for organic materials and bulk soil for which a plateau was already reached between 1 and 2 h. However, a similarly slow increase of the δ^2H_t values with time during vacuum drying at constant temperature was observed for some clay minerals (Faucher & Thomas, 1955; O'Neil & Kharaka, 1976). Likewise, Schimmelmann et al. (2006) reported an asymptotic convergence to a plateau for kerogen-H. Thus, full equilibrium of the clay minerals with the steam occurs only at equilibration times, which are not feasible for routine measurement. Therefore, we decided to run our equilibration for 16 h, because after 16 h the change in the δ^2H_t value was only minor. Thereby, we accept that our δ^2H_n
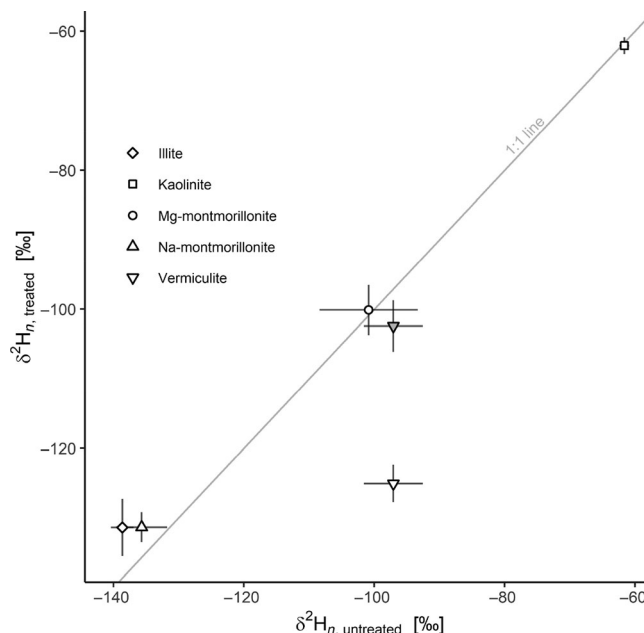

FIGURE 6 Relationship between the δ^2H_n values of untreated bulk clay minerals and those of the clay fraction of kaolinite, illite, Mg- and Na-montmorillonite and vermiculite collected with a clay separation method ('treated') shown with open symbols. For vermiculite, the bulk δ^2H_n value calculated from the separate measurements of the clay, '≤silt' (includes some clay) and sand fractions is additionally shown with a grey filled symbol. Error bars show the SD ($n = 3$, each per treatment batch). For the bulk value of vermiculite, the SD was calculated by Gaussian error propagation from the individual errors of the three particle-size fractions.

values include some strongly bound interlayer water of phyllosilicates. We consider the associated error as acceptable, because the alternative vacuum-drying methods using constant drying temperatures of 100–250°C (Bauer & Vennemann, 2014; Gilg et al., 2004; VanDe-Velde & Bowen, 2013) also leave an unknown concentration of non-structural H in the sample. The latter is particularly true if the sample consists of a mixture of minerals, which commonly occurs in soil clay fractions. This is related to the fact that the drying temperature required to remove all non-structural H depends on the type of mineral, which has been shown with the help of thermogravimetric analyses (Beyer & von Reichenbach, 2002; Brigatti et al., 2013; Guggenheim & Van Groos, 2001; Joussein et al., 2005; Steudel, 2008). Moreover, dehydration and dehydroxylation ranges may even overlap for some clay minerals, such as palygorskite (Heller-Kallai, 2013).

Our finding that the biotite standard contained some exchangeable H (Table 3) might result in a small variation of the δ^2H values measured in different laboratories at different temperatures if the contribution of exchangeable H is not eliminated as in our approach. However,

TABLE 5 Means and SD ($n = 2$–3) of organic C concentrations in bulk soils (subscript bulk) and the clay fraction (subscript clay), potential cation-exchange capacity (CEC_{pot}) in bulk soils and clay fractions, dithionite-citrate-bicarbonate-soluble Fe concentrations (Fe_d) and contributions of grain-size fractions to the total sample mass

Sample	$C_{org,bulk}$ (mg g^{-1})	$CEC_{pot,bulk}$ (mmol$_c$ kg^{-1})	Fe_d (mg g^{-1})	Sand (mass-%)	Silt (mass-%)	Clay (mass-%)	$C_{org,clay}$ (mg g^{-1})	$CEC_{pot,clay}$ (mmol$_c$ kg^{-1})
Mg-montmorillonite	0.4 ± 0.02	1113 ± 37	0.6 ± 0.0	1 ± 0.4	11 ± 4	88 ± 4	0.5 ± 0.1	n.a.
Illite	0.6 ± 0.01	89 ± 9	8.9 ± 0.1	49 ± 5.7	32 ± 3	20 ± 9	0.8 ± 0.1	n.a.
Kaolinite	0.2 ± 0.01	29 ± 4	1.2 ± 0.1	1 ± 0.4	16 ± 3	84 ± 2	0.5 ± 0.0	n.a.
Na-montmorillonite	1.2 ± 0.2	743 ± 12	3.5 ± 0.2	2 ± 0.2	13 ± 4	85 ± 4	0.5 ± 0.1	n.a.
Vermiculite	0.1 ± 0.05	n.a.	0.6 ± 0.1	91 ± 0.4	6 ± 1	3 ± 1	3.6 ± 1.0	n.a.
KA-1	57.7 ± 0.6	247 ± 22	7.5 ± 0.7	10 ± 1.1	25 ± 10	65 ± 10	13.5 ± 1.7	296 ± 12
KA-2	22.5 ± 0.2	57 ± 6	4.1 ± 0.2	62 ± 2.9	22 ± 7	16 ± 7	30.2 ± 3.7	144 ± 3
Oso	61.9 ± 2.2	89 ± 3	9.4 ± 0.1	34 ± 1.0	52 ± 1	15 ± 0	35.7 ± 2.4	121 ± 11

Abbreviation: n.a., not available.

TABLE 6 Mean δ^2H_n values of the clay fractions (subscript 'clay'), the soil organic matter (subscript 'SOM') and δ^2H_n values in the clay fractions corrected by the C-bonded H contribution of residual soil organic matter ($\delta^2H_{n,inorg.clay}$)

Sample	$\delta^2H_{n,clay} \pm$ SD (‰)	$f_{H,SOM}$ (−)	$\delta^2H_{n,SOM}$ (‰)	$\delta^2H_{n,inorg.clay}$ (‰)
KA-1	-101.0 ± 6.8	0.149	-106.5	-100.0
KA-2	-108.6 ± 2.8	0.326	-106.5	-109.7
Oso	-99.0 ± 0.6	0.334	-129.0	-83.9

Note: $f_{H,SOM}$ is the contribution of H in soil organic matter to the total non-exchangeable H concentration.

the size of the exchangeable H pool might even be smaller at room temperature.

We attribute the high precision of the δ^2H_n value of kaolinite and the Oso clay fraction to their large structural H fraction and a corresponding small exchangeable H fraction (Table 4). In turn, the bigger error of the δ^2H_n measurements of the swellable vermiculites and partly also the Mg-montmorillonite is attributable to the large exchangeable H fraction (Table 4).

We observed large differences between the δ^2H_n values of clay minerals in our study and δ^2H_t measurements of the same material in other studies (Δ^2H_{n-t}). For untreated Mg-montmorillonite (SCa-3), the Δ^2H_{n-t} value was −18‰ and for illite (IMt-1 vs. IMt-2 from the same origin) −36‰ compared with the results of VanDeVelde and Bowen (2013), which we estimated from a figure. For the treated clay fraction of Na-montmorillonite (SWy-1 vs. SWy-3 from the same origin), the Δ^2H_{n-t} value was 14‰ in both cases, relative to the δ^2H_t value for the fraction <2 μm before leaching of Menegatti et al. (1999) and the δ^2H_t of the clay fraction of Fagan (2001), which was similarly treated as ours. We attribute these differences to the fact that the exchangeable H fraction, which ranged from 17% to 64% of the total H concentrations in the three clay minerals (Table 4), was less completely removed than in our study, before the δ^2H_t values were

determined by Menegatti et al. (1999), Fagan (2001) and VanDeVelde and Bowen (2013). However, our δ^2H_n value for treated Na-montmorillonite (SWy-3) was in close agreement with the measurement of Kanik et al. (2022) of Na-saturated SWy-1 from the same origin, which was similarly treated as ours, showing a Δ^2H_{n-t} value of only 0.5‰. Likewise, the result of Bauer and Vennemann (2014) using 200°C vacuum drying for untreated SWy-1 was close to ours, with a Δ^2H_{n-t} value of −1‰.

4.2 | Effect of the clay separation on the δ^2H_n values of clay minerals

The recovery of only 1% of the bulk sample in the clay fraction of the vermiculite (Table 4) was much lower than the 10% reported in the literature (Steudel, Batenburg, et al., 2009). The major reason for our low yield of the clay fraction was the fact that part of the clay fraction was included in the silt fraction, which we accepted to speed up the clay separation process. We cannot rule out that the H_2O_2 treatment to remove SOM resulted in some swelling of vermiculite moving part of the clay fraction to a larger particle-size class (Obut & Girgin, 2002; Üçgül & Girgin, 2002; Valášková & Martynková, 2012). A similar influence of the particle

size on the δ^2H values, like for our vermiculite, was reported for biotite and muscovite (Qi et al., 2014, 2017).

However, macrocrystalline vermiculite originating from a clay deposit differs mineralogically from pedogenic vermiculites in soil clay fractions (Douglas, 1989). The macrocrystalline vermiculite possesses an exclusively trioctahedral structure, includes crystals from sand to clay size, and the OH-dipole of the hydroxyl groups is oriented perpendicular to the sheet plane (Malla, 2002). The usually submicroscopic soil vermiculite can be di- and trioctahedral (Jasmund & Lagaly, 1993). Particularly, dioctahedral vermiculite occurs frequently and is usually smaller than medium silt size (Malla, 2002). Moreover, the OH-dipole of the hydroxyl groups in soil vermiculite is oriented oblique to the dioctahedral sheet plane causing different cation interactions (Malla, 2002). Finally, the potential swelling of vermiculite in our H_2O_2 treatment is less pronounced for microcrystalline soil vermiculite than for macrocrystalline vermiculite from a clay deposit. Therefore, the used macrocrystalline vermiculite is likely not representative for soil vermiculite, so that we consider the observed shift in δ^2H_n values between the bulk vermiculite and its clay fraction as irrelevant for soil clay fractions.

Our finding that there was no effect of the treatment of the samples with H_2O_2 on the δ^2H_n values of the clay minerals contrasted with reports of Hyeong and Capuano (2000) and VanDeVelde and Bowen (2013). We therefore speculate that in the previous work, the apparent effect of the H_2O_2 treatment on the δ^2H values of the treated samples was attributable to re-adsorption of air moisture after drying.

The finding that the organic C concentrations in three of the eight clay fractions were lower than in the bulk samples (Table 5), although the clay fraction usually contains a higher organic C concentration than the bulk sample (Eusterhues et al., 2005; Kaiser et al., 2002; von Lützow et al., 2007) underlines the general efficacy of the H_2O_2 treatment. In our approach to mathematically remove the influence of the remaining SOM in the clay fractions after the H_2O_2 treatment (Equation (4), Table 6), we assumed that the clay separation procedure did not change the δ^2H_n values of the organic matter. However, Leifeld and Kögel-Knabner (2001) observed that the H_2O_2 treatment attacks non-polycyclic aromatic (e.g., lignin) and O-substituted aliphatic compounds (e.g., sugars) more than alkyl-C, while Mikutta et al. (2005) reported that an H_2O_2 treatment enriches aliphatic and pyrogenic compounds, which includes polycyclic aromatic compounds. Von Lützow et al. (2007) found that SOM was not degraded by H_2O_2 if it was protected by hydrophobic SOM moieties such as alkyl-C and black carbon. We are not aware of any study quantifying how this preferential removal of selected organic compounds influences the δ^2H_n values of residual SOM.

5 | CONCLUSIONS

The steam equilibration method previously used for bulk soils and SOM can be used for precise measurements of δ^2H_n values in clay fractions of soils and clay minerals, provided the contact of the clays with ambient air humidity after equilibration can be entirely avoided. To achieve this, the samples must be handled in a water vapour-free Ar atmosphere. This technique should be universally applicable to other hygroscopic materials. Thus, our first hypothesis is supported.

We did not detect a significant effect of the classical clay fractionation treatment including removal of Fe oxides and carbonates, reduction of SOM and dispersion of the remaining material on the δ^2H_n values of clay minerals. However, the incomplete destruction of SOM required a correction of the data, which relied on the unproven assumption that the H_2O_2 treatment did not change the δ^2H_n values of the SOM. Therefore, we consider our second hypothesis as only supported with this constraint. Future work should focus on a more complete destruction of SOM that does not change the δ^2H_n values of the soil clay fractions.

AUTHOR CONTRIBUTIONS

Stefan Merseburger: Data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); validation (lead); writing – original draft (lead). **Arnim Kessler:** Investigation (supporting); writing – review and editing (supporting). **Yvonne Oelmann:** Conceptualization (equal); funding acquisition (equal); investigation (supporting); supervision (supporting); writing – review and editing (supporting). **Wolfgang Wilcke:** Conceptualization (equal); funding acquisition (equal); investigation (supporting); methodology (supporting); project administration (lead); resources (lead); supervision (lead); writing – review and editing (lead).

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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