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Mineral Clays for Cleaning Tidelines on Paper-Based Artworks

Alimatou Desbrière, Anne-Laurence Dupont*, Thalia Bajon-Bouزيد and Isabelle Drieu la Rochelle

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Abstract: Clay minerals possess a number of properties such as ion exchange capability, alkaline pH, adsorptive, swelling and plastic behavior, most of which are governed by their interactions with water. They have the capacity to interact with soluble molecules, which is particularly interesting for art conservation treatments. For all these reasons clays deserve to be considered for green and sustainable paper conservation interventions. In this work two phyllosilicates with different properties, namely montmorillonite and sepiolite, were investigated for the removal of tidelines on artificially aged paper samples. Water exchange, cleaning efficiency and pH were evaluated comparing the clays to gellan gum, a benchmark cleaning hydrogel. A pouch made with regenerated cellulose was used so as to avoid direct contact of the minerals with the paper. The water sorption capacity of the clays combined with the specific permeability of the cellulosic membrane allowed for a homogeneous and easy to control cleaning. The formation of new tidelines, an inherent risk to any local conservation treatment of paper, was avoided. As an example, sepiolite was used for the local cleaning of a paper-based artwork's multiple tidelines.

Keywords: Montmorillonite, sepiolite, gellan, water damage, green conservation

1. Introduction

1.1 Focus on tidelines

Brown lines, also called water marks or 'tidelines', are a manifestation as much as a source of damage, caused by the formation of a wet-dry interface that affects many historical manuscripts, artworks and books (Hutchins 1983, Eusman 1995, Dupont 1996a&b). Tidelines are aesthetically problematic by way of intrusive localized browning, and as such are detrimental to an artwork's readability. They are also problematic at the chemical level as they are a sign of degradation (concentrated acidity and mechanical

*Corresponding author: Anne-Laurence Dupont, Centre de Recherche sur la Conservation des Collections (CRC, CNRS UAR 3224), Muséum National d'Histoire Naturelle, 36 rue Geoffroy St Hilaire 75005 Paris, France.

E-mail: anne-laurence.dupont@mnhn.fr, <https://orcid.org/0000-0003-0341-4850>

Alimatou Desbrière, Institut National du Patrimoine, Département des restaurateurs, Paris, France. E-mail: alimatou.desbriere@gmail.com

Thalia Bajon-Bouزيد, Textile conservation studio, private practise, Paris, France. E-mail: thbajonbouزيد@gmail.com

Isabelle Drieu la Rochelle, Paper conservation studio, private practise, Puteaux, France. E-mail: isa.dlr@wanadoo.fr

fragility). They are usually difficult to remove or attenuate, and wet cleaning increases the risk of producing additional wet-dry interfaces, especially when applied locally. For all these reasons, tidelines are tricky to remediate with conservation treatments.

The term catastrophic is not too strong to characterize the tideline phenomenon since it only takes a few minutes to a few hours to create a tideline. In aged discoloured papers, migration of coloured water-soluble products to the wet-dry interface are expected, but brown lines can also form on pure cellulosic papers or textiles (containing no other biopolymer or additive) even if they have been freshly washed in distilled water beforehand, and are free from coloured degradation products (Bone 1934, Bogaty et al. 1952).

In the laboratory, a tideline is created simply by suspending a sheet of paper vertically, with the lower end immersed in distilled water by a few centimeters. Water rises by capillarity and a brown line quickly appears at the upward moving interface. The brown line darkens slowly before stabilizing in a few hours. The interface boundary fluoresces sharply under UV even before colour appears under visible light (Bone & Turner 1950, Dupont 1996a, Pedersoli and Ligterink 2001). Tideline formation at the wet-dry interface in cellulosic materials, textiles as well as sheets of paper, was observed and described in several early publications (Bone 1934, Bone & Turner 1950, Madaras & Turner 1953, Schaffer et al. 1950, Fox 1965 a&b). Because of the complexity of the chemical reactions triggered, the phenomenon has long been perplexing. Recent research has demonstrated that both acid-catalysed hydrolysis and oxidation reactions occur during the migration of water, through *in-situ* formation and drainage of saturated and unsaturated carboxylic acids, as well as reactive oxygen species such as hydroperoxides and hydroxyl radicals (Souguir et al. 2008, Jeong et al. 2012). Cellulose degradation triggered by free radical mechanisms is favoured during the water migration by the acids, as well as by the high availability of oxygen and water and by the trace metal cations present in paper (iron, copper, etc). These reactive chemical species can explain the fast degradation observed and measured. However, as more recently shown, there is more to the phenomenon since, simultaneous to this, the formation of carbohydrate derivatives with antioxidant properties, such as furan compounds, produced through dehydration reactions (Sladkevich et al. 2016), as well as, the presence among the drained ions, of species with an acid buffering capacity (calcium, magnesium) that can crystallize at the interface, trigger antagonistic effects to the degradation (Jeong et al. 2012). In the tideline area the degradation reactions are thus partly counteracted, whereas in the wet portion of the paper, buffering ions are swept along with the water migration, leaving cellulose more prone to degradation (Jeong et al. 2014). The identification in tideline extracts of unsaturated compounds arising from successive dehydration and cyclisation of sugars could explain the yellowish to brownish colour (Sladkevich et al. 2016).

This bulk of research confirms that tidelines are a source of degradation and should be removed in order to stabilize the paper. The only applicable conservation remediation action is wet-cleaning, whether with water or solvents. In most tidelines, the coloured compounds are, at least in part, water-soluble (Schaffer et al. 1950, Eusman 1995, Dupont 1996a, Jeong et al. 2012). Yet, since water is precisely one of the causes of the degradation, it should be supplied carefully, in limited amount and in a tightly controlled fashion, in order to limit the risk of formation of new wet-dry interfaces.

The use of low pressure vacuum is an effective way to remove tidelines thanks to the powerful forced throughflow. However, this technique would typically fail if the paper is very thick or dense, or on the contrary too fragile to withstand the pressure. This technique is also excluded for wet-cleaning of painted surfaces, such as in the case study presented in section 3.4, which only allows for a one-sided approach. In

that case, using poultice materials is a reasonable option. When the water supply needs to be limited and controlled, hydrogels are often used. Gels are also advisable in cases where, whether for mechanical, structural, compositional or aesthetic reasons, the use of traditional cleaning techniques may not be appropriate (Warda et al. 2007, Botti et al. 2011, Couvert & Dupont 2014).

Additionally, parameters such as pH and conductivity can be modified to optimize the cleaning and/or favour ions exchange between the hydrogel and the paper, such as for deacidification or local bleaching of artworks on paper (Botti et al., 2011, Barbisan 2016). Polysaccharide gels such as gellan gum, agar and agarose are now part of the toolbox of the paper conservator (Angelova et al. 2017). In particular, hydrogels have been used for tideline removal (Barbisan 2016, Barbisan & Dupont 2017, Liang et al. 2017, Chardon 2018). However, other natural green materials possess similar characteristics. Among these, clays have a number of properties that are in tune with paper conservation needs and ethics and have the potential to expand the array of products compatible with paper treatments. Clays have been used in conservation on a variety of materials such as for objects and paintings (Paleri & Curri 1981, Lorenzen 1992, Lefevre & Pre 1996, Bourguignon 2009, Khashimov 2013, Barabant et al. 2015), textiles (Thomson 1994, Lemiski 1998, Bouzid 2002, Charley 2004, Bonpas-Benet 2005, Toubert 2015), and occasionally paper (Delnef 2001, Bastier 2007). However, on paper, they have seldom been explored other than for adhesive residue removal (Smith et al. 1984, Warda et al. 2007), mostly because they are suspected of leaving powdery residue on the paper surface (Sullivan et al. 2017).

1.2 Focus on clay minerals

Clays, or silicates, are among the most widespread naturally occurring minerals on earth. Their unit assembly, called tetrahedron (T), is a $(\text{SiO}_4)^4-$ anionic group where the four oxygen atoms are arranged around a central silicon atom to form a pyramid. A wide variety of naturally occurring silicate minerals is produced by the tetrahedra interlinking and sharing one, two, three or four apex oxygens. In octahedral sheets (O) the connections are made by sharing the edges of the pyramid. These assemblies form large polymeric molecules organized in a wide range of nanostructured hybrid materials, which make them suitable for environmental, agricultural, pharmaceutical, cosmetic, papermaking applications, and an array of other industrial purposes (Wypych & Satyanarayana 2004). They are also catalysts in chemical reactions and have been used for pigment manufacture across all eras of humankind.

With such a wide range of uses and applications, clays are ancient materials as much as they are twenty-first century materials (Bergaya et al. 2006). Their physical properties such as particle size (generally less than 2 microns), shape (unique crystal structure, layer and sheet superstructure), surface area (up to $800 \text{ m}^2 \text{ g}^{-1}$), porosity, as well as their surface chemistry and surface charge give them special properties and are fundamental parameters intimately related to their applications. Among these properties, the ion exchange capabilities, the pH, and the adsorptive, swelling and plastic behaviour are of particular interest for conservation purposes. Most of these properties are governed by the clay-water interactions and are thus interdependent. One example is the cation exchange capacity (CEC), which is described in the literature as the quantity of cations (generally Al^{3+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Na^+ , K^+ , and H^+) exchangeable with the environment at a given pH. These cations are held by the negatively charged surface layer of clay minerals arising from the substitution of silica cations (Si^{4+}) by aluminum cations (Al^{3+}) in the sheet.

CEC is a notion mostly used to characterize soils (Gillott 1987) but one can foresee potential applications in paper conservation wet treatments, where cations can be withdrawn or delivered to the paper substrate. The initial sorption of water operates via the hydration of these cations. CEC thus falls by definition under the category of adsorption phenomena, another characteristic of clay minerals. Adsorption follows physical (non-ionic) or electrostatic interaction and exchange mechanisms. Organic cations are preferentially exchanged over inorganic cations, and some clay minerals can adsorb anions, although this capacity is usually smaller than the CEC. Closely related to the CEC is the pH buffer capacity, which is the property of the material to retain or hold acid or bases without changing its pH (Jeon & Nam 2019). The buffer capacity of a clay mineral depends on the amount of cations and anions that can be released into solution (in fact exchanged for H^+ and OH^-). For instance, montmorillonite buffers better at high pH and less under neutral and slightly acid conditions (Van Breemen & Wielemaker 1974).

Porosity, which is represented by the volume of voids to the total volume, is also an important parameter in the clay-water interactions and is linked to the specific surface area (SSA) (surface area per unit weight or volume). The penetration of water and organic molecules can also occur into the interlayer spaces of clay minerals (intercalation) and explains the swelling capacity. Clay minerals are electron acceptors and/or donors in organic reactions. Here the pH is instrumental since there is a point of zero charge where the clay mineral carries equal number of positive and negative charges (pH_0), and therefore on either side of this value, the interactions will occur preferentially with opposite charge species.

Lastly, the plasticity of clay-water systems is another key property in relation to paper conservation treatment. This capacity of shape deformation of clay minerals under the influence of a force without rupture allows them to retain their shape after the applied force has been removed. With this property, the material can closely mould the surface geometry to which it is applied and the contact remains until it is disrupted (Andrade et al. 2011).

In summary, there is a variety of modes of interaction and exchange between clay minerals and organic molecules. For all these properties clay minerals deserve to be considered for green and sustainable paper conservation treatments.

Clays are divided into several categories with distinctive features, among which phyllosilicates have been explored for cleaning conservation treatments (Paleni & Curri 1981, Lorenzen 1992, Thomson 1994, Da Silveira 1997, Lefevre & Pre 1996, Lemiski 1998, Delnef 2001, Bouzid 2002, Bajon-Bouzid 2003, Charley 2004, Chomienne 2005, Bastier 2007, Bourguignon 2009, Barabant et al. 2015, Bonpas-Benet 2015, Khashimov 2013, Williams 2013, Toubert 2015). For instance halloysite, kaolinite, vermiculite, laponite, sepiolite and smectite, the best-known variety of which is montmorillonite, are phyllosilicates.

In this work two phyllosilicates with different properties, namely montmorillonite and sepiolite were investigated for the removal of tidelines on paper. In both clays, the sheets are arranged in a 2:1 layer structure, based on the repeating pattern of a central octahedral sheet between two tetrahedral sheets (also defined as TOT structure). The cohesion between each sheet is ensured by interlayer cations, and weak bonds through van der Waals forces, electrostatic forces, or hydrogen bonds. The interlayer space makes possible the addition of new elements in that volume. Montmorillonite (**Figure 1a**) is a hydrous magnesium aluminum silicate $[(Si_4)(Al_{2-y}Mg_y)O_{10}(OH)_{2-y}M^+ \cdot nH_2O]$ (Bergaya et al. 2006, Uddin 2018). Sepiolite (**Figure 1b**) is a hydrous magnesium silicate $[(Si_{12}Mg_8O_{30})(OH)_4(OH_2)_4 \cdot 8H_2O]$, in the form mostly

described as fibers, ribbons or fiber bundles. The formulas found in the literature are often oversimplistic since in their natural form, these clays contain other mineral impurities and traces of other ions such as calcium, sodium and iron (Uddin 2008, Suárez & García-Romero 2011).

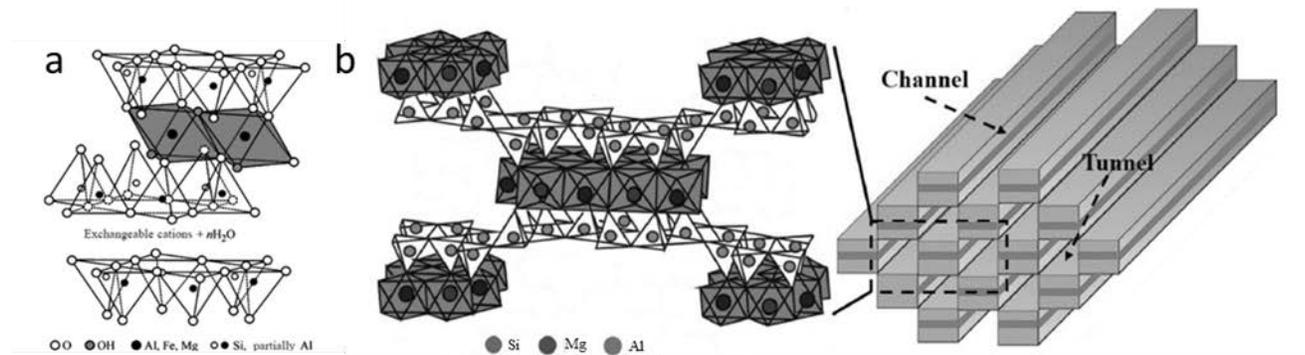


Figure 1: Schematic crystal structure of (a) montmorillonite (Golubeva, Korytkova, and Gusarov 2005) and (b) sepiolite (right: nanofibrous structure of with channels and tunnels) (Zhou et al. 2017).

The purpose of this work is to provide an overview of the main properties of clays that can be useful in paper conservation for water-based cleaning treatments, and explore how they can be implemented for the removal of tidelines on paper artworks.

2. Materials and methods

2.1 Paper samples

Canson drawing paper C with grain was used (224 g.m^{-2}) to make the samples. It is described by the manufacturer as acid-free, with no optical brighteners. The microscopic observation of the fibers indicates a mix of cotton linters and bleached chemical woodpulp (hardwood kraft and softwood sulphite). The presence of starch, probably used to increase paper dry and wet strength or printability, was evidenced using the iodine microchemical test. Calcium carbonate filler is present as verified by the FTIR band at 875 cm^{-1} in Attenuated Total Reflectance mode (ATR) (Nicolet 6700 spectrometer). The spectra showed no specific bands for gelatine or neutral sizing (alkyl ketene dimers or alkenyl succinic anhydride).

2.2 Artificial ageing

Six strips of paper ($3 \text{ cm} \times 10 \text{ cm}$), long side in the machine direction, were placed in glass tubes (Wheaton hybridization tubes, 145 mL) (approximately 4 g of paper per tube). The paper strips as well as the tubes were conditioned at 23°C and 50% relative humidity (rH) for 48 hours before capping tightly (screw cap and teflon/silicon septum). The tubes were then artificially aged at 100°C for 5 days in a dry oven, according to TAPPI T 573 pm-09, where the rH inside the tubes is approximately 50%. Tidelines formed on the samples when they were suspended vertically, the lower end dipped 5 cm in tap water (**Figure 2**).

When freshly formed, tidelines are relatively easy to clean (Dupont 1996a). For this reason, in order to obtain strongly coloured and more difficult to remove tidelines, which would better mimic an old tideline on a paper artwork, the samples were artificially aged again in the same manner as before, at 100°C for 5 days (TAPPI T 573 pm-09).



Figure 2: Tidelines formed on the artificially aged samples by dipping their lower end of the paper in water for 1h30 (machine direction is vertical).

2.3 Clay minerals used

The choice was made to use natural clay minerals. The second prerequisite was that they had to be easily available to conservators and affordable. Bentonite (Optigel CL®, Abemus) and sepiolite (Kremer Pigmente) were chosen. They are henceforth called B and S.

Their intended industrial use is as rheological additives for paints and emulsions. Both show a thixotropic behavior, an interesting feature for the application of a conservation treatment. The technical data sheets indicate that these products are not made of pure mineral, with no further information. In bentonite, the principal clay mineral constituent is montmorillonite and in sepiolite 15 % of other types of clay minerals are said to be present, as well as Al₂O₃ (2.4%) and Fe₂O₃ (0.9%). Table 1 gathers some of the specifications given by the suppliers and, where indicated, found in the literature.

Table 1. Some properties of sepiolite and bentonite.

	pH ^a	SSA (m ² g ⁻¹)	CEC (milliEq/100g)	Sorption	Dimensions (μm)
Sepiolite	8.8 ± 0.5	320	3-20 ^b	280%	Avg Fiber length = 2 Avg fiber diameter 0.02
Bentonite	10 ± 1	40-800*	80-120 ^b	unspecified	1-5

^apH of aqueous suspensions: 10% (w/v) sepiolite and 2% (w/v) bentonite. ^bKumari and Mohan (2021).

2.4 Cleaning tests with poultices

Thick pastes were prepared with Bentonite and Sepiolite by mixing the clays powder in deionized water 30% w/v until they became smooth. S swells faster than B. For the latter a thorough kneading was required to disrupt the lumps.

In order to avoid leaving residues on the paper surface or embedding powder into the cellulose fibers, the clays were inserted in a cylindrical membrane made of regenerated cellulose (Precision Zephyr® HS Visrex® from Viskase®) (**Figure 3**). This permeable membrane has neutral pH, and a sufficient wet strength to withstand handling during the treatment. Its intended use is for food and biomedical applications. It has been tested in conservation for the cleaning of textiles with clay (Bouzid 2002, Charley 2004, Bonpas-Benet 2015.). Before use, the membrane was soaked in deionized water, first at room temperature for about 30 minutes, and then at 100°C during about 10 minutes to remove the additives, following the protocol by Bouzid (2002). One side of the membrane was tightly closed with a clamp and the clay paste was packed inside, avoiding air pockets. Then the opposite end of the membrane was closed with a second clamp and the flat pouch of about 13 cm × 8 cm (approx. 30 g) was readily applied on the paper samples surface (**Figure 3**).



Figure 3: Regenerated cellulose membrane filled with B (left) and S (right) ready to be used.

In order to compare the results with a benchmark cleaning product, gellan gum was used (called G henceforth). This polysaccharide hydrogel has been widely documented for paper cleaning purposes (Warda et al. 2007, Iannuccelli & Stotgiu 2010 and 2012, Botti et al. 2011, Couvert 2012, Couvert & Dupont 2014, Delattre 2015, Mazzuca et al. 2014, Barbisan 2016, Angelova et al. 2017). It is a linear polysaccharide secreted by the bacterium *Sphingomonas elodea* (formerly referred to as *Pseudomonas elodea*), which consists of glucose, glucuronic acid and rhamnose (Nishinari & Doi 1993). It is available in two forms depending on the degree of acylation of glucose, high acyl (HA) and low acyl (LA). Low acyl gellan produces a rigid gel and is the form most often used for paper cleaning. Gellan reacts with mono- and polyvalent cations to form a gel, notably Na⁺, K⁺, Mg²⁺ and Ca²⁺, the latter being the most efficient. The commercial product used, Kelcogel® CG-LA (CP Kelco), was prepared at a concentration of 2.5% (w/v) in an aqueous calcium acetate solution (0.4 gL⁻¹) at room temperature, and then heated to 80-85°C according to the protocol by Placido (2012).

2.5 pH measurements

To confirm the supplier's specifications, the pH of the clays in dilute suspensions was measured in the same conditions as indicated in the technical data sheets (aqueous solutions 2% w/v for B and 10% w/v for S), using a combined pH electrode InLab Expert Pro (Mettler Toledo).

Additionally, some complementary measurements of the clay pastes and the hydrogel prepared with deionized water (B 30% w/v, S 20% w/v, G 2.5% w/v) were performed. Surface pH measurements of the clays and the gellan gum were carried out with an InLab Surface electrode (Mettler Toledo). The pH of the water in which the clays were suspended for 2 hours (supernatant) was measured also with a combined pH electrode InLab Expert Pro (Mettler Toledo).

The buffer and ion exchange capacity was characterized by measuring the surface pH of the clays after they were suspended in dilute acetic acid (AcOH) solutions. The AcOH solutions were prepared with glacial acetic acid (17.42 M), by diluting approximately 10^3 , 5×10^3 , 10^4 and 5×10^4 times, and their pH was measured. They were named dil1, dil2, dil3, dil4, respectively. After 30 minutes, the clay/AcOH suspensions were centrifuged, and the supernatant was separated from the bottom pellet. The pH of the bottom clay pellets was measured with the surface electrode and the pH of the AcOH supernatant was measured with the combined electrode. Based on the K_a of AcOH at 25 °C (1.78×10^{-5} M), this allowed to calculate the concentration of protons buffered by the clays.

2.6 Water desorption measurements

The water discharge was evaluated simply by weighing the paper samples before and immediately after they had been in contact over the whole surface with the clay pouches (B & S 30% w/v) or with the hydrogel (2,5% w/v), in room conditions (22°C, 47% RH) for various periods of time (5 to 290 minutes). Three repeat measurements were made per sample type.

2.7 Cleaning efficiency evaluation

The cleaning was evaluated both visually and by colour measurements, three hours after the application of the clay pouches and the gellan gel on the tideline area under light weight (200 g). This duration was chosen because it is the longest time reported in previous studies for the cleaning of tidelines. Adopting the worst-case scenario aimed at magnifying possible side effects, since longer application time enhances the risk of creating new tidelines. Three different strips of paper with tidelines were tested per cleaning material.

Photographs of both sides of the paper samples were taken with identical camera and lighting conditions (angle, film sensitivity, focal distance, opening, obturator speed) in visible and UV light (365 nm). A colour chart was used to process the images with Photoshop CC® in a standardized fashion.

Colour measurements on the tideline area before and after cleaning were recorded with a hand-held spectrophotometer CM-26dG (Konica Minolta) equipped with an integrating sphere. The configuration was in reflectance mode with the specular component excluded, using a 3 mm diameter measurement aperture. D65 Standard Illuminant and 8° Standard Observer were used (ISO 5631-2 standard). The colorimetric coordinates L^* , a^* and b^* were calculated in the CIE*Lab76 Color System. Three repeat measurements were done per sample using a cardboard guide where holes were punched to place the reading probe on the

exact same location on the tideline before and after the cleaning. Based on the (L,a,b)* values, the total colour change ΔE^* occurred on a given sample before and after cleaning was calculated as $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$.

XRF imaging measurements were carried out to evaluate the impact of the clays on the chemical elements composition of the paper. A Micro X-ray Fluorescence Spectrometer (M6 Jetstream, Bruker) with a 450 μm^2 polychromatic beam (0-50 keV) was used. The beam is produced by an X-ray tube with a rhodium anode (50 kV, 600 μA). The instrument is equipped with a 100 μm -thick beryllium window and polycapillary optics are used to focus the X-ray beam. The X-ray detector is a 30 mm^2 SDD. Scans every 450 μm^2 of 1000 ms/pixel were juxtaposed to cover the whole area of the samples where the poultices were applied.

3. Results and discussion

3.1 pH and buffering capacity of clays

The pH of bentonite fell within the supplier's specification range, while the pH of sepiolite was slightly below the announced pH. At the concentrations used for cleaning, gellan gum had a slightly acidic surface pH, and the clay pastes were alkaline, B being the most alkaline (**Table 2**).

Table 2: pH of the poultices in aqueous solutions (2% w/v for B and 10% w/v for S) (surface electrode (s), combined electrode (c)). Standard deviations are given when available.

	pH
G 2.5% (s)	6.00 \pm 0.19
B 2% (w/v) (c)	9.90
B 30% (w/v) (s)	10.58 \pm 0.01
S 10% (w/v) (c)	7.95
S 20% (w/v) (s)	8.55 \pm 0.04

Table 3: Buffering capacity of the clays (pH upon contact with diluted acetic acid, AcOH) (surface electrode (s), combined electrode (c)).

		dil4	dil3	dil2	dil1
Bentonite 30% (w/v)	AcOH solution (c)	6.75	5.85	4.43	3.93
	AcOH solution after contact w/clay (c)	8.87	6.82	5.04	4.34
	clay after contact w/AcOH (s)	10.30	10.34	10.20	8.58
sepiolite 20% (w/v)	AcOH solution (c)	6.75	5.85	4.43	3.93
	AcOH solution after contact w/clay (c)	7.03	6.45	4.58	4.10
	clay after contact w/AcOH (s)	8.13	8.04	6.86	6.55

Table 3 gathers the pH measurements performed to evaluate the buffering capacity of the clays (proton exchange) after they were suspended in the dilute acetic acid solutions. This buffering capacity was quite extended in the acidic pH range for both clays. **Figure 4** illustrates this and shows that B has a stronger acid buffering capacity than S, by maintaining its initial pH when in contact with a more concentrated AcOH solution. AcOH being a weak acid, considering its K_a it was calculated that B buffered up to about 3.7×10^{-5} M $[H_3O^+]$ (dil2, pH = 4.43), beyond which its pH dropped abruptly (steep slope of the blue curve between dil1 and dil2). S was able to buffer at least 1.4×10^{-6} M $[H_3O^+]$ (dil3, pH = 5.85), and probably a little more considering the shallow slope of the red curve from dil2 to dil3. This buffering difference was attributed to the higher initial pH of B (**Table 1**).

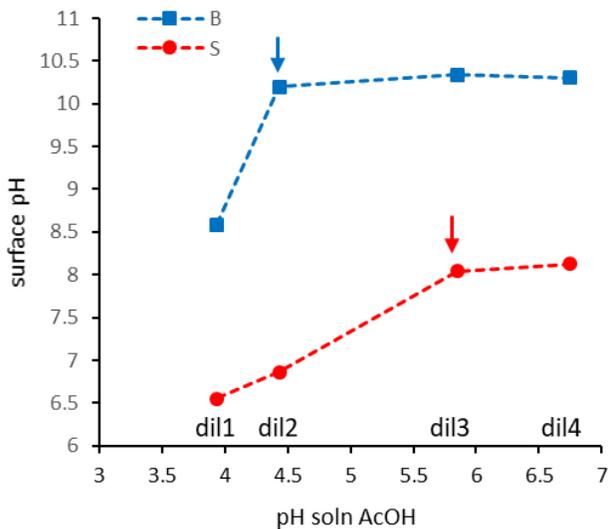


Figure 4: Surface pH of bentonite (B) and sepiolite (S) as a function of the pH of dilute acetic acid solutions (dil 1, dil2, dil3 and dil4), in which they have been suspended for 30 minutes. The arrows indicate the buffering capacity limit.

The second observation was that, after suspension with the clays, the pH of all the AcOH solutions increased, and the less acidic the solution (more diluted), the larger its pH raise (up to an alkaline pH for dil4) (**Table 3**). This indicates that not only can the clays buffer protons up to a certain concentration, but that they do so by exchanging alkaline species in the medium. It is known that two major pH buffering reactions of clay minerals are protonation or deprotonation of edge sites, and proton exchange of basal sites (Jeon & Nam 2019). The uptake of protons is thus accompanied by a release of alkaline cations, a characteristic of the CEC. This two-ways action is without doubt an asset for cleaning acids from paper and introducing alkaline cations at the same time.

3.2 Water desorption

The clays can absorb or deliver (depending on the flow direction) aqueous solutions from/to the substrate they are in contact with, in different amount and at various rates. For the reasons listed in the introduction, it is relevant in conservation treatments to anticipate how much water will be brought into the paper, and

measure the speed of delivery to evaluate whether it can be easily controlled. The water desorption from the clay poultices into the paper samples was evaluated in terms of weight gain of the paper samples (**Figure 5a**), as well as in terms of delivery rate (**Figure 5b**).

The gellan hydrogel desorbed significantly more water than the clays and did so more rapidly. After 290 minutes in contact with gellan G, the paper samples had adsorbed water to 73% their initial weight, whereas B and S delivered about 21% and 34% water with respect to the samples weight (**Figure 5a**). Moreover, the water delivery by S and B was more than twice and three times slower than by G, respectively (**Figure 5b**). For both clays the bulk of the water was delivered within 50 minutes. For the three materials, the rate was significantly higher at the beginning of the contact (after 5 min) than at the end (290 min), by 20, 17 and 11 times for G, B and S, respectively. These results indicate that in the conditions used for the experiment, the clays can allow for a better control of the flow of water delivered to the paper than the hydrogel.

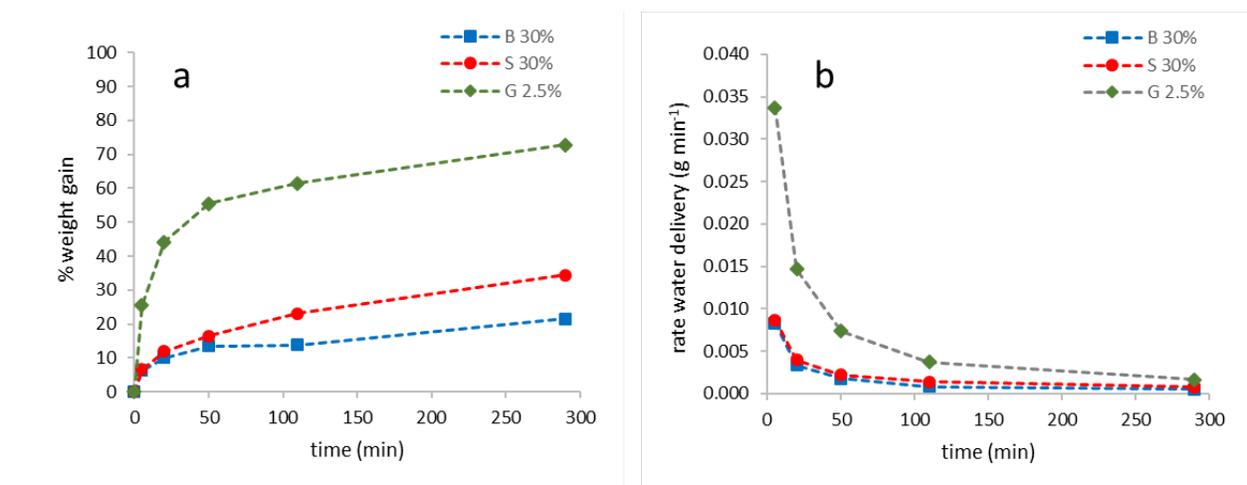


Figure 5: (a) Weight gain (%) of the paper samples due to water absorption as a function of contact time with the poultices, (b) Rate of water delivery of the poultices as a function of contact time with the paper samples.

3.3 Cleaning efficiency

Based on the colour measurements, gellan gum was the most efficient for cleaning the brown line, with a colour difference ΔE^* before vs after cleaning of 5.9. Both B and S slightly reduced the browning. However, with ΔE^* of 2.1 and 3, respectively, the colour difference is barely perceptible with the naked eye (Richardson & Saunders 2007).

This result has to be discussed in more general terms. The experiment showed that to evaluate the cleaning of tidelines based solely on colour measurements was misleading. One reason is that the measuring aperture covered an area of paper around the thin tideline, where a brownish halo had sometimes formed due to the migration of the coloured species, especially on the samples cleaned with G. Therefore the sample was never exactly the same before and after cleaning in the measured area. Moreover the measurement did not take into account the new tidelines formed beyond the initial tideline, as explained below. Therefore the average ΔE^* value departed from the visual perception.

For these reasons, a visual inspection based on photography was carried out to provide an overall appraisal closer to the human eye experience. The observation of the samples under visible and UV light allowed to evaluate the cleaning efficiency and the lateral migration of water in the paper after the application of bentonite (**Figure 6**), sepiolite (**Figure 7**) and gellan hydrogel (**Figure 8**).

None of the three cleaning materials was able to retrieve the brown degradation products on paper completely, which was not unexpected. However, they did attenuate the browning to various extent (depending on the intensity of the tideline), which resulted in different visual impacts.

Both clays diminished the browning more efficiently than the gellan hydrogel (**Figures 6-8**). Moreover, they created less or no new tidelines. On the contrary new tidelines were visible immediately after the application of G, as confirmed by the UV images where wavy fluorescent lines are visible on both sides of the original tideline (**Figure 8**). Fluorophores are precursors of chromophores in tidelines, and the appearance of fluorescent lines on the paper after cleaning foretells the development of new brown lines (Bone & Turner 1950, Dupont 1996a, Pedersoli and Ligterink 2001). On **Figures 6** and **7**, only slight fluorescence appears after cleaning, hence the cleaning achieved on these samples with either of the two clays is most likely to be more durable than with gellan gum.

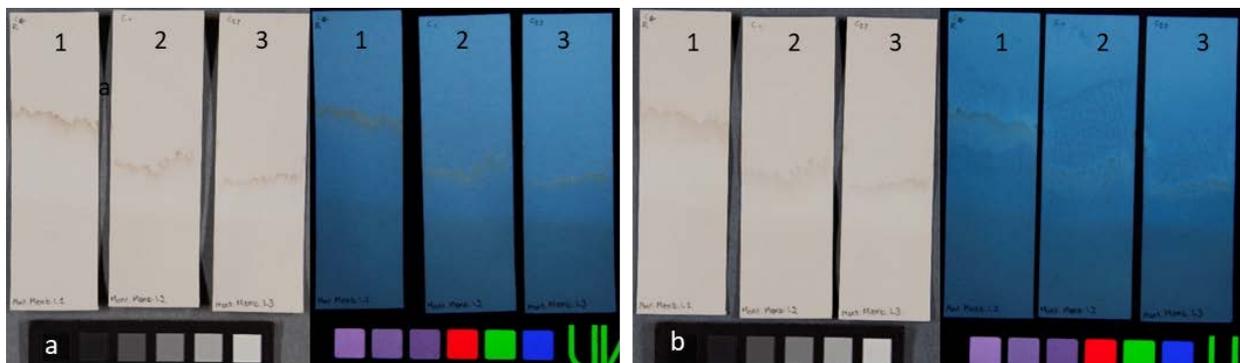


Figure 6: Images in visible light (left) and UV radiation at 365 nm (right) of Canson paper samples with tidelines 1–3: (a) before cleaning and (b) after cleaning with bentonite.

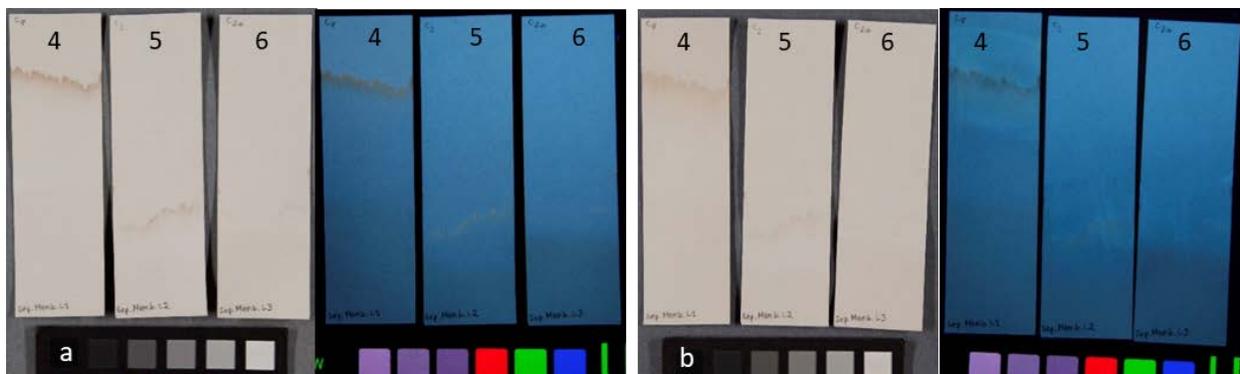


Figure 7: Images in visible light (left) and UV radiation at 365 nm (right) of Canson paper samples with tidelines 4–6: (a) before cleaning and (b) after cleaning with sepiolite.

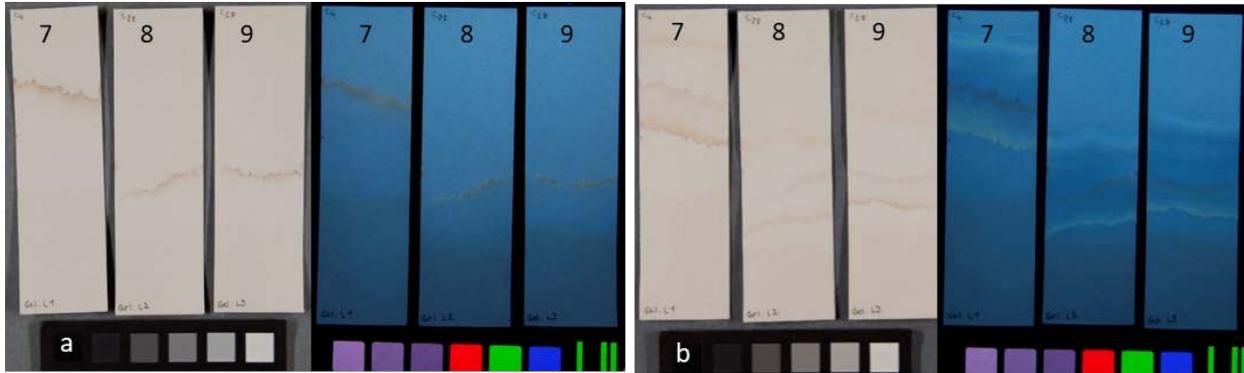


Figure 8: Images in visible light (left) and UV radiation at 365 nm (right) of Canson paper samples with tidelines 7–9: (a) before cleaning and (b) after cleaning with gellan hydrogel.

All the elements detected on the XRF spectra were evenly distributed on the samples, the most abundant of which was calcium, since CaCO_3 filler was present in the paper (spectra not shown). There was no difference between the control paper and the areas where B and S had been applied, showing that the poultices did not modify the chemical composition of the paper to any measurable extent with XRF. In particular the iron oxides reported to be present in sepiolite on the supplier's data sheet were not among the species that could migrate in the paper. These results also indicate that the tidelines are mostly formed by the accumulation of organic compounds.

3.4 Application to a paper-based artwork

Clay poultices were used to attenuate the multiple tidelines on a large artwork, an oil painting on Montgolfier paper mounted on a wood frame (*Le Roi de Pique, Jeu de carte*, by François Deney, 1949, Centre national des arts plastiques) (**Figure 9**). The painting represents the King of spades, and is one of four screen panels depicting each a face card. The back of the paper bears graphite and charcoal sketches by the artist.



Figure 9: Photographs of *Roi de pique, Jeu de cartes* (François Deney, 1949, Cnap). Tidelines are circled (in red: tidelines on recto and verso, in blue: tidelines on verso only) ©A. Dequier (Inp).

Some of the tidelines are visible on both sides of the artwork (circled in red) and others only on the back side (circled in blue) (**Figure 9**). The former are diffuse and moderately dark on the back side and more discolored on the front (paint) side. The latter are narrow tidelines (**Figure 10 a&c**). It is unknown when they occurred, but certainly before the ones circled in red, which date from a water damage in 2017 (**Figure 10 a&b**).

A surface cleaning was carried out to sanitize the paper and improve its aesthetic appearance as well as the readability of the graphite drawings on the verso, which was disrupted by the multiple tidelines. The artwork was previously unmounted from the wooden frame. Sepiolite was used locally for the attenuation of some of the tidelines. Preliminary testing ensured that the sizing was not affected (drop absorption test) and the graphite medium was not modified by the clay poultice application (results not shown).



Figure 10: Photographs of (a) the back of the artwork with both types of tidelines. The arrows indicate the direction of the water migration (b) detail of 2017 tidelines and (c) the tidelines that heavily disrupt the readability of the graphite drawing on the verso.

The poultice was prepared as described in the experimental section (30% w/v in distilled water), placed in the regenerated cellulose membrane and clamped to form a little pouch (**Figure 3**). Several of these pouches had to be applied simultaneously to cover the whole tideline area to be cleaned. Then a poultice at a higher concentration (50% w/v) was applied to partly reabsorb the humidity as well as more brown products. A final step involved the application of dry sepiolite in a pouch made with Japanese paper (32 gm⁻²). Japanese paper was used instead of the membrane because the latter could not be used with dry clay. This step allowed to avoid making new tidelines, and continue to re-absorb degradation products at the same time as progressively drying the area. For the strongest tidelines (circled in red), a protocol that sandwiched the artwork between two poultices with different clay concentrations (30% w/v and 50% w/v) was followed (Bouziid 2002). The more concentrated poultice was placed on the back side of the artwork so as to force the water flow from the front to the back. Each step lasted a few minutes (15 minutes at most), although time was not recorded precisely since the level of cleaning was monitored visually. The three steps were repeated between 2 and 4 times until the browning was clearly attenuated and the cleaning did not progress further.

This local treatment was tested on all the strongest tidelines with the poultices placed on the verso or in sandwiches (on the paper parts that covered the frame). As after the first step, some of the tidelines (circled

in blue) were not visually attenuated, the following steps were not pursued. On the contrary, the other tidelines (circled in red) responded well to the local treatment and were clearly diminished. **Figure 11** shows an example where only two successive applications of the three-steps cycle were needed. **Figure 12** shows an area with strong tidelines before and after the sandwich cleaning.

As mentioned earlier, cleaning the entire surface of the artwork to reduce the overall yellowing of the paper by locally applying clay poultice was not possible. This limitation is partly due to the format of the cellulosic membrane used to encase the clay, which only allows making pouches of a given width (13 cm). A global surface cleaning treatment using gellan gum was thus carried out after the local applications of sepiolite. The procedure and details of this part of the treatment can be found in Desbrière (2021).

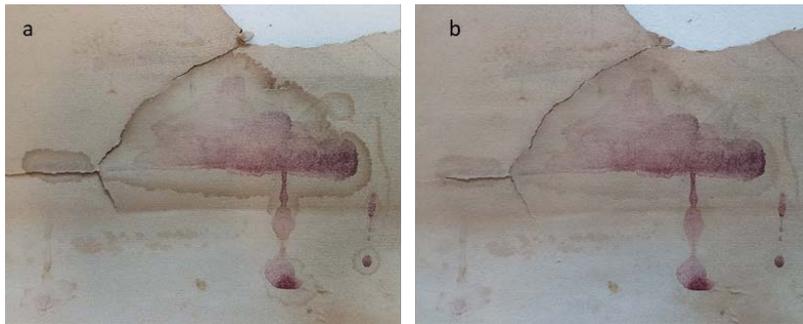


Figure 11: Photographs of the recto area with red pigment and tidelines (a) before and (b) after 2 successive three-steps cycles applied on the back side.

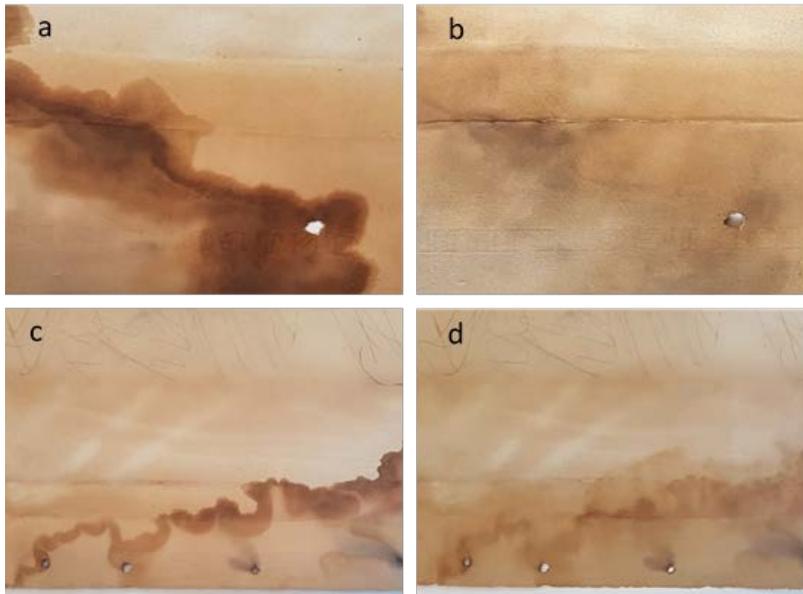


Figure 12: Photographs of two areas with strong tidelines (a and c) before and (b and d) after clay sandwich treatment.

4. Conclusions

Clays are natural products that have a number of remarkable properties, which enable them to be used in conservation, in particular for paper treatments. To cite a few, their alkaline pH, capacity of absorbing organic molecules, water sorption/desorption capacity and high specific surface, are properties that makes clays well-suited as green and sustainable paper conservation materials, especially for local surface cleaning treatments. In this work, two phyllosilicate clays, sepiolite and bentonite, were tested on artificially aged paper samples with tidelines and were shown to achieve a satisfactory cleaning. The water sorption capacity of the clays combined with the permeability of the cellulosic membrane used as a pouch allowed a limited and slow release of water, which permitted a homogeneous and easy to control cleaning. The formation of new tidelines, an inherent risk to any local treatment of paper and a threat for the artefact's stability, was avoided. Following these results, a clay poultice was then used for the local cleaning of an artwork's multiple tidelines and gave satisfactory results. More work needs to be carried out, especially to allow cleaning larger surfaces with clays, but this work opens the route for the use of clays as a new tool for the local cleaning of artworks on paper.

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