Clays Clay Miner., Vol. 70, No. 6:837–849, 2022
https://doi.org/10.1007/s42860-023-00221-z

ORIGINAL PAPER

Comparison of Pretreatment Methods for Organic-matter Removal and their Effects on the Hydrogen Isotope (δ^2H) Composition of Kaolinite

Arpita Samanta · M. K. Bera · Sruthi P. Sreenivasan · Anindya Sarkar

Accepted: 9 February 2023 / Published online: 14 March 2023
© The Author(s), under exclusive licence to The Clay Minerals Society 2023

Abstract The hydrogen isotopic composition (δ^2H) of authigenic clay minerals has been used extensively in paleoclimate studies. The separation of clay minerals from sediments/soils, using various chemicals, is a prerequisite for isotope ratio measurements, where carbonate, Fe-(oxyhydr)oxides, and organic matter are removed successively from the sediments for a greater clay yield. The commonly adopted organic matter-removal method using hydrogen peroxide (H_2O_2) is thought to either alter directly the pristine δ^2H values of the smectite clay minerals or to introduce organic hydrogen-bearing impurities through the ineffective removal of organic matter. The objective of the present study was to test whether H_2O_2 treatment can alter the δ^2H values of kaolinite (Kln) by comparing two organic matter-removal methods, namely, H_2O_2 and disodium peroxodisulfate ($Na_2S_2O_8$) combined with a neutral buffer. In doing so, kaolinite-rich, old (~56 Ma) sediment samples and pure kaolinite internal laboratory reference materials were used to understand the effectiveness and suitability of the above-mentioned methods in clay-sample preparation for δ^2H measurements. The δ^2H values of the H_2O_2-treated aliquots show smaller δ^2H values than those for the $Na_2S_2O_8$-treated aliquots. Estimated ambient water $\delta^{18}O$ values (−4‰) from the $Na_2S_2O_8$-treated aliquots agreed well with the bio-phosphate (fish vertebrae) based environmental water $\delta^{18}O$ estimation (−3.3‰). The present study indicated, therefore, that δ^2H values obtained after $Na_2S_2O_8$ treatment are likely to be more realistic for paleoclimate reconstruction.

Keywords δ^2H · Early-Eocene equatorial precipitation · Kaolinite · Organic matter-removal method

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s42860-023-00221-z.

A. Samanta (✉)
Department of Geology, Asutosh College, Kolkata 700026, India
e-mail: arpitas25@gmail.com

M. K. Bera · S. P. Sreenivasan · A. Sarkar
Department of Geology and Geophysics, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

Introduction

The geochemistry of authigenic (both neoformed and transformed; Pozo & Calvo, 2018) clay minerals, particularly oxygen ($\delta^{18}O$) and hydrogen (δ^2H some time referred to as δD) isotopic compositions, is a potential tool for quantitative reconstruction of past climates (Andrzejewski & Tabor, 2020; Bukalo et al., 2019; Gilg, 2000; Gilg et al., 2004; Girard et al., 2000; Oyebanjo et al., 2018; Tabor & Montañez, 2005). Complete removal of organic matter from the soil/sediment samples without affecting the mineral phase is a prerequisite for studying the structure, physicochemical

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

properties, and, most importantly, isotopic composition of clay minerals for paleoclimate study. The incomplete removal of organic matter from phyllosilicates hinders the determination of their mineralogy (Tributh & Lagaly, 1991), and isotope values (mainly δ^2H, Hyeong & Capuano, 2000) may also affect inferences based on infrared (IR) and differential thermal analysis (Mitchell & Farmer, 1962). The well known organic matter-removal methods include treatment with hydrogen peroxide (H_2O_2, Jackson, 2005), disodium peroxodisulfate ($Na_2S_2O_8$) combined with various neutral buffers (Menegatti et al., 1999), sodium hypochlorite (NaOCl, Anderson, 1963), ozone, Br_2, low-temperature plasma ashing, and stepped-heating (for a summary see Gilg et al., 2004; Sheppard & Gilg, 1996). Among these methods, H_2O_2 treatment is the most popular and is used commonly during sample preparation for δ^2H analysis (Andrzejewski & Tabor, 2020; Bechtel & Hoernes, 1993; Bechtel et al., 1999; Jackson, 2005; Mizota & Longstaffe, 1996; Oyebanjo et al., 2018). However, the efficacy of organic matter-removal by H_2O_2 has been questioned, especially for samples containing > 1 wt.% total organic carbon (TOC; Hyeong & Capuano, 2000). Further, Hyeong and Capuano (2000) also suggested that H_2O_2 can alter significantly the δ^2H values of clays, e.g. from ~ −8‰ in pure smectites (e.g. smectite reference material H26) to ~ −13‰ in smectite-rich shale samples (Hyeong & Capuano, 2000). Studies have shown that treating clays with $Na_2S_2O_8$ combined with various kinds of neutral buffers is more effective at organic-matter removal (>98 wt.% of the initial TOC, Meier & Menegatti, 1997) than H_2O_2 (Mikutta et al., 2005). An easier method of $Na_2S_2O_8$ treatment (using sodium bicarbonate as a buffer) showed that the δ^2H values remained unchanged after leaching (with $Na_2S_2O_8$ only) for less susceptible illite and kaolinite but smectite was altered by up to ~ −28‰ (Meier & Menegatti, 1997; Menegatti et al., 1999). No data exist on the effects of various organic matter-removal treatments for kaolinite, the most widely used clay mineral for paleoclimate studies. A possibility exists that H_2O_2 treatment may alter the δ^2H values of kaolinite, as has been found for smectite (Hyeong & Capuano, 2000). The purpose of the present study was to investigate the effect of commonly used H_2O_2 and $Na_2S_2O_8$ treatments on δ^2H values of kaolinite separated from the late Paleocene/early Eocene (~ 56–52 Ma) Cambay Shale samples.

Geology of the Study Area

The Cambay Shale sediments were deposited in India's western margin rift basin. The rift basin formed when India was being separated from Madagascar between the early Jurassic and late Cretaceous. The late Paleocene–early Eocene (~56–52 Ma) Cambay Shale sediments, deposited in a marginal marine setup with an abundant terrestrial organic matter supply, directly overlie the late Cretaceous Deccan Trap flood basalt (see Samanta et al., 2013, 2016 for a detailed geological setup). The sediments were derived mostly from weathering of the Deccan Trap basalts, occurring below the thick canopy of the late Paleocene–early Eocene tropical rainforest (Bansal et al., 2022; Prasad et al., 2009). Despite their old depositional age, the Cambay Shale sediments were never buried deeply and remained close to the subsurface (<1–1.5 km depth), which is evident from the: (1) exceptionally well preserved original aragonitic shells of bivalves with intact outermost organic layer (periostracum); (2) low thermal maturity index (T_{max} values ranging between 400 and 423°C); and (3) preserved angiosperm biomarkers (see Dutta et al., 2012 for details).

Materials and Methods

Sediment samples were obtained from a well drilled near the village of Valia (latitude: 21°35′50″ N; longitude: 73°12′2″ E; see Samanta et al., 2013 and references therein for depositional age assignment). Shale samples from four discrete depths of the Cambay Shale were selected for kaolinite clay separation and hydrogen isotopic analysis. The shale samples were selected primarily based on their color (grayscale color) so that they cover a range of TOC values.

Separation of bulk clay from the sediment samples requires a few pretreatment steps to remove carbonate, iron (oxyhydr)oxide phases, and organic matter, which may act as binding agents (Mehra & Jackson, 1960). Sediment samples were treated successively with HCl (37%; Merck, India, EMPARTA® ACS grade), citrate-bicarbonate-dithionite (trisodium citrate [> 99%, Merck, India], $NaHCO_3$ [Merck, India, EMPLURA® grade], and sodium dithionite [purified, > 85%, Lobachemie, India], following Mehra & Jackson, 1960), and H_2O_2 (30%; Merck, India,

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

EMPLURA®ISO grade) with repeated rinsing, centrifuging for removal of carbonate, iron (oxyhydr) oxide phases, and organic matter, respectively. Apart from the usual cleaning using neutral pH detergent (Extran®) and Elix® (Merck, 10—12 Mohm cm at 25°C) water, all laboratory glassware was cleaned with Milli-Q® (18.2 Mohm cm at 25°C) water before use, and the same water was used in sample and reagent preparation at various stages. The freshly prepared Milli-Q® water was used during the wet chemistry and never stored for > 2–3 days.

Approximately 5 g of gently crushed samples (samples were not lithified) were treated with > 100 mL of 0.5 N HCl at ~60°C in 250 mL borosilicate glass beakers until effervescence stopped. This de-carbonation process generally took a few hours, depending on the presence of carbonate types (Ca, Ca-Mg, Fe, or Mn). Once effervescence stopped, the samples were washed repeatedly with Milli-Q® water by centrifuging 4 or 5 times at 4000 rpm (15 cm rotor diameter, 2683 × *g*) for 10 min. The neutralized samples were then dried in a microprocessor-controlled hot air-circulation oven at 60°C, where the actual temperature never exceeded the set temperature by > 2°C. A portion of each of the dried samples was then transferred to a clean 500 mL borosilicate glass beaker and treated with citrate-bicarbonate-dithionite (CBD) solution to remove iron (oxyhydr)oxide phases. The CBD solution was freshly prepared by adding 45 mL of 0.3 M sodium citrate solution, 5 mL of 1 M sodium bicarbonate solution, and 2 g of sodium dithionite to each 0.5 g sample. The whole CBD solution containing the samples was kept in a water bath at 80°C for a maximum of ~2 h with intermittent stirring. The color change of the sample from black/dark-gray to light gray was a good indicator of the completeness of the reaction; the time taken increased from ~2 to 4 h depending on the amount of iron (oxyhydr)oxide present in the samples (Meier & Menegatti, 1997; Menegattiet al., 1999; Mikutta et al., 2005). The samples were then allowed to cool to room temperature and centrifuged four or five times with Milli-Q® water at 4000 rpm (2683 × *g*) for 10 min. A portion of the dried sample was then treated with 30% H_2O_2 at room temperature (~25°C) to remove the organic matter. In doing so, a 250 mL beaker was wrapped in multiple layers of aluminum foil to prevent direct exposure to light and kept for a minimum period of 2 h, an intermediate period of 24 h, and a maximum period of 48 h, with intermittent shaking. The varied-time (2 to 48 h) H_2O_2 treatment was only conducted for the kaolinite internal laboratory reference materials. The core samples were treated for a total of 48 h.

As discussed above, several studies have suspected that H_2O_2 treatment may alter the δ^2H values of the clay samples. Therefore, a portion of each of the CBD-treated samples was treated with sodium peroxodisulfate ($Na_2S_2O_8$, > 95%, Merck, India) in combination with sodium bicarbonate ($NaHCO_3$ [Merck, India, EMPLURA® grade]) used as a buffer, in parallel with H_2O_2 treatment to remove organic matter. In doing so, each sample was dispersed in Milli-Q® water (70 mL of water for each 200 mg sample). A total of ~1:50 $Na_2S_2O_8$:OM mass ratio was slowly added to it, keeping the pH of the solution > 7 by intermittently adding small aliquots of $NaHCO_3$ ($NaHCO_3$:$Na_2S_2O_8$ mass ratio ≈ 1.1) when the pH dropped below 5. This procedure was conducted at ~80°C for a maximum of ~1 h (see Meier & Menegatti, 1997; Menegatti et al., 1999 for details). However, except for the internal laboratory reference materials and one dark-colored sample (244 m), which were treated for ~1 h, the rest of the samples stopped changing color after ~20–30 min and were removed from the bath after ~30–40 min. After centrifuging four or five times at 4000 rpm (2683 × *g*) to remove sulfates, a few mL of 0.5 N HCl was added to the samples to remove any carbonates that formed during the reaction. The samples were again centrifuged at 4000 rpm (2683 × *g*) to remove any excess acid and salts.

After completion of HCl, CBD, and H_2O_2 or $Na_2S_2O_8$ treatments, the samples were transferred to a 250 mL beaker, and 5.5 g L^{-1} sodium hexametaphosphate (Merck, India, 96%) was added to the samples for dispersion (Sperazza et al., 2004). A small amount of dispersed sample was poured into a 1 L borosilicate graduated cylinder with 1000 mL of Milli-Q® water for gravity settling. The depth of the water column, containing a particular size fraction, was calculated by 'Stokes Law' using *Sedicalc* (Krumm, 2006) software and later concentrated by a centrifuge method for making oriented glass slides. To check whether the grain size (in the clay size range) has any effect on the clay mineralogy, various size fractions of one Cambay Shale sample, i.e.: (1) bulk sample (having all size fractions between 2 and 0.2 μm); (2) 2 to 1 μm; (3) 1

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

to 0.5 μm; (4) 0.5 to 0.2 μm; and (5) < 0.2 μm were analyzed in a Rigaku desktop X-ray diffractometer operating with CuKα radiation between 2 and 60°2θ with a step size of 0.02°2θ and count time per step of 1 s (Fig. 1). The bulk clay samples containing the 2–0.2 μm size fractions were selected for the δ^2H analysis. In addition, two kaolinite internal laboratory reference materials (BDLK2 and BDLK3) collected from a kaolinite deposit formed over a Precambrian basement rock were also processed. As mentioned, the reference materials were subjected to H_2O_2 treatment for a minimum of 2 h and a maximum of 48 h to assess its effect on δ^2H values, if any. About 1–2 mg of vacuum-dried (70°C for 24 h) clay samples were packed into tin capsules and analyzed immediately by placing them onto the automated carousel atop a Temperature Conversion Elemental Analyzer (TC-EA; Thermo Scientific, Bremen, Germany; Fig. 2a; following Sharp et al., 2001). The sample capsule was plunged inside the graphite crucible housed in a glassy carbon reactor surrounded by a ceramic insulator tube under a continuously He-flushed (purity 99.999%, flow rate of ~100 mL min^{-1}) condition. The lower part of the reactor was filled with glassy carbon granules, pre-conditioned at ~1450°C. The base of the reactor was plugged with silver wool, which also adsorbed sulfur and other halogen gases produced during the pyrolysis. Gases produced by the high-temperature reduction were then allowed to pass through a gas chromatographic column (molecular sieve 5 Å) maintained at 80°C to separate other trace gases from the target H_2. The purified H_2 was introduced into a Delta^{plus}XP mass spectrometer (Thermo Scientific, Bremen, Germany) via a ConFlo interface housed at the National Facility for Stable Isotope Geochemistry, Department of Geology and Geophysics, Indian Institute of Technology (IIT) Kharagpur. Only ~10% of the H_2 from the reaction tube went into the open split (maintained at ~2 mL min^{-1} He), which dilutes and sends the gas to the mass spectrometer, and the remaining ~90% of the gas was expelled through the vent. The ConFlo interface also generated reference H_2 pulses, so individual sample H_2 peaks could be measured against those of a reference gas (Fig. 2b). This procedure is comparatively fast, requires a small amount of sample, and provides 100% yield for hydrogen. Routine H_3^+-correction was employed before analyzing each set of samples. Raw delta (δ) values were calculated with respect to a laboratory tank of H_2. The tank H_2 was used as a primary reference gas. Raw δ values were calculated using the following relationship:

$$\delta_X = \left(\frac{R_X}{R_R} - 1\right) \times 1000 \text{ (in ‰ with respect to VSMOW)} \quad (1)$$

where R_X = D/H ratio in the sample and R_R = D/H ratio in the reference (the δ^2H of the laboratory tank was assumed to be 0‰).

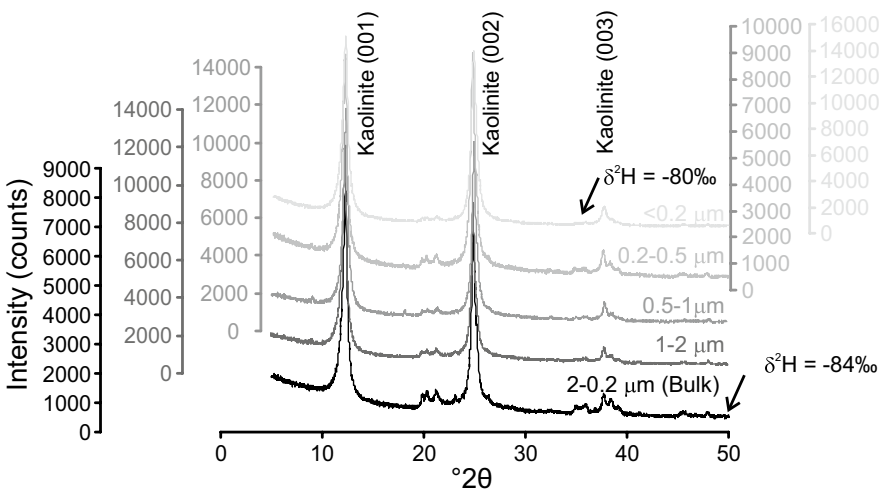

Fig. 1 XRD data (CuKα) showing the presence of kaolinite only in all size fractions of a single Cambay Shale sample and δ^2H values of bulk and the finest (<0.2 μm) size fractions treated with H_2O_2; note no appreciable difference in δ^2H values between the size fractions studied

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

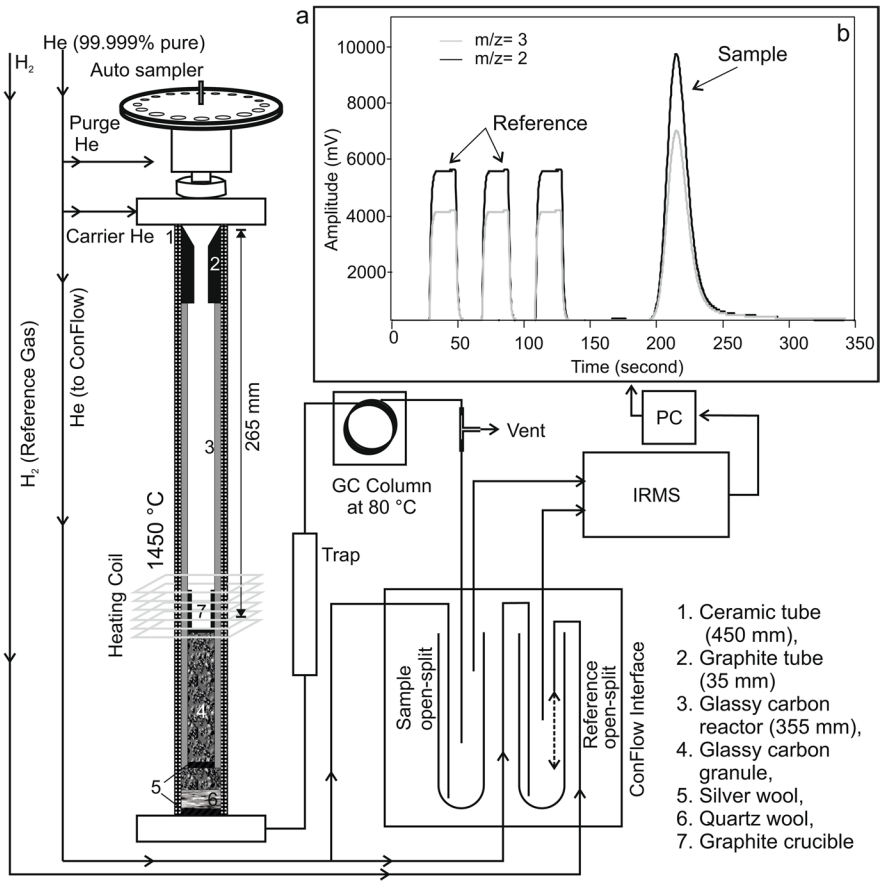

Fig. 2 **a** Schematic diagram of the high-temperature TC-EA reactor showing the flow of He carrier gas through the GC column into the mass spectrometer. **b** Typical chromatograms of the H_2 reference and sample gases

Before routine analysis of the clay samples, the reproducibility of the TC-EA-Delta^{plus}XP mass spectrometer system was monitored by analyzing the NBS-22 (oil) certified reference material. In doing so, many aliquots of NBS-22 were measured over a large range of H^+ ion beam amplitude (mV), and the raw δ^2H (vs. tank H_2) was estimated (Table 1; Fig. 3a). The raw δ^2H values of NBS-22 exhibited good reproducibility (±2‰) over a very large range of beam amplitude (mV) varying between ~2000 and ~31,000 mV, which is similar to those obtained elsewhere by both dual inlet and online continuous flow techniques (Sanyal et al., 2010; Sharp et al., 2001). Such good reproducibility of the NBS-22 δ^2H values indicated the system's stability over a wide range of ion currents. The reproducibility becomes better (~0.8‰) with a restricted/narrower range of H^+ ion beam amplitude (mV), as was shown by Coplen and Qi (2010).

Natural clays can have a wide range of δ^2H values depending on the meteoric/environmental water hydrogen isotopic composition with which the clay had equilibrated. While glacial meltwaters at high altitudes or latitudes can be extremely depleted in deuterium, tropical waters, affected by evaporation, may be significantly enriched in deuterium (Dansgaard, 1964). Because the resistance of the amplifier of the mass spectrometer does not behave linearly with minor ion current, the system is required to be referenced with respect to reference materials of widely varying isotope compositions before measurement of any unknown samples (Coplen & Qi, 2010; Qi et al., 2014). During the present work, this was obtained by analyzing three reference materials

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

Table 1 Amplitude of the H^+ ion beam and raw δ^2H values vs. values from tank H_2 (raw)

Sample	Amplitude (mV)	Raw δ^2H (‰)	Sample	Amplitude (mV)	Raw δ^2H (‰)
NBS-22	7367	1636	NBS-22	8063	1639
NBS-22	17520	1636	NBS-22	6272	1639
NBS-22	2148	1637	NBS-22	4798	1638
NBS-22	31282	1638	NBS-22	9383	1637
NBS-22	9426	1633	NBS-22	6194	1632
NBS-22	18130	1634	NBS-22	3697	1638
NBS-22	23324	1635	NBS-22	7551	1637
NBS-22	10708	1636	NBS-22	12621	1638
NBS-22	16430	1634	NBS-22	9018	1638
NBS-22	21146	1634	NBS-22	12624	1636
NBS-22	24393	1636	NBS-22	14075	1637
NBS-22	4838	1639	NBS-22	12294	1635
NBS-22	11929	1635	NBS-22	15910	1634
NBS-22	6950	1639	NBS-22	11979	1633
NBS-22	24062	1635	NBS-22	15886	1634
NBS-22	8933	1640		Mean ± 1σ	1636 ± 2

having widely different δ^2H values (Fig. 3b). These are NBS-22$_{VSMOW}$ oil (−116.9 ± 0.8‰; Coplen & Qi, 2010), AP-223$_{VSMOW}$ (−80‰), and AP-227$_{VSMOW}$ (−49‰; internal cellulose nitrate reference materials obtained from Physical Research Laboratory, Ahmedabad). Using the slope and intercept obtained from recommended and measured δ^2H values of the reference materials, NBS-22 – AP-223 – AP-227 (Fig. 3b), the final δ^2H values (VSMOW) of multiple aliquots of ground biotite certified reference material NBS-30 were calculated as unknown samples. The δ^2H values of the kaolinite samples were calculated in the same way as mentioned above. The accuracy of the analysis was checked by comparing the measured and recommended δ^2H values of the primary NBS-30 certified reference material. Because δ^2H values of NBS-30 show a grain-size dependency (see Qi et al., 2014 and references therein for details), the NBS-30 was powdered with the help of an agate mortar and pestle before being introduced into the TC-EA for high-temperature reduction. As observed by previous workers, the δ^2H values of NBS-30 crystals showed a clear grain size-dependent trend, and the measured δ^2H values became closer to recommended δ^2H values (−65.7 ± 2‰; Qi et al., 2014) only when the grain size was <74 µm (−64‰, Qi et al., 2014). The measured values of NBS-30 (n = 3), as an unknown sample, yielded a δ^2H value of −64.2 ± 0.3‰ (VSMOW) which agreed well with the recommended value of −65.7 ± 2‰ (see Qi et al., 2014). Hereafter, all δ^2H values are reported with respect to VSMOW unless otherwise mentioned specifically.

Total organic carbon (in wt.%) of all decarbonated (HCl-treated), H_2O_2-treated, and $Na_2S_2O_8$-treated bulk clay samples (size fraction 2–0.2 µm) were measured in a Flash 2000 Elemental Analyzer (Thermo Scientific, Bremen, Germany) attached to a Thermo Delta V Advantage continuous flow isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany) at the Department of Geology and Geophysics, IIT Kharagpur, India (see Samanta et al., 2013, for details).

Results

The X-ray diffraction (XRD) data of all size fractions, i.e. (1) bulk sample (having all size fractions between 2 and 0.2 µm), (2) 2 and 1 µm, (3) 1 and 0.5 µm, (4) 0.5 and 0.2 µm, and (5) <0.2 µm suggested that irrespective of size, all size fractions represent kaolinite only (Fig. 1). The δ^2H values of the bulk clay and the finest fraction (<0.2 µm) did not show an appreciable difference even when treated with H_2O_2.

Two samples of organic matter-free (below detection limit), pure kaolinite internal laboratory reference materials BDLK2 and BDLK3 showed similar δ^2H

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

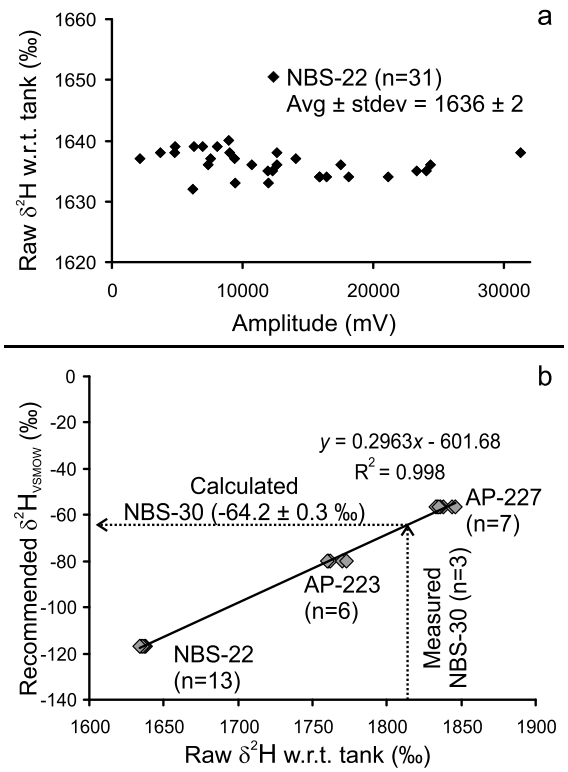

Fig. 3 **a** The stability of the Elemental Analyzer-DeltaplusXP mass spectrometer system over a large range of ion-current (represented as collector voltage). **b** Results of δ^2H stretching experiment using three reference materials having widely different δ^2H values. Measured and calculated values for NBS-30 Biotite reference material treated as an unknown are also shown using dotted lines (see text for details; w.r.t. = with respect to)

values of −77 ± 2‰ and −80 ± 2‰, respectively, for H_2O_2-treated, $Na_2S_2O_8$-treated, and untreated samples (Table 2). No significant difference was observed even when H_2O_2 treatment duration was varied from a minimum of 2 h to a maximum of 2 days. The δ^2H values of kaolinite extracted from the Cambay Shale using H_2O_2 treatment exhibited a range between −73 and −78‰ (average ~ −75‰), whereas kaolinite extracted from the same samples using $Na_2S_2O_8$ treatment showed larger values, varying from −48 to −56‰ (average ~ −53‰; Table 3; Fig. 4).

The TOC of the decarbonated samples varied from 0.12 to 5.15 wt.%. However, after organic-matter removal/oxidation, the TOC varied from 0.05 to 3.58 wt.% for the H_2O_2-treated samples and 0.03 to 0.07 wt.% for $Na_2S_2O_8$-treated samples (Table 3; Fig. 4).

Table 2 δ^2H values of kaolinite internal laboratory reference materials (BDLK2 and BDLK3) using various organic matter-removal techniques

Internal laboratory reference materials	BDLK2	BDLK3
δ^2H, ‰ (VSMOW) without treatment	−79	−78
δ^2H, ‰ (VSMOW) $Na_2S_2O_8$ treatment	−77	−82
δ^2H, ‰ (VSMOW) H_2O_2 treatment (2 h)	−75	−79
δ^2H, ‰ (VSMOW) H_2O_2 treatment (1 day)	−80	−82
δ^2H, ‰ (VSMOW) H_2O_2 treatment (2 days)	−76	−78
Mean ± 1σ	−77 ± 2	−80 ± 2

Discussion

The $\delta^{18}O$ and δ^2H values of both detrital (having a nearby source; Oyebanjo et al., 2018) and authigenic (formed during the early diagenesis; Girard et al., 2000) clay minerals found in sediments can be excellent recorders of the ambient climate. However, depending on the source and mineralogy, the δ^2H values of the clay minerals can show large variability. The general assumption is that the finer fraction (< 0.2 μm) of the clay represents the authigenic minerals formed during early water–rock interaction, whereas the coarser fraction generally represents the detrital fraction (Andrzejewski & Tabor, 2020; Bukalo et al., 2019; Oyebanjo et al., 2018; Tabor & Montañez, 2005). Therefore, a detailed size-fraction analysis of one representative sample was performed before the δ^2H measurements to check whether the clays studied represent a mixture of both detrital and authigenic populations. All size fractions were characterized by kaolinite only (Fig. 1) and showed no appreciable difference in δ^2H values between the bulk (2–0.2 μm) and finest (>0.2 μm) fraction, even when treated with H_2O_2. Hence, the 2–0.2 μm size fraction (i.e. bulk clay fraction) was selected for δ^2H analysis for the rest of the samples.

Hyeong and Capuano (2000) and Menegatti et al. (1999) showed that both H_2O_2 and $Na_2S_2O_8$ treatment alter the δ^2H values of their smectite reference materials. The authors suggested that this may be due to the exchange of H^+ ions, adsorbed primarily on interlamellar surfaces of smectite, with H^+ coming from H_2O_2 (intermediate cation in Fenton-like reactions, Mikutta et al., 2005 and references therein). The δ^2H values of two pure kaolinite

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

Table 3 δ^2H values (all values with respect to VSMOW) of kaolinite separated from Cambay shale using various organic matter-removal techniques and calculated meteoric water δ^2H values under assumed equilibration temperatures of 28°C

Sample depth (m) (TOC, %, after HCl-assisted decarbonation)		239.5 (0.55)	244 (5.15)	287 (0.12)	298.5 (0.24)
Material		Gray shale	Carb. Shale	Gray shale	Gray shale
H_2O_2-treated (for 2 days) samples	Kaolinite δ^2H ‰ (TOC in %)	−73 (0.05)	−78 (3.58)	−76 (0.07)	−73 (0.12)
	Estimated meteoric water δ^2H ‰ at 28°C	−43	−48	−46	−43
$Na_2S_2O_8$-treated samples	Kaolinite δ^2H ‰ (TOC in %)	−52 (0.05)	−56 (0.07)	−48 (0.04)	−54 (0.03)
	Estimated meteoric water δ^2H ‰ at 28°C	−22	−25	−17	−23

The TOC, in % after HCl-assisted decarbonation, and $Na_2S_2O_8$ and H_2O_2 treatments are also provided

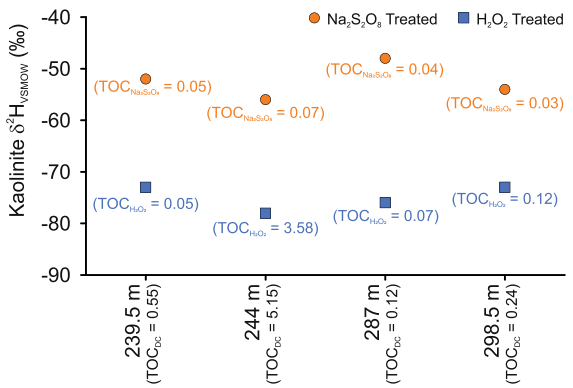

Fig. 4 Comparison of kaolinite δ^2H_{VSMOW} (‰) values after treatments with H_2O_2 and $Na_2S_2O_8$. The total organic carbon (%) after HCl-assisted decarbonation (TOC_{DC}), H_2O_2 ($TOC_{H_2O_2}$), and $Na_2S_2O_8$ ($TOC_{Na_2S_2O_8}$) treatments are also shown for comparison

internal laboratory reference materials (BDLK2 and BDLK3) were measured without any pretreatment as well as after the H_2O_2 (after 2 h, 1 day, and 2 days of reaction time) and $Na_2S_2O_8$ treatments to evaluate the effect, if any, of the treatment, on the δ^2H values (Table 2). No appreciable difference in δ^2H values was observed between the treated and untreated kaolinite reference materials. The δ^2H values obtained for these pure kaolinite reference materials subjected to these two treatments were -77 ± 2 and -80 ± 2‰, respectively, and are very similar within experimental error (Table 2). Even H_2O_2 treatment for 2 days did not alter the kaolinite δ^2H values. Also important to note is that, before H_2O_2 and $Na_2S_2O_8$ treatment, the kaolinite internal laboratory reference materials were subjected to routine HCl and CBD treatment. One may assume, therefore, that, apart from H_2O_2 and $Na_2S_2O_8$, the HCl and CBD treatments did not alter the hydrogen isotopic composition of these kaolinite internal laboratory reference materials. The possibility exists that not enough free H^+ was present during the HCl reactions (0.5 N HCl) to cause hydrogen isotopic exchange, i.e. all H^+ may have been consumed during carbonate dissolution or the reaction rate was too slow to show any significant effect on the δ^2H values.

When subjected to different pretreatment methods, however, a substantial difference in δ^2H values was observed for the kaolinites separated from Cambay Shale. When comparing δ^2H values of H_2O_2- and $Na_2S_2O_8$-treated kaolinite from these shale samples, H_2O_2-treated samples were ~20–30‰ less than the $Na_2S_2O_8$-treated aliquots (Fig. 4). TOC data highlight that the $Na_2S_2O_8$ treatment was more efficient for organic-matter removal (Table 3; Fig. 4). The δ^2H values of the investigated shale samples, along with their TOC data, suggested that for sediment samples with high TOC (carbonaceous shale 244 m), the H_2O_2 treatment is not sufficient, resulting in partial retention of the organic phases, which may eventually contaminate the samples during their δ^2H measurement. The present observation concerning the inefficient removal of organic matter during the H_2O_2 treatment has also been reported by many previous workers, e.g. Hyeong and Capuano (2000), Meier and Menegatti (1997), Menegatti et al. (1999), and Mikutta et al. (2005). Three possible reasons for the observed difference in the average δ^2H values of ~22‰ between H_2O_2 and $Na_2S_2O_8$-treated samples could be: (1) the presence of residual organic matter after H_2O_2 treatment; (2) hydrogen isotopic exchange between H_2O_2 and kaolinite's 'outer hydroxyl' group (Fig. 5; Ledoux & White, 1964); and (3) dissolution (and possible reprecipitation) of kaolinite during the H_2O_2 treatment (Fig. 5; Cama & Ganor, 2006; Chin & Mills, 1991; Mikutta et al.,

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

2005; Yang & Steefel, 2008). So, a simple mass-balance estimation was performed to understand whether the presence of residual organic matter can cause the observed ~22‰ difference between H_2O_2- and $Na_2S_2O_8$-treated samples. In doing so, it was estimated from the chemical formula that kaolinite has a hydrogen mass fraction of 1.56 wt.% and organic matter (CH_2) has a hydrogen mass fraction of 14.29 wt.%. The organic-matter chemical formula, i.e. CH_2, was chosen on purpose to estimate the maximum possible depletion to be expected in δ^2H values when samples are contaminated with organic matter. Any other natural soil/sedimentary organic matter, e.g. cellulose, lignin, etc., contains a much smaller amount of hydrogen, ~6%. If the clay δ^2H value is ~−53‰ (average of the $Na_2S_2O_8$-treated samples) and the organic matter δ^2H value is ~−120‰ ($\Delta D^{Water}_{C3PlantOM}$~−120‰, Leaney et al., 1985; ($\Delta D^{Water}_{sedimentaryorganicmatter}$~−80 to −110‰, Schimmelmann et al., 2006), the presence of 1 wt.% organic matter in the treated clay can shift the δ^2H values by ~5–6‰. The observed difference of ~20‰ between H_2O_2- and $Na_2S_2O_8$-treated samples requires ~5 wt.% organic matter in the H_2O_2-treated samples. The TOC (wt.%) data suggested that the TOC of the H_2O_2-treated samples was < 1 wt.% (except for one sample), however. The presence of residual organic matter after H_2O_2 treatment cannot explain the observed difference in δ^2H values. Interestingly, a study by Barnette et al. (2011) showed that a linear relationship exists between δ^2H and $\delta^{18}O$ values of H_2O_2 solutions purchased across the United

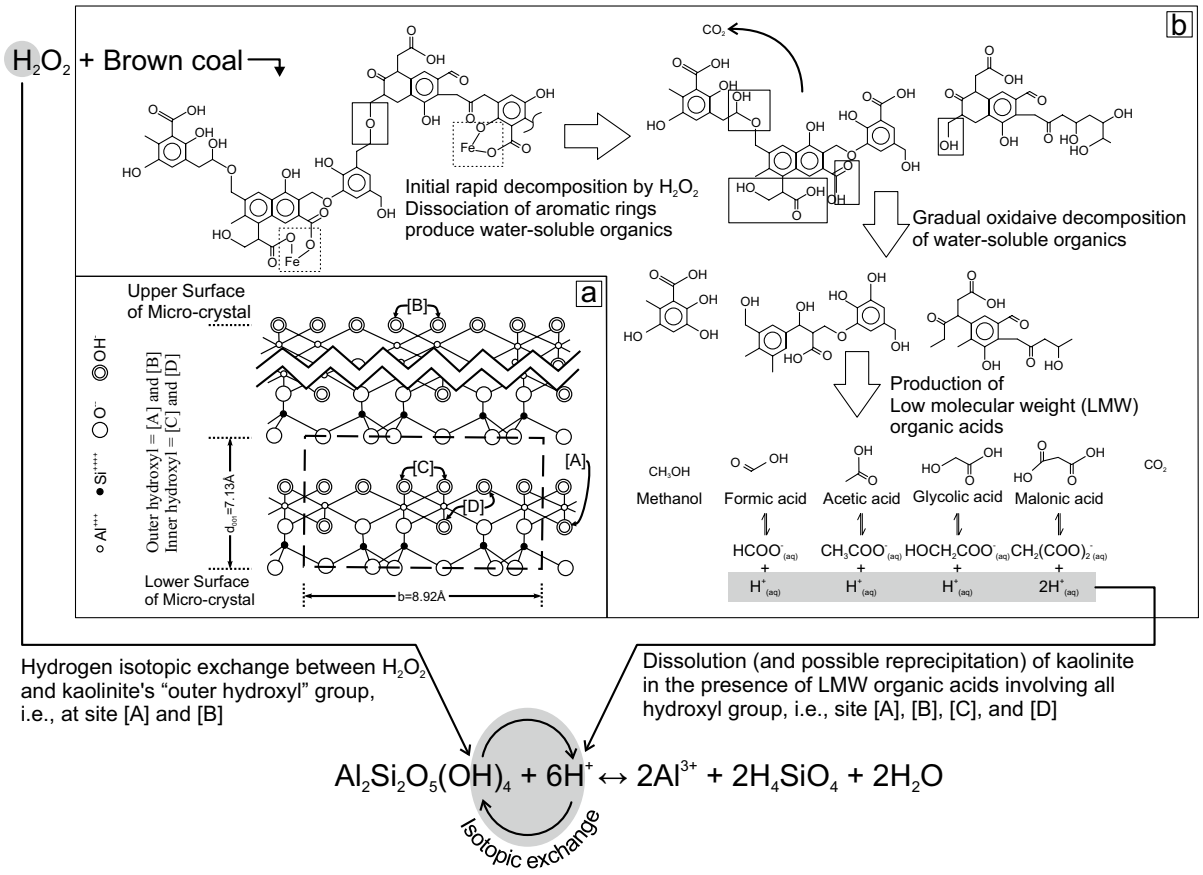

Fig. 5 Schematic diagram showing **a** the projection of the kaolinite crystal structure on the (100) plane (modified after Ledoux & White, 1964) and **b** the proposed mechanism for the H_2O_2 oxidation of Brown coal and formation of low-molecular-weight organic acids (modified after Miura et al., 1996). Two important processes, i.e. hydrogen isotopic exchange between H_2O_2 and kaolinite's "outer hydroxyl" group and dissolution (and possible reprecipitation) of kaolinite in the presence of low molecular-weight organic acids produced during the H_2O_2 treatment, are also shown

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

States and in Mexico, which nearly parallels the Local Meteoric Water Line (LMWL) and the δ^2H values can be as low as −235‰. So, a possibility exists that ^2H-depleted H_2O_2 can cause a significant depletion in the clay δ^2H values through hydrogen isotopic exchange of the kaolinite's 'outer hydroxyl' group (Fig. 5a). However, the small ratio (~1:130; see Supplementary Material for detailed calculations) of the ~0.2 μm size kaolinite's 'outer hydroxyl' and 'inner hydroxyl' groups can only cause a minimal shift (~−1.4‰) during the isotopic exchange between highly ^2H-depleted H_2O_2 (−235‰), and most ^2H-enriched $Na_2S_2O_8$-treated kaolinite (~−53‰). Therefore, following Mikutta et al. (2005), H_2O_2 treatment was suspected possibly to promote the organic-assisted dissolution of poorly crystalline minerals at low pH. During this dissolution (±reprecipitation) process, isotope exchange between mineral and H_2O_2 may cause the lowering of the δ^2H values of kaolinite clays. Previous studies have shown that oxidation of organic matter (coal/lignite) using H_2O_2 produces a large quantity of low-molecular-weight organic acids, e.g. formic acid, acetic acid, glycolic acid, succinic acid, and malonic acid (Fig. 5; Doskočil et al., 2014; Miura et al., 1996). Because the low-molecular-weight organic acids are more efficient at dissolution and sometimes reprecipitation of silicates or kaolinite compared to the inorganic acids, even at low temperatures (Cama & Ganor, 2006; Chin & Mills, 1991; Yang & Steefel, 2008), the organic-assisted dissolution (±reprecipitation in selected cases) during the H_2O_2 treatment may be the reason for this discrepancy (Fig. 5). $Na_2S_2O_8$ treatment, on the other hand, is likely to be less harmful to the minerals (Mikutta et al., 2005) as it is performed at a neutral to basic pH and thus lacks free H^+ to affect the δ^2H of kaolinite..

In a further attempt to understand which of the average kaolinite δ^2H values (i.e. H_2O_2-treated [−75‰] or $Na_2S_2O_8$-treated [−53‰]) is more realistic, soil/environmental water δ^2H values were estimated using a branched glycerol dialkyl glycerol tetraether-based paleotemperature estimation of ~28°C (Naafs et al., 2018) from nearby early Eocene lignite deposits at Matanomadh and Panandhro, and a hydrogen isotope fractionation factor of the kaolinite–water system provided by Gilg and Sheppard (1996; Table 3). The calculated soil/environmental water δ^2H values for the H_2O_2 and $Na_2S_2O_8$ treated kaolinite were −45 and −22‰, respectively (Table 3). Using the relationship between the $\delta^{18}O$ and δ^2H values of global precipitation water, i.e. the global meteoric water line (Dansgaard, 1964), the estimated early Eocene equatorial precipitation $\delta^{18}O$ for the H_2O_2- and $Na_2S_2O_8$-treated kaolinite are −7 and −4‰, respectively. Bera et al. (2010) reported a phosphate $\delta^{18}O$ value of 18.1‰ from fish vertebrae recovered from the equivalent stratigraphic horizon (i.e. above the characteristic carbon isotopic excursion of the Paleocene–Eocene Thermal Maximum) of nearby Vastan Mine (see Samanta et al., 2016 for detailed stratigraphic correlation). Following the revised phosphate–water fractionation equation for biogenic apatite (Pucéat et al., 2010), the environmental (lagoonal) water $\delta^{18}O$ value of −3.3‰ was estimated from the phosphate $\delta^{18}O$ value (at 28°C). The estimated environmental water $\delta^{18}O$ values from these two independent proxies, i.e. $Na_2S_2O_8$-treated kaolinite δ^2H values (−4‰) and fish vertebrae phosphate (−3.3‰), agree well with each other. Alternatively, the environmental water $\delta^{18}O$ value of −7‰, obtained from the H_2O_2-treated kaolinite, requires an abnormally small d-excess ($=\delta^2H - 8*\delta^{18}O$; Dansgaard, 1964) value of ~−19‰. As such a low d-excess value is unrealistic for the equatorial marginal marine precipitation, the $Na_2S_2O_8$-treated kaolinite δ^2H values are proposed to be more realistic.

An important observation is that such a difference in δ^2H values between H_2O_2- and $Na_2S_2O_8$-treated samples was not seen for the kaolinite internal laboratory reference materials. The possibility exists that: (1) the very small organic matter content of these kaolinite reference materials was insufficient to cause organic-assisted dissolution (±reprecipitation); and/or (2) a better crystallinity (greater structural order) of the kaolinite internal laboratory reference materials, obtained from a kaolinite deposit formed over a Precambrian basement rock (Aparicio & Galan, 1999), prevented organic-assisted dissolution at low pH and possible disintegration/transformation (following Mikutta et al., 2005).

Based on these observations and also on the data of pretreatment experiments on kaolinite reference materials, the conclusion is that $Na_2S_2O_8$ treatment is a better method for both complete removal of organic matter and preservation of pristine δ^2H values for paleoclimate analysis compared to H_2O_2 treatment.

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

Conclusions

The present study showed that the commonly used H_2O_2 pretreatment for extracting clay minerals from organic matter-rich sediments (e.g. carbonaceous shales) is inefficient at removing organic matter. The $Na_2S_2O_8$ treatment was more efficient. Further, the smaller δ^2H values of the H_2O_2-treated aliquots compared to the $Na_2S_2O_8$-treated aliquots raised suspicion about the possible alteration of the pristine δ^2H values during H_2O_2 treatment. Because H_2O_2 treatment of organic material-bearing sediment produces low-molecular-weight organic acids, which have the potential to cause organic-assisted dissolution ($\pm$reprecipitation) of the clay minerals, the possibility exists that H_2O_2 treatment can lead to alteration of the pristine isotopic composition. The excellent agreement between the estimated environmental water $\delta^{18}O$ values from two independent proxies, i.e. biogenic phosphate and $Na_2S_2O_8$-treated kaolinite, further suggested that $Na_2S_2O_8$ treatment is less harmful to the clay minerals as the treatment is performed under neutral to mildly basic pH condition that helps to retain the pristine isotopic composition. The present study, therefore, recommends $Na_2S_2O_8$ treatment for clay mineral separation for isotopic study.

Acknowledgements The present work was initiated by A. Samanta during her Ph.D. studies; she thanks IIT Kharagpur for the fellowship. A. Samanta is also grateful to Asutosh College for providing the necessary permission to carry out further research. A. Sarkar acknowledges the Department of Science and Technology (DST), New Delhi, for funding a research project on Paleogene sediments of western and northwestern India, under which the fieldwork was conducted and samples were procured. All isotope data were generated in the Diamond Jubilee Stable Isotope Mass Spectrometer Laboratory at IIT Kharagpur. All of the authors thank R. Ramesh (PRL, Ahmedabad) and P. Sengupta (Jadavpur University) for providing the cellulose nitrate and kaolinite reference materials. An in-depth review by an anonymous reviewer, by Prof. J. M. Wampler, by Prof. Peter Ryan (Associate Editor), and by Prof. Joseph W. Stucki (Editor in Chief) helped improve the manuscript significantly.

Authors' contributions All authors equally contributed to conceiving the problem, sample collection, experiment design, data interpretation, and MS writing. A. Sarkar arranged the funding. All authors confirm that they have seen the manuscript and agree to its submission to *Clays and Clay Minerals*.

Funding The Department of Science and Technology (DST) and the Indian Institute of Technology Kharagpur, India.

Data availability All of the data used in the manuscript are provided in the tables and supplementary material.

Code availability Not Applicable.

Declarations

Conflicts of interest/Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Anderson, J. U. (1963). An improved pretreatment for mineralogical analysis of samples containing organic matter. *Clays and Clay Minerals, 10*(1), 380–388.

Andrzejewski, K., & Tabor, N. J. (2020). Paleoenvironmental and paleoclimatic reconstruction of Cretaceous (Aptian-Cenomanian) terrestrial formations of Texas and Oklahoma using phyllosilicates. *Palaeogeography, Palaeoclimatology, Palaeoecology, 543*, 109491.

Aparício, P., & Galán, E. (1999). Mineralogical interference on kaolinite crystallinity index measurements. *Clays and Clay Minerals, 47*(1), 12–27.

Bansal, M., Morley, R. J., Nagaraju, S. K., Dutta, S., Mishra, A. K., Selveraj, J., Kumar, S., Niyolia, D., Harish, S. M., Abdelrahim, O. B., & Hasan, S. E. (2022). Southeast Asian Dipterocarp origin and diversification driven by Africa-India floristic interchange. *Science, 375*(6579), 455–460.

Barnette, J. E., Lott, M. J., Howa, J. D., Podlesak, D. W., & Ehleringer, J. R. (2011). Hydrogen and oxygen isotope values in hydrogen peroxide. *Rapid Communications in Mass Spectrometry, 25*(10), 1422–1428.

Bechtel, A., & Hoernes, S. (1993). Stable isotopic variations of clay minerals: A key to the understanding of Kupferschiefer-type mineralization. *Germany. Geochimica et Cosmochimica Acta, 57*(8), 1799–1816.

Bechtel, A., Savin, S. M., & Hoernes, S. (1999). Oxygen and hydrogen isotopic composition of clay minerals of the Bahloul Formation in the region of the BouGrine zinc–lead ore deposit (Tunisia): Evidence for fluid–rock interaction in the vicinity of salt dome cap rock. *Chemical Geology, 156*(1–4), 191–207.

Bera, M. K., Bhattacharya, K., Sarkar, A., Samanta, A., Kumar, K., & Sahni, A. (2010). Oxygen isotope analysis of bone and tooth enamel phosphate from paleogene sediments: Experimental techniques and initial results. *Journal of the Geological Society of India, 76*(3), 275–282.

Bukalo, N., Ekosse, G. I., Odiyo, J., & Ogola, J. (2019). Paleoclimatic implications of hydrogen and oxygen isotopic compositions of Cretaceous-Tertiary kaolins in the Douala Sub-Basin Cameroon. *Comptes Rendus Geoscience, 351*(1), 17–26.

Cama, J., & Ganor, J. (2006). The effects of organic acids on the dissolution of silicate minerals: A case study of oxalate catalysis of kaolinite dissolution. *Geochimica et Cosmochimica Acta, 70*(9), 2191–2209.

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

Chin, P. K. F., & Mills, G. L. (1991). Kinetics and mechanisms of kaolinite dissolution: Effects of organic ligands. *Chemical Geology, 90*(3–4), 307–317.

Coplen, T. B., & Qi, H. (2010). Applying the silver-tube introduction method for thermal conversion elemental analyses and a new δ^2H value for NBS 22 oil. *Rapid Communications in Mass Spectrometry, 24*(15), 2269–2276.

Dansgaard, W. (1964). Stable isotopes in precipitation. *Tellus, 16*(4), 436–468.

Doskočil, L., Grasset, L., Válková, D., & Pekař, M. (2014). Hydrogen peroxide oxidation of humic acids and lignite. *Fuel, 134*, 406–413.

Dutta, S., Bhattacharya, S., Mallick, M., Shukla, A. C., & Mann, U. (2012). Preserved lignin structures in early eocene Surat lignites, Cambay Basin, Western India. *Journal of the Geological Society of India, 79*(4), 345–352.

Gilg, H. A. (2000). D-H evidence for the timing of kaolinization in Northeast Bavaria, Germany. *Chemical Geology, 170*(1–4), 5–18.

Gilg, H. A., & Sheppard, S. M. (1996). Hydrogen isotope fractionation between kaolinite and water revisited. *Geochimica et Cosmochimica Acta, 60*(3), 529–533.

Gilg, H.A., Girard, J.P., & Sheppard, S.M. (2004). Conventional and less conventional techniques for Hydrogen and oxygen isotope analysis of clays, associated minerals and pore waters in sediments and soils. In: *Handbook of Stable Isotope Analytical Techniques.* Elsevier, pp. 38–61.

Girard, J. P., Freyssinet, P., & Chazot, G. (2000). Unraveling climatic changes from intraprofile variation in oxygen and hydrogen isotopic composition of goethite and kaolinite in laterites: An integrated study from Yaou, French Guiana. *Geochimica et Cosmochimica Acta, 64*(3), 409–426.

Hyeong, K., & Capuano, R. M. (2000). The effect of organic matter and the H_2O_2 organic-matter-removal method on the δD of smectite-rich samples. *Geochimica et Cosmochimica Acta, 64*(22), 3829–3837.

Jackson, M. L. (2005). *Soil Chemical Analysis: Advanced Course*. UW-Madison Libraries Parallel Press.

Krumm, S. (2006). SediCalc (Free Geological Software). GeoZentrum Nordbayern, Universität Erlangen-Nürnberg. http://www.geol.uni-erlangen.de/sedicalc.

Leaney, F. W., Osmond, C. B., Allison, G. B., & Ziegler, H. (1985). Hydrogen-isotope composition of leaf water in C3 and C4 plants: Its relationship to the hydrogen-isotope composition of dry matter. *Planta, 164*(2), 215–220.

Ledoux, R. L., & White, J. L. (1964). Infrared study of the OH groups in expanded kaolinite. *Science, 143*(3603), 244–246.

Mehra, O.P., & Jackson, M.L. (1960). Fe oxide removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. *In: Proceeding of the 7th National Conference on Clays and Clay minerals* (editor: A. Swineford. Pergamon Press, UK), pp. 317–327.

Meier, L. P., & Menegatti, A. P. (1997). A new, efficient, one-step method for the removal of organic matter from clay-containing sediments. *Clay Minerals, 32*(4), 557–563.

Menegatti, A. P., Frueh-Green, G. L., & Stille, P. (1999). Removal of organic matter by disodium peroxodisulphate: Effects on mineral structure, chemical composition and physicochemical properties of some clay minerals. *Clay Minerals, 34*(2), 247–257.

Mikutta, R., Kleber, M., Kaiser, K., & Jahn, R. (2005). Organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. *Soil Science Society of America Journal, 69*(1), 120–135.

Mitchell, B. D., & Farmer, V. C. (1962). Amorphous clay minerals in some Scottish soil profiles. *Clay Minerals Bulletin, 5*(28), 128–144.

Miura, K., Mae, K., Okutsu, H., & Mizutani, N. A. (1996). New oxidative degradation method for producing fatty acids in high yields and high selectivity from low-rank coals. *Energy & Fuels, 10*(6), 1196–1201.

Mizota, C., & Longstaffe, F. J. (1996). Origin of Cretaceous and Oligocene kaolinites from the Iwaizumi clay deposit, Iwate, northeastern Japan. *Clays and Clay Minerals, 44*(3), 408–416.

Naafs, B. D. A., Rohrssen, M., Inglis, G. N., Lähteenoja, O., Feakins, S. J., Collinson, M. E., Kennedy, E. M., Singh, P. K., Singh, M. P., Lunt, D. J., & Pancost, R. D. (2018). High temperatures in the terrestrial mid-latitudes during the early Palaeogene. *Nature Geoscience, 11*(10), 766–771.

Oyebanjo, O., Ekosse, G. I., & Odiyo, J. (2018). Hydrogen and oxygen isotope composition of selected Cretaceous and Paleogene/Neogene kaolins from Nigeria: Paleoclimatic inferences. *Applied Clay Science, 162*, 375–381.

Pozo, M., & Calvo, J. P. (2018). An overview of authigenic magnesian clays. *Minerals, 8*(11), 520.

Prasad, V., Farooqui, A., Tripathi, S. K. M., Garg, R., & Thakur, B. (2009). Evidence of late Palaeocene-early Eocene equatorial rain forest refugia in southern Western Ghats, India. *Journal of Biosciences, 34*(5), 777–797.

Pucéat, E., Joachimski, M. M., Bouilloux, A., Monna, F., Bonin, A., Motreuil, S., Morinière, P., Hénard, S., Mourin, J., Dera, G., & Quesne, D. (2010). Revised phosphate–water fractionation equation reassessing paleotemperatures derived from biogenic apatite. *Earth and Planetary Science Letters, 298*(1–2), 135–142.

Qi, H., Coplen, T. B., Olack, G. A., & Vennemann, T. W. (2014). Caution on the use of NBS 30 biotite for hydrogen-isotope measurements with online high-temperature conversion systems. *Rapid Communications in Mass Spectrometry, 28*(18), 1987–1994.

Samanta, A., Bera, M. K., Ghosh, R., Bera, S., Filley, T., Pande, K., Rathore, S. S., Rai, J., & Sarkar, A. (2013). Do the large carbon isotopic excursions in terrestrial organic matter across Paleocene-Eocene boundary in India indicate intensification of tropical precipitation? *Palaeogeography, Palaeoclimatology, Palaeoecology, 387*, 91–103.

Samanta, A., Bera, M. K., & Sarkar, A. (2016). Climate-modulated sequence development in a tropical rift basin during the Late Palaeocene to Early Eocene super greenhouse Earth. *Sedimentology, 63*(4), 917–939.

Sanyal, P., Sarkar, A., Bhattacharya, S. K., Kumar, R., Ghosh, S. K., & Agrawal, S. (2010). Intensification of monsoon, microclimate and asynchronous C4 appearance: Isotopic evidence from the Indian Siwalik sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology, 296*(1–2), 165–173.

Schimmelmann, A., Sessions, A. L., & Mastalerz, M. (2006). Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences, 34*, 501–533.

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press

Sharp, Z. D., Atudorei, V., & Durakiewicz, T. (2001). A rapid method for determination of Hydrogen and oxygen isotope ratios from water and hydrous minerals. *Chemical Geology, 178*(1–4), 197–210.

Sheppard, S. M. F., & Gilg, H. A. (1996). Stable isotope geochemistry of clay minerals: "The story of sloppy, sticky, lumpy and tough" Cairns-Smith (1971). *Clay Minerals, 31*(1), 1–24.

Sperazza, M., Moore, J. N., & Hendrix, M. S. (2004). High-resolution particle size analysis of naturally occurring very fine-grained sediment through laser diffractometry. *Journal of Sedimentary Research, 74*(5), 736–743.

Tabor, N. J., & Montañez, I. P. (2005). Oxygen and hydrogen isotope compositions of Permian pedogenic phyllosilicates: Development of modern surface domain arrays and implications for paleotemperature reconstructions. *Palaeogeography, Palaeoclimatology, Palaeoecology, 223*(1–2), 127–146.

Tributh, H., & Lagaly, G. (1991). Identifizierung und Charakterisierung von Tonmineralen. Berichte der Deutschen Ton- und Tonmineralgruppe Giessen, Germany. *Institut für Bodenkunde und Bodenerhaltung*, 37–85.

Yang, L., & Steefel, C. I. (2008). Kaolinite dissolution and precipitation kinetics at 22°C and pH 4. *Geochimica et Cosmochimica Acta, 72*(1), 99–116.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

https://doi.org/10.1007/s42860-023-00221-z Published online by Cambridge University Press