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Effect of water on elastic and creep properties of self-standing clay films

Benoit Carrier,[†] Matthieu Vandamme,^{*,†} Roland J.-M. Pellenq,^{‡,¶,§} Michel Bornert,[†] Eric Ferrage,^{||} Fabien Hubert,^{||} and Henri Van Damme^{‡,¶,§}

[†]*Université Paris-Est, Laboratoire Navier (UMR 8205), CNRS, ENPC, IFSTTAR, F-77455 Marne-la-Vallée, France.*

[‡]*Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States.*

[¶]*Centre Interdisciplinaire des Nanosciences de Marseille, CNRS (UPR 7251), Campus de Luminy, 13288 Marseille Cedex 09, France.*

[§]*<MSE>2, UMI 3466, CNRS-MIT, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States.*

^{||}*Université de Poitiers/CNRS, UMR 7285 IC2MP, 86022 Poitiers, France.*

E-mail: matthieu.vandamme@enpc.fr

Abstract

We characterized experimentally the elastic and creep properties of thin self-standing clay films, and how their mechanical properties evolved with relative humidity and water content. The films were films of clay montmorillonite SWy-2, obtained by evaporation of a clay suspension. Three types of films were manufactured, which differed by their interlayer cation: sodium, calcium, or a mixture of sodium with calcium. The orientational order of the films was characterized by X-ray diffractometry. The films were mechanically solicited in tension, the resulting strains being measured by Digital

9 Image Correlation. We measured the Young’s modulus and the creep over a variety
10 of relative humidities, on a full cycle of adsorption-desorption for what concerns the
11 Young’s modulus. Increasing relative humidity made the films less stiff and made them
12 creep more. Both the elastic and creep properties depended significantly on the inter-
13 layer cation. For the Young’s modulus, this dependence must originate from a scale
14 greater than the scale of the clay layer. Also, hysteresis disappeared when plotting
15 the Young’s modulus vs. water content instead of relative humidity. Independent of
16 interlayer cation and of relative humidity greater than 60%, after a transient period,
17 the creep of the films was always a logarithmic function of time. The experimental
18 data gathered on these mesoscale systems can be of value for modelers that aim at
19 predicting the mechanical behavior of clay-based materials (e.g., shales) at the engi-
20 neering macroscopic scale from the one at the atomistic scale, for them to validate the
21 first steps of their upscaling scheme. They provide also valuable reference data for
22 bioinspired clay-based hybrid materials.

23 Introduction

24 Understanding the short and long-term mechanical behavior of clay-based materials and the
25 sensitivity of this behavior to water is relevant for a variety of applications. For instance, a
26 deep disposal facility for high-level and intermediate-level long-lived nuclear waste is being
27 developed in France, in a clayey sedimentary rock called argillite:¹ after a few hundred years,
28 confinement of the radionuclides must be ensured by the geological barrier for more than
29 100,000 years, during which the mechanical integrity of the barrier needs to be guaranteed, in
30 spite of the expected variations of thermal and hygric conditions. Also, the stability of slopes
31 —and therefore the risk of landslides— is governed not only by the short-term mechanical
32 behavior of soils, but by their long-term behavior as well.² Finally, a better understanding
33 of the mechanical behavior of shales —a heterogeneous rock that often contains clay— is of
34 value not only to optimize the process of hydraulic fracturing used in the shale gas industry,

35 but also to ensure the stability of boreholes in conventional oil and gas reservoirs, for which
36 the sealing formation is often made of shales.³

37 Macroscopically, some clays expand significantly with water,⁴ partly as a consequence of
38 the swelling of the slit-shaped or lens-shaped void space between the individual clay layers
39 or between stacks of clay layers.⁵ Also, the macroscopic mechanical properties of clay-based
40 materials are known to be sensitive to relative humidity. For instance, uniaxial compression
41 experiments on argillite⁶⁻⁸ show that their Young's modulus and strength depend signifi-
42 cantly on the water content. Equivalent trends are observed when the elastic properties are
43 measured by nanoindentation.⁹ The creep properties of clay materials are also sensitive to
44 water: the coefficient of secondary consolidation (which characterizes the long-term creep of
45 soils in general) depends on the water content.¹⁰

46 The sensitivity to water of macroscopic clay materials stems from the sensitivity to water
47 of the individual clay layer itself. Several recent studies aim at better characterizing and
48 modeling the response of clay-based materials under hydromechanical loading through so-
49 called bottom-up (or upscaling) approaches, in which the goal is to predict the macroscopic
50 behavior by starting from the microscopic level of the clay layer^{7,11}. However, the hydrome-
51 chanical behavior at the scale of the clay layer and the relationship between the behavior
52 of the layer and that of the upper scales need to be better characterized. Moreover, the
53 gap between the scale of the clay layer and the macroscopic scale is huge, which makes the
54 elaboration and the validation of upscaling schemes more difficult.

55 Here, we propose and manufacture clay materials at a scale that is intermediate between
56 the scale of the clay layer and the scale of macroscopic natural clay-based materials. The
57 materials we design are self-standing films of pure clay with a thickness of a few dozen
58 micrometers, which are much larger than individual clay layers (whose thickness is on the
59 order of the nanometer) and can be probed mechanically, but remain much smaller and
60 much simpler than macroscopic natural clay-based materials. For instance, we showed in a
61 previous work that the swelling of those films with variations of relative humidity can be easily

62 inferred from the swelling of the slit-shaped void space between the individual clay layers
63 (i.e., the so-called interlayer space).¹² Here, we characterize the orientational order and the
64 mechanical properties of those films, which can be of value for instance for modelers aiming at
65 validating the first steps of their upscaling scheme. The idea of manufacturing such films and
66 characterizing their mechanical properties is readily inspired from the work of Zabat et al.
67 which, to our best knowledge, is the first textural and mechanical study of self-standing clay
68 films.^{13,14} Actually, self-standing clay films with good transparency have been manufactured
69 and used for several decades for spectroscopic (UV-Visible, IR, fluorescence) and structural
70 (X-ray) studies of clay-organic intercalates, including their sensitivity to water.¹⁵⁻¹⁷ Clay-
71 based films have also been investigated as mimics of nacre¹⁸⁻²⁰.

72 In the present work, we prepared thin films of montmorillonite, on which we performed
73 tensile tests in order to characterize an elastic property (i.e., the Young's modulus) and a
74 viscous property (i.e., creep). In order to assess the effect of water, the tensile tests were
75 performed over a wide range of relative humidities. Since the mechanical behavior of clays
76 and their sensitivity to water depend on the interlayer cation, we manufactured films from
77 montmorillonites with various interlayer cations: sodium, calcium, and a mixture of sodium
78 with calcium. First, we present the materials and methods. Then, we introduce the results
79 and discuss them.

80 **Materials and methods**

81 **Materials**

82 We prepared materials from a natural montmorillonite SWy-2 purchased from the Source
83 Clay Repository of the Clay Mineral Society. SWy-2 is a low-charge Wyoming montmo-
84 rillonite, whose structural formula is $(Al_{3.23}Mg_{0.56}Fe_{0.42})(Si_{7.89}Al_{0.11})O_{20}(OH)_4(Ca_{0.16}Na_{0.36}$
85 $K_{0.03})$ ²¹: naturally, the clay SWy-2 contains both sodium and calcium interlayer cations, in a
86 ratio of about 2 to 1. Only the clay fraction with particles smaller than 2 μm was conserved,

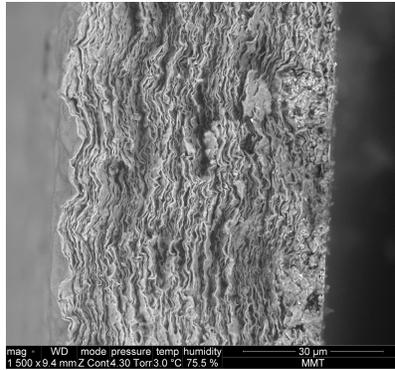
87 following the process described by Arroyo et al.²² The material was then homoionized with
88 either sodium cations or calcium cations. Thus, we obtained three types of montmorillonite
89 which differed by their interlayer cation, from which we prepared three types of clay films:
90 films from the natural SWy-2 clay (which contained both sodium and calcium interlayer
91 cations, and were coined ‘raw-SWy-2’), films from the SWy-2 clay homoionized with sodium
92 (which were coined ‘Na⁺-SWy-2’), and films from the SWy-2 clay homoionized with calcium
93 (which were coined ‘Ca²⁺-SWy-2’). The films were manufactured by evaporation of a clay
94 suspension. The thickness of the prepared films was a few dozens of microns. The meth-
95 ods to homoionize the raw material and to prepare the clay films are described in detail
96 elsewhere.¹² SEM pictures of the films are given in Fig. 1.

97 We measured the elastic stiffness of the three types of clay films. We measured the
98 creep properties of the films Na⁺-SWy-2 and Ca²⁺-SWy-2 only. In order to perform those
99 various measurements, upon application of a mechanical load to the sample, we needed to
100 measure the strain of the sample: those measurements were performed by Digital Image
101 Correlation (DIC), which is introduced later. Note that we also measured elsewhere the
102 adsorption isotherms of the films,¹² and how the films swelled when relative humidity was
103 varied.¹² In parallel of the mechanical characterization here performed, we also conducted
104 a characterization of the orientational order of the obtained films, which is the focus of the
105 next section.

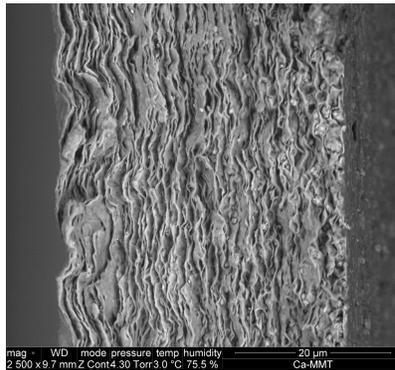
106 **Characterization of orientational order of clay films**

107 We considered the films to be transverse isotropic, with the plane of transverse isotropy being
108 that of the films.²³ We characterized the orientational order of particles in the obtained films
109 by analyzing experimental rocking curves. The basic principle of this technique is to operate
110 at a fixed 2θ value, corresponding here to the 001 Bragg reflection of the clay material
111 under investigation, and to rotate the entire system of an angle α with respect to the film
112 orientation. Accordingly, analysis of experimental intensity provides direct information on

a) raw-SWy-2



b) Ca²⁺-SWy-2



c) Na⁺-SWy-2

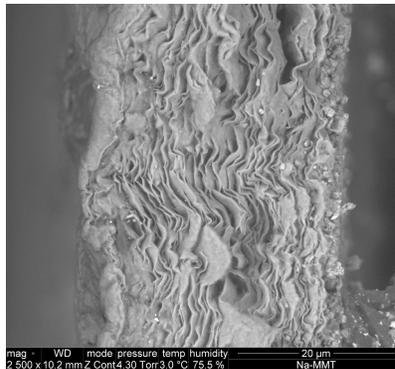


Figure 1: SEM pictures of the edge of the manufactured clay films, at a relative humidity of 75.5 %: a) raw-SWy-2, b) Ca²⁺-SWy-2, and c) Na⁺-SWy-2. The pictures were acquired by L. Wang at the LMS laboratory at Ecole Polytechnique (Palaiseau, France).

113 the proportion of particles forming an angle α with the film geometry. The experimental
114 curves were acquired at ambient temperature ($\sim 25^\circ\text{C}$) and relative humidity ($\sim 40\%$) in
115 transmission conditions on an Empyrean Panalytical X-ray diffractometer equipped with an
116 X'Celerator detector operating in receiving slit mode. The step size was 0.15 and $0.5^\circ\alpha$ in
117 the $0-7$ and $7-90^\circ\alpha$ angular ranges, respectively, with a time per step of 10 s. The angular
118 α range probed in this study for each sample depended on both the position of the 001
119 reflection of the sample and the relative position of the sample holder with respect to the
120 sample in the fixed 2θ geometry, the sample holder inducing a shadow for both incident and
121 transmitted X-ray beam.

122 The experimental rocking curves, and how they were analyzed,²³⁻²⁵ are provided in Sup-
123 porting Information. More information on the overall degree of particle orientation in
124 the different films can be obtained through the calculation of the scalar order parameter
125 $S = \langle (3 \cos^2 \alpha) - 1 \rangle / 2$, where $\langle X \rangle$ holds for the ensemble average of the volumetric
126 quantity X .²⁶ This order parameter S can range from $S = 0$ for an isotropic medium to
127 $S = 1$ for a perfectly anisotropic medium (i.e., with all particles oriented perfectly parallel
128 in the film). The order parameter S of the films raw-SWy-2, Ca^{2+} -SWy-2, and Na^+ -SWy-2
129 was 0.69 , 0.79 , and 0.66 , respectively. From those relatively high values, we infer that the
130 clay particles exhibited a preferential orientation in the clay film, as supported by direct ob-
131 servation (see Fig. 1). Also, as suggested by this same direct observation, values of the order
132 parameter S confirm that the Na^+ -SWy-2 film and the raw-SWy-2 film were less ordered
133 than the Ca^{2+} -SWy-2 film.

134 **Measurement of strain by DIC**

135 We measured the elastic stiffness of the three types of clay films, but the creep properties of
136 the films Na^+ -SWy-2 and Ca^{2+} -SWy-2 only. In order to perform those various measurements,
137 upon application of a mechanical load to the sample, the strains were characterized by
138 using digital image correlation (DIC), which is a contact-free technique.²⁷ DIC consists in

139 acquiring images of the surface of the sample with a digital camera at various times during
140 the experiment. Then, each image is compared with an image of the surface of the sample
141 in its state of reference (i.e., here, before any load was applied to the sample). Points chosen
142 in the reference image are identified in the image of the deformed sample by matching the
143 gray levels: thus, at a given time, the displacement of various points at the surface of the
144 sample is measured. The two-dimensional strain of the observed surface is obtained by
145 spatial differentiation of the displacements, and average strains over regions of interest are
146 obtained from contour integrals.⁶

147 To take images of the samples during the tests, a Pike camera from Allied Vision Tech-
148 nology was used. The CCD sensor was 2048×2048-pixels-wide with pixels with a width of
149 7.4 μm and the gray levels were encoded on 8 bits. To improve the contrast of the images,
150 carbon powder was scattered all over the surface of the films. The camera was equipped with
151 optics from Schneider Kreuznach (Apo-Componon 90 mm lens) with appropriate extension
152 tubes (makro system), so that a pixel in the images represented approximately 25 μm (i.e.,
153 optical magnification was about 0.3). During experiments at ambient relative humidity, we
154 used another Pike camera (Allied Vision Technology) with a lower resolution: the 2/3-inch
155 CCD sensor was 1388×1038-pixels-wide with pixels with a width of 5.5 μm . The images
156 were acquired continuously during the tests at a minimum interval of 250 ms. All images
157 were then analyzed by DIC with the in-house software CMV.⁶ We used 30-pixels-wide cor-
158 relation windows. First-order affine shape functions were combined with a zero-centered
159 normalized cross-correlation criterion, and subpixel accuracy was obtained by means of a
160 biquintic interpolation of the gray levels.²⁷ The physical size of a correlation window was
161 730 μm with the higher resolution camera. With the lower resolution camera, the physical
162 size of the correlation window was 1 mm (pixel size in the images of about 30 μm , optical
163 magnification of about 0.18).

164 We estimated from the analysis of controlled rigid body motions²⁸ that the error on the
165 average strain measured by DIC was 6×10^{-5} , which is small with respect to the magnitude

166 of the strains in this study, which were on the order of 10^{-3} . For a detailed description of
167 how we estimated this error, see the Ph.D. thesis of Carrier.²⁹

168 **Method for measurement of Young's modulus**

169 We aimed at measuring the Young's modulus in the direction parallel to the film. In order
170 to measure this modulus, we performed tensile experiments on the clay films, at various
171 controlled relative humidities. The clay films were stressed in tension in a direction parallel
172 to the films.

173 First, in each prepared film, samples which were 9.3-mm-wide and 80-mm-long were cut
174 with sharp blades. The ends of each sample were reinforced with sandpaper before being
175 placed in the grips of the tensile test machine. The free length of the sample was equal to
176 50 mm. Figure 2 displays the experimental setup.

177 The tensile tests were carried out under controlled relative humidities in an environmental
178 chamber made of PMMA and built around the testing machine. The relative humidity was
179 controlled with saturated salt solutions. Compressed air was blown into a salt solution
180 so that it reached the desired relative humidity. The humidified air was then injected in
181 the environmental chamber. Thus, the pressure in the chamber was slightly higher than
182 in the room and the relative humidity in the chamber was less sensitive to leaks than if
183 no overpressure had been applied. Equilibration of the chamber required only about 30
184 minutes. The relative humidity and temperature were recorded continuously with a thermo-
185 hygrometric sensor. Equilibration of the films with the relative humidity in the environmental
186 chamber required about one hour.

187 During the tensile tests, we controlled the displacement of the upper grip to perform
188 one or two loading-unloading cycles. A force sensor recorded continuously the force with an
189 accuracy of 1 mN. To compute the Young's modulus of the clay films, we used the slope of
190 the unloading portion of the force-strain curve, together with the section of the sample at any
191 relative humidity. To estimate this section, first, we measured the thickness of the samples at

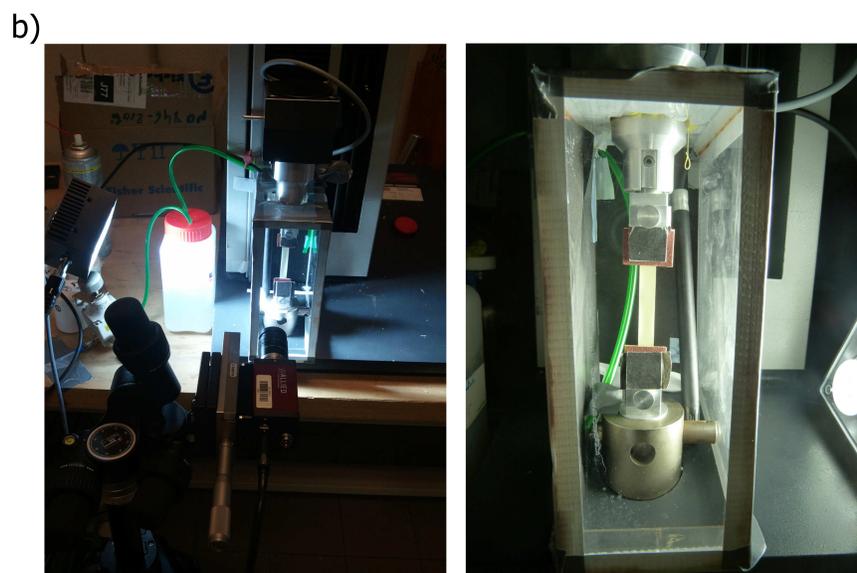
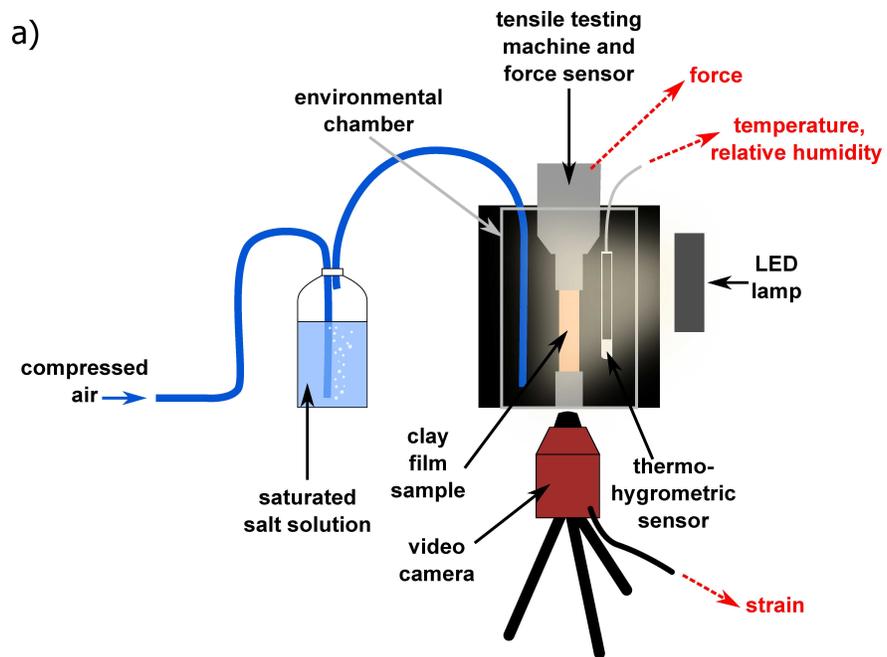


Figure 2: Experimental setup for the measurement of elastic stiffness: a) schematics and b) pictures.

192 a reference relative humidity of 35 % with an Environmental Scanning Electron Microscope
193 FEI Quanta 600 available at LMS at École Polytechnique. We estimated the thickness at
194 other relative humidities as follows. First, adsorption isotherms measured elsewhere¹² made
195 it possible to estimate the water content at a given relative humidity. Second, we estimated
196 the thickness at this water content by considering a linear relationship between thickness
197 and water content, the validity of such linear relation being supported by data gathered by
198 Carrier et al.;¹² the slope of this linear relation was fitted on this set of data.

199 A typical stress-strain curve, acquired at ambient conditions (i.e., temperature of about
200 25°C and relative humidity of about 25 %) is provided as Supporting Information. From
201 this data, we infer that, in all tensile tests performed in this study, for which strains were
202 always smaller than 0.3%, strains were sufficiently small to remain in the linear elastic
203 regime. Also, by loading and unloading 20 times a Ca²⁺-SWy-2 film at various displacement
204 rates, ranging from 0.3 $\mu\text{m/s}$ to 32 $\mu\text{m/s}$ (see Supporting Information), we could observe
205 no damage during the successive loading-unloading cycles and we could conclude that the
206 Young's modulus did not depend on the displacement rate. Finally, by performing tensile
207 experiments under ambient conditions on various films made with all materials (see again
208 Supporting Information), we concluded that relative uncertainties on the measured Young's
209 moduli were all smaller than 19 %, thus proving that both manufacturing and measurement
210 were repeatable.

211 **Method for measurement of creep property**

212 We aimed at measuring a creep property of the clay films, i.e., how the clay films deform over
213 time under a constant load. Creep experiments were performed on the films Ca²⁺-SWy-2
214 and Na⁺-SWy-2, whose geometry was the same as for the samples dedicated to the elastic
215 characterization. The free length of the samples was equal to 50 mm.

216 Figure 3 displays the experimental setup we used to perform creep tests. One end of the
217 sample was placed in a fixed grip and the other end was fixed to a mobile ball slide which

218 could move linearly on a rail. The sample was loaded by a weight attached to a string, itself
219 attached to the mobile ball slide. A pulley transformed the vertical gravitational force into a
220 horizontal force on the ball slide. In order to minimize friction, the mobile part had a linear-
221 motion bearing at the contact with a lubricated rail. Before performing any experiment, we
222 calibrated the device: to measure the friction, we loaded the device with various weights. For
223 each weight, we measured the force transmitted by the ball slide with a force sensor having
224 an accuracy of 1 mN. We fitted the data with a linear function. The slope of this function
225 was equal to 1 and the extrapolation to a measured force equal to zero gave a friction of
226 0.11 ± 0.1 N. In all results presented in this study of the creep properties, every applied
227 force was corrected by taking into account this friction. To be consistent from one sample
228 to another, the load will be expressed in force per clay layer, i.e., the force transmitted to
229 the sample divided by the number of clay layers in the thickness of the sample, which was
230 estimated by dividing the surface density of the dry film by the surface density of a clay
231 layer.

232 To perform creep tests at various relative humidities, the creep test device was placed in an
233 environmental chamber. The relative humidity was controlled with saturated salt solutions
234 and measured with a hygrometric sensor. Figure 3 shows the experimental setup. Again,
235 the strains of the samples were measured by taking images of the samples and analyzing
236 them with DIC, with the same camera and correlation procedure as the ones presented in
237 Sec. 2.3. Before each creep test, the sample was placed in a chamber in equilibrium with
238 pure water to equilibrate it at a relative humidity close to 100 %. Water was then replaced
239 with a saturated salt solution to bring the chamber to the desired relative humidity. The
240 hydric starting points of all creep tests were therefore located on the desorption branch of
241 the adsorption isotherms.

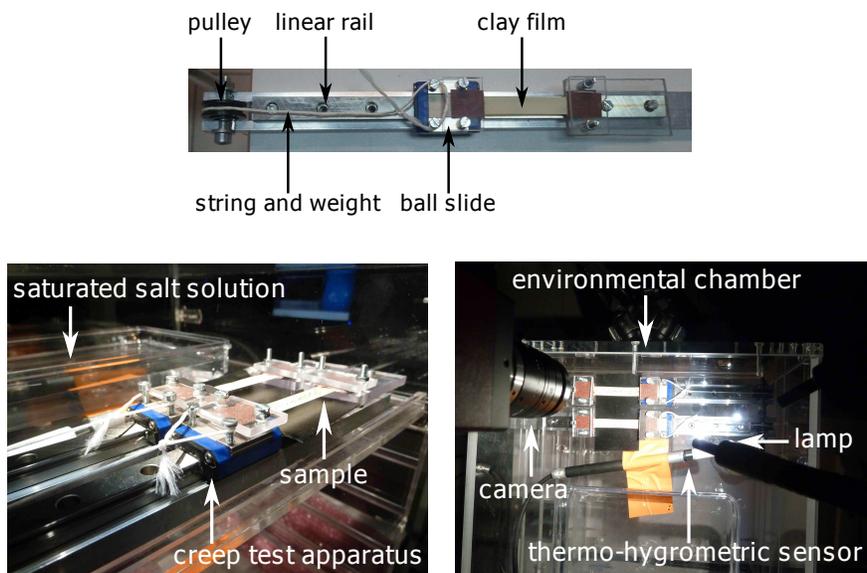


Figure 3: Pictures of the experimental setup to measure tensile creep under controlled relative humidity.

Results and discussion

Effect of water content on Young's modulus

Figure 4 displays the Young's modulus of the raw-SWy-2, Ca^{2+} -SWy-2, and Na^{+} -SWy-2 films versus relative humidity and water content. Several samples of each material were tested: we observed a good reproducibility of the tests. The Ca^{2+} -SWy-2 film was the stiffest one, with Young's moduli ranging from 2.4 GPa at high water content to 6.2 GPa at low water content, while the Young's moduli of the Na^{+} -SWy-2 film ranged from 1.0 GPa to 5.6 GPa. The raw-SWy-2 film exhibited an intermediate behavior: at low water content, its Young's modulus was smaller than the one of the Ca^{2+} -SWy-2 film (5.6 GPa versus 6.2 GPa, respectively); however, at a water content of 0.2 g/g of dry clay, its Young's modulus was higher than the one of the Ca^{2+} -SWy-2 film (3.3 GPa versus 2.8 GPa).

The nature of the cation had a clear impact on the elastic properties of clay films at a given water content. The film made with Ca-exchanged montmorillonite (i.e., the Ca^{2+} -SWy-2 film) was always stiffer than the film made with Na-exchanged montmorillonite (i.e., the Na^{+} -SWy-2 film). But we also observed an effect of the nature of the cation on the softening

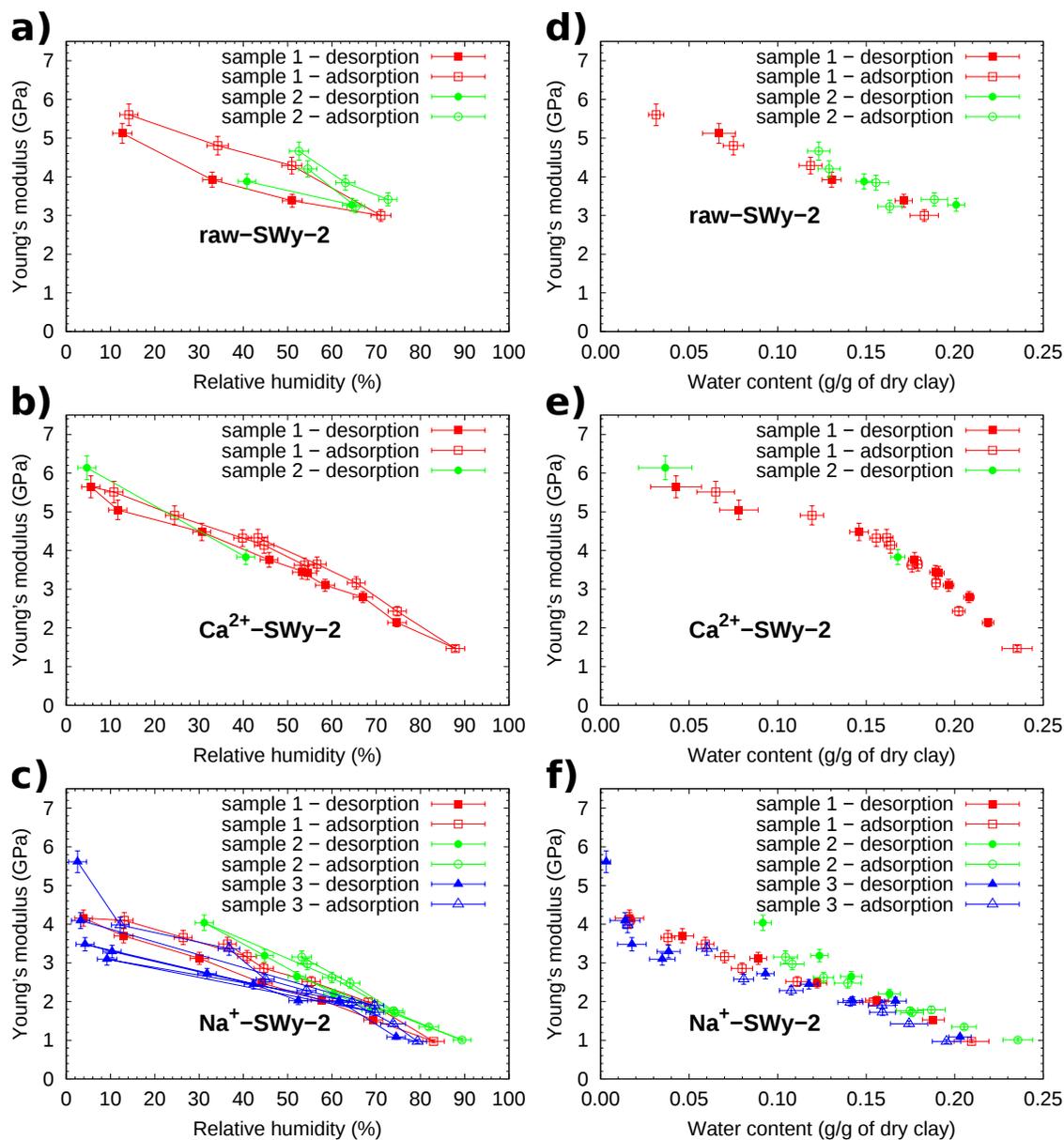


Figure 4: Young's modulus of clay films as a function of relative humidity and water content: (a) and (d) raw-SWy-2-raw, (b) and (e) Ca²⁺-SWy-2, (c) and (f) Na⁺-SWy-2. For each material, several samples were tested at various relative humidities.

257 of the films with the increase of water content. Between the smallest and the largest water
 258 contents (i.e., about 0.02 g/g and 0.24 g/g, respectively), the ratio of the Young's moduli
 259 was equal to approximately 6 for the Ca²⁺-SWy-2 films while it was equal to approximately
 260 3 in the case of the Na⁺-SWy-2 films. The Young's modulus of the Ca²⁺-SWy-2 films was
 261 therefore much more sensitive to water than that of the Na⁺-SWy-2 films. Again, the films

262 made with the natural clay raw-SWy-2 exhibited an intermediate behavior. The difference
263 in sensitivity to the water content, in particular between the Ca^{2+} -SWy-2 films and the
264 Na^+ -SWy-2 films, is quite surprising as, over a full adsorption/desorption cycle, the water
265 contents of the films varied over an identical range.

266 Part of the decrease of stiffness upon an increase of water content is a geometrical effect
267 consecutive to an increase of basal spacing.³⁰ In order to obtain results insensitive to this
268 geometrical effect, we now choose to focus no more on the Young's modulus of the clay films,
269 but on a normalized stiffness. This normalized stiffness was computed as the slope of the
270 force-strain curve divided by an estimate of the number of clay layers in the film, the basal
271 spacing of a dry clay layer (i.e., 9.55 Å, which corresponds to about 1050 layers through the
272 thickness of a 1- μm -thick film), and the width of the sample. Note that, with this definition,
273 the normalized stiffness can also be said to be equal to the slope of a stress-strain curve,
274 where the stress is calculated by dividing the applied force by the cross-sectional area of
275 the dry film, whatever the hydric conditions of the experiment are. The number of clay
276 layers in the thickness of a film was estimated (see Sec. 2.5) to be approximately equal
277 to 25000, 16000, and 40000 for Ca^{2+} -SWy-2, Na^+ -SWy-2, and raw-SWy-2, respectively.
278 Figure 5 displays this normalized stiffness upon a full adsorption/desorption cycle for the
279 three types of films tested. As expected, all samples exhibited a softening upon hydration
280 and a stiffening upon dehydration with a hysteresis between the two branches. Moreover,
281 the Ca^{2+} -SWy-2 and raw-SWy-2 films were stiffer than the Na^+ -SWy-2 film, all the more so
282 as the relative humidity was low.

283 As can be observed in Figs. 4 and 5, the dependence of the Young's modulus on the
284 relative humidity exhibited a significant hysteresis for the raw-SWy-2 samples, but no hys-
285 teresis for the Ca^{2+} -SWy-2 films. Interestingly, the same figures show that, when plotting
286 the Young's modulus versus the water content, this hysteresis almost fully disappeared for
287 all samples. Therefore, upon a cycle of adsorption/desorption, the hysteresis observed on
288 the Young's modulus is mostly due to the fact that water is adsorbed in a hysteretic man-

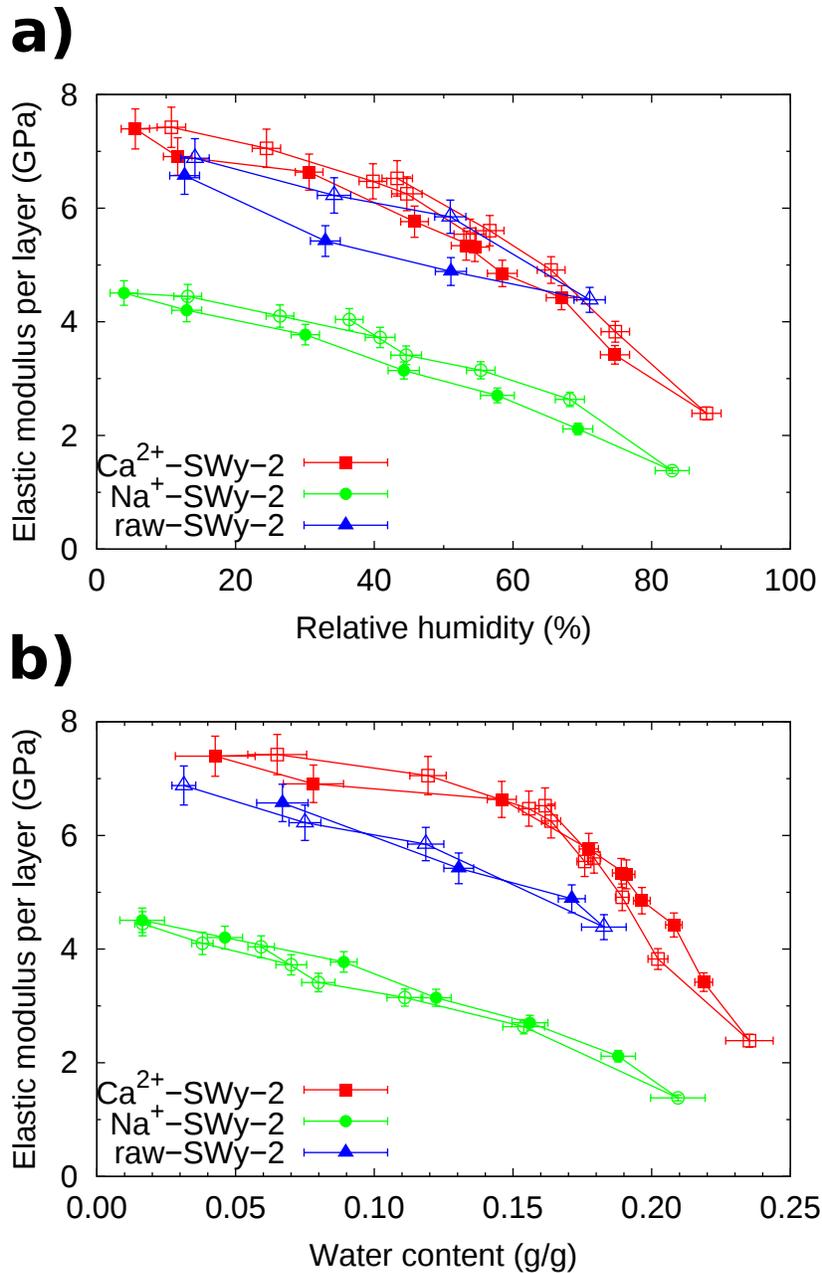


Figure 5: Normalized stiffness of films Ca^{2+} -SWy-2, Na^{+} -SWy-2, and raw-SWy-2, as a function of (a) relative humidity and (b) water content. Hollow and filled symbols correspond to the adsorption and desorption branches, respectively.

289 ner: in particular, the film on which no hysteresis was observed for the elastic properties
 290 (i.e., the Ca^{2+} -SWy-2 film) is indeed the film on which no hysteresis is observed for the
 291 adsorption isotherm.¹² When focusing on the swelling of clay films induced by variations of
 292 relative humidity, one also observes that plotting swelling versus relative humidity exhibits

293 a hysteresis, but that plotting swelling versus water content exhibits no hysteresis.¹² Those
294 observations on hysteresis strongly suggest that the natural state variable on which swelling
295 or elastic properties depend is the water content.

296 **Discussion on effect of interlayer cation**

297 Figure 5 shows that, at a given relative humidity, the normalized stiffness was larger for the
298 Ca^{2+} -SWy-2 film than for the Na^{+} -SWy-2 film. Such result can seem somewhat counter-
299 intuitive since, at low relative humidities, adsorption isotherms¹² and X-ray diffraction re-
300 sults^{31,32} show that the water content and the basal spacing are larger for montmorillonite
301 homoionized with calcium than with sodium. Also, the raw-SWy-2 film —although it con-
302 tains more sodium cations than calcium cations— exhibited a normalized stiffness close to
303 the one of the Ca^{2+} -SWy-2 film.

304 The experimental results show that, even at a given water content, the mechanical prop-
305 erties of the clay films depended on the nature of the interlayer cation: at a given water
306 content, the Ca^{2+} -SWy-2 film was always stiffer than the Na^{+} -SWy-2 film, while the film
307 made with natural montmorillonite (i.e., the raw-SWy-2 film, which contained both Na^{+}
308 and Ca^{2+} cations) exhibited an intermediate behavior. This result is not consistent with
309 the mechanical behavior of the clay layer as evaluated from numerical simulations. Indeed,
310 molecular dynamics computations showed a limited impact of the nature of the interlayer
311 cation on the elastic properties of the layer, except in the driest states:³⁰ as soon as the first
312 water layer is formed, no dependence of the coefficients of the stiffness tensors on the in-
313 terlayer cation is observed. However, the dependence of the elastic properties of clay-based
314 materials on the interlayer cation was also observed by Wang et al.,³³ who measured the
315 elastic properties of epoxy-clay composites, from which they inferred the elastic properties
316 of the clay minerals only, after subtracting the mechanical contribution of the epoxy by us-
317 ing micromechanical relations: their results show that Ca-rich montmorillonites are stiffer
318 than Na-rich montmorillonites. Note however that the water content of their samples was

319 not controlled and therefore was very uncertain. To our knowledge, there is no other work
320 available in the literature in which the mechanical properties of a same clay with various
321 interlayer cations are compared.

322 If the reason for the dependence of the elastic properties of clay-based materials on the
323 nature of the interlayer cations cannot be found at the scale of the clay layer, it must be
324 found at a scale above. Indeed, the nature of the cation has also an effect on the size and the
325 arrangement of the clay particles and on the mesostructure of the material^{34,35}. Experiments
326 show that exfoliating smectite layers with calcium counterions is very difficult³⁶⁻³⁸ and that
327 Ca-exchanged smectite layers form thicker tactoids in solution than Na-exchanged smectite
328 layers³⁵. A microscopic reason for those observations can be that cohesive forces between
329 neighboring layers depends on the counterion.²⁹ Indeed, the cohesion of clay systems is
330 mainly governed by electrostatic interactions (rather than by Van der Waals ones), so that it
331 is in particular sensitive to the valence of the counterion. Note that cohesion can vary even
332 if stiffness does not, so that the fact that Ca-rich clays are more cohesive than Na-rich clays
333 is not inconsistent with the molecular simulations of Carrier et al.,³⁰ which show that, at a
334 given water content, the counterion has no effect on the stiffness of the stack of clay layers.

335 In addition, our X-ray diffraction measurements show that the order parameter S is larger
336 in the Ca-exchanged than in the Na-exchanged sample, showing that the orientational order is
337 better in the former case. One can expect that the elastic properties of the film depend on this
338 orientational order since the stiffness coefficients of clay particle that are solicited by tensile
339 loading of the film depend on the orientation of the particle with respect to the film. Another
340 microstructural feature that could play a role in the mechanical properties of the film is how
341 the contacts between neighboring clay particles are spatially organized, as these contacts
342 govern how stresses are being transmitted throughout the film. Intuitively, one could expect
343 that a larger average area of contact would translate into a greater stiffness. It may be that,
344 in our self-standing films, the average area of contact between clay particles in Ca-exchanged
345 montmorillonite differs from that in Na-exchanged montmorillonite: as a result, for the same

346 uniaxial force applied to the film, the stresses (and in particular the shear stresses) acting
347 at the scale of the clay particle would depend on the interlayer cation. Such mesostructural
348 difference could explain our experimental observation that Ca-exchanged films were stiffer
349 than Na-exchanged films. In short, the macroscopic hydromechanical behavior of clays
350 depends strongly on the structure at scales larger than the scale of the clay layer and on the
351 orientational order. This mesostructure should be taken into account in a realistic model
352 to obtain a good estimate of the Young's modulus of an ensemble of particles, may it be
353 ordered or not.

354 **Effect of water on creep property**

355 The results presented in this section were obtained with the experimental setup displayed
356 in Fig. 3 according to the protocol described in Sec. 2.5. Figure 6(a) displays the typical
357 deformations of a clay film with time. At $t = 0$ s, a load equal to $26.1 \mu\text{N}$ per clay layer
358 was applied and was kept constant during the test. The samples exhibited an instantaneous
359 elastic deformation. The creep strain was then calculated as the difference between the total
360 strain and this instantaneous elastic deformation: thus, the creep strain was the delayed
361 part of the deformation. In Fig. 6(a), the creep strain of two Ca^{2+} -SWy-2 films is displayed
362 in function of time, on a logarithmic scale. After 500 to 600 s, the deformation was a
363 logarithmic function of time. Actually, such feature of a creep strain that evolves linearly
364 with the logarithm of time after a transient period was observed for all films. By analogy
365 with what is done in soil mechanics,³⁹ we introduce a creep coefficient α defined as the slope
366 of the creep strain versus logarithm of time curve:

$$\alpha = \frac{d\epsilon}{d(\ln t)}. \quad (1)$$

367 For each tensile creep experiment, this creep coefficient was back-calculated from the data
368 acquired once the non-logarithmic transient period is exhausted.

369 In Fig. 6(a), tests performed on two Ca^{2+} -SWy-2 films are displayed: the first one was
370 performed at a relative humidity of 92.0 ± 2.9 % and the second one at a relative humidity
371 of 77.7 ± 2.0 %. The test at 92.0 % was stopped when the sample failed, while we stopped
372 the test at 77.7 % before failure. Relative humidity had a very clear impact on the creep
373 rate. The creep strain was a linear function of the logarithm of time for both tests and the
374 slope α of this function (which we named creep coefficient) was larger at a higher relative
375 humidity: the creep coefficient α was equal to 0.22 % at a relative humidity of 92 % but to
376 0.05 % at a relative humidity of 78 %.

377 The observed logarithmic feature of creep is reminiscent of the creep of macroscopic clay-
378 based materials or of soils, which is also known to evolve logarithmically with time after a
379 transient period.³⁹ However, macroscopically, soils are usually tested in compression or in
380 shear, not in tension. The fact that, here, a logarithmic creep was also observed in tension
381 makes it possible to discard one possible explanation for the origin of such logarithmic creep,
382 which is the free volume dynamics theory. Free volume dynamics can explain why the density
383 of vibrated columns of granular materials evolve logarithmically with time^{40,41}, by stipulating
384 that, when the density of the column increases, the free volume between grains decreases,
385 and hence their ability to move and the creep rate. Such theory has also been proposed to
386 explain why the creep of cementitious materials is a logarithmic function of time in the long
387 term.⁴² But, for what concerns our experiments on clay films, since the applied stresses are
388 tensile, the free volume must increase with time, thus making it impossible to explain why
389 the creep rate would decrease over time. Other potential theories to explain this logarithmic
390 creep, sometimes proposed for other materials that exhibit this same feature (e.g., cement
391 or sand), are, among others: relaxation of internal prestresses,⁴³ presence of energy barriers
392 that two solids (e.g., two clay layers) need to overcome in order to slide over each other,⁴⁴
393 or breakage of bonds or particles.⁴⁵

394 Figure 6(b) displays the creep strain of two Na^+ -SWy-2 films in function of time, on
395 a logarithmic scale. The two tests were performed at the same relative humidity, but at

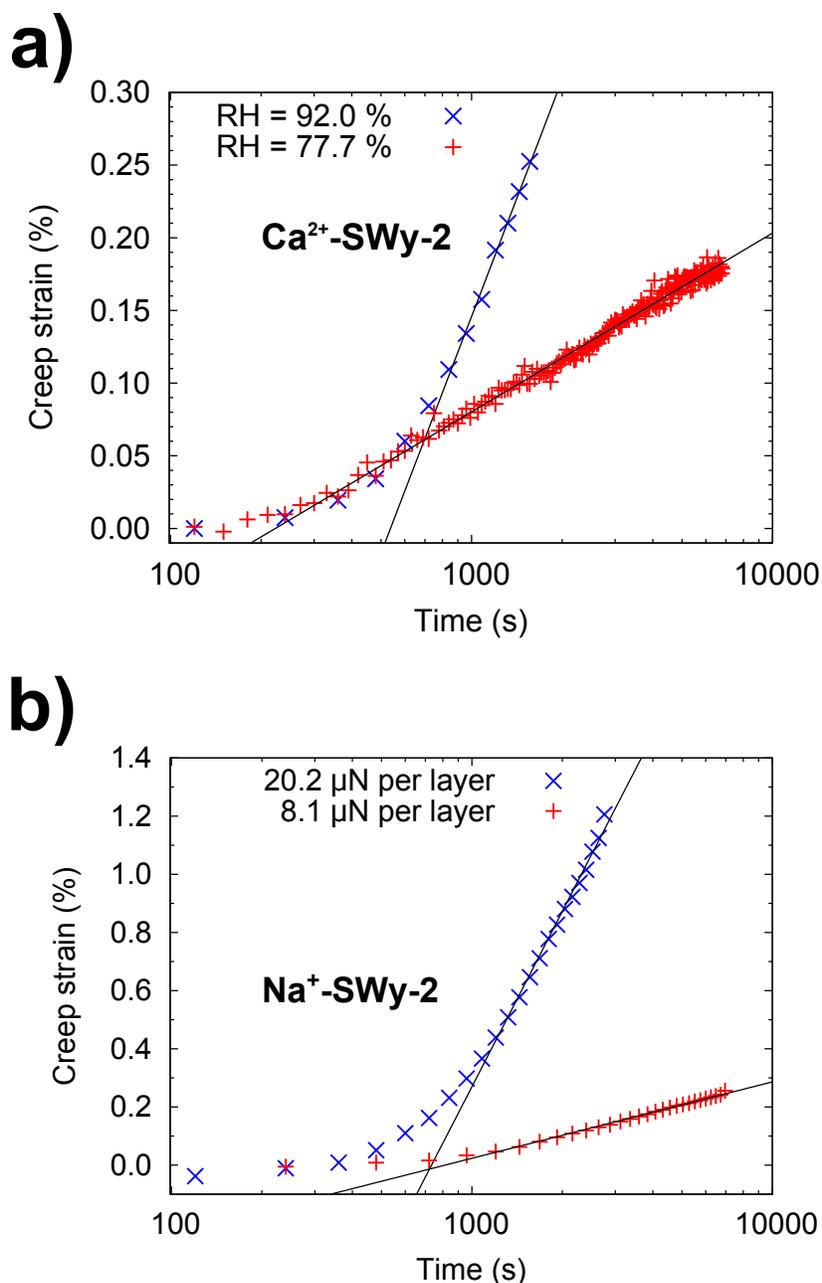


Figure 6: (a) Creep strain of films of Ca^{2+} -SWy-2 as a function of time (logarithmic scale) at various relative humidities. The force transmitted to the samples was identical for both tests (i.e., $26.1 \mu\text{N}$ per clay layer). (b) Creep strain of Na^{+} -SWy-2 films as a function of time at various applied forces. The relative humidity was identical for both tests ($\sim 92\%$).

396 various loads (8.1 and $20.2 \mu\text{N}$ per clay layer, respectively). The test with a load equal to
 397 $20.2 \mu\text{N}$ per layer was stopped when the sample failed, while we stopped the test with a load
 398 of $8.1 \mu\text{N}$ per layer before failure. For both films, after a transient period, the creep strain

399 was a logarithmic function of time. The amplitude of the creep increased with load: for a
400 load equal to $8.1 \mu\text{N}$ per clay layer, the creep coefficient α was equal to 0.12 %, while this
401 creep coefficient was equal to 0.91 % for a load equal to $20.2 \mu\text{N}$ per layer. Therefore, the
402 amplitude of creep increased faster than the load: when the load was multiplied by 2.5, the
403 creep coefficient α increased by a factor 4.3. A more thorough study of the effect of the load
404 on the creep coefficient is presented next.

405 Figure 7 displays the creep coefficient α in function of load for Ca^{2+} -SWy-2 films and Na^{+} -
406 SWy-2 films at a given relative humidity. Four sets of data are displayed, which correspond
407 to 2 experiments: a first experiment on two samples cut out from the same Ca^{2+} -SWy-2 film
408 and on two samples cut out from the same Na^{+} -SWy-2 film, and a second experiment on a
409 sample cut out from another Ca^{2+} -SWy-2 film and on a sample cut out from another Na^{+} -
410 SWy-2 film. In each experiment, all samples were tested at the same time while located in the
411 same environmental chamber. The 2 experiments were performed at different times but with
412 the same environmental chamber. When the films were loaded during the same experiment,
413 for both materials, the creep coefficient was an increasing function of load in a roughly linear
414 manner. However, experiments performed at different times were not consistent with each
415 other. Although the relative humidities measured in the two experiments were close to each
416 other (e.g., $77.5 \pm 2.8 \%$ and $77.7 \pm 2.5 \%$ for the two sets of data on the Ca^{2+} -SWy-2
417 films), because of the experimental difficulty in controlling temperature and relative humidity
418 precisely, the uncertainty on the actual local relative humidity with which the films were in
419 equilibrium may be up to 5 %. Moreover, at relative humidities around 80 %, the creep
420 coefficient α was very sensitive to relative humidity, as is shown next. Such uncertainty
421 could explain the discrepancy between the sets of experiments 1 and 2 displayed in Fig. 7.
422 In any case, experiments under the very same environmental conditions suggested that the
423 creep coefficient depends on the load and that this dependence is quite linear. Therefore, we
424 introduce the creep compliance κ (expressed in Pa^{-1}), defined by:

$$\kappa = \alpha \frac{bd}{F}, \quad (2)$$

425 where F is the force applied by clay layer, b is the width of the sample ($b = 9.3$ mm for
 426 all creep tests), and d is the basal spacing of a dry clayer (i.e., 9.55 Å). The results of all
 427 creep tests, at all relative humidities and for both types of films, are given as Supporting
 428 Information.

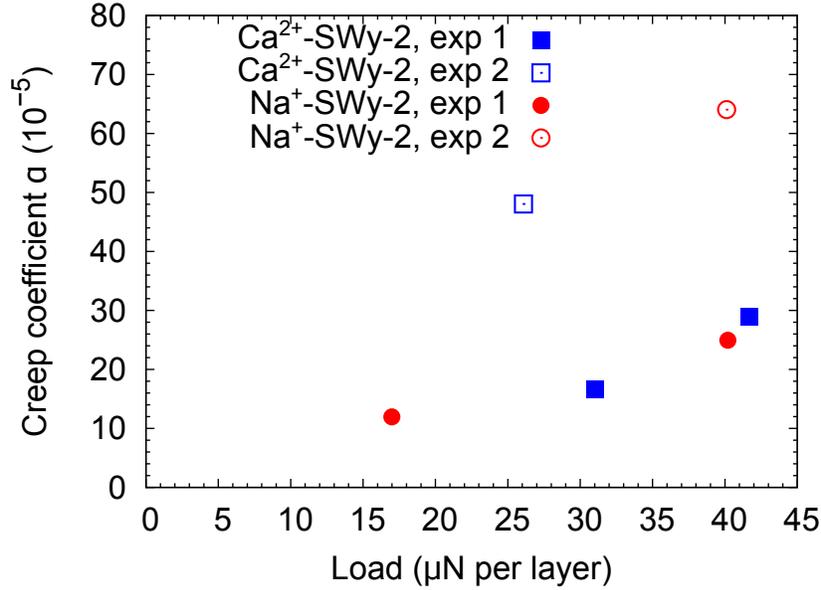


Figure 7: Creep coefficient α as a function of load at a given relative humidity. For each film, exp 1 and exp 2 correspond to two different experiments. During experiment 1, two identical films were loaded at the same time in the same environmental chamber. The relative humidity was equal to 77.5 ± 2.8 % and 81.3 ± 1.5 % for Ca²⁺-SWy-2 and Na⁺-SWy-2, respectively. Experiment 2 was performed on different films, at a different time. The relative humidity was equal to 77.7 ± 2.5 % and 80.3 ± 2.3 % for Ca²⁺-SWy-2 and Na⁺-SWy-2, respectively.

429 Figure 8 displays the creep compliance κ in function of relative humidity for both the
 430 Ca²⁺-SWy-2 and Na⁺-SWy-2 films. The error bars on the creep compliance are only visible
 431 for the data with the lowest creep compliance, which correspond to films that creep the
 432 least, and on which the noise on the creep measurement was thus the largest. At a given
 433 relative humidity, the creep compliance was much higher for the Na⁺-SWy-2 films than for
 434 the Ca²⁺-SWy-2 films, by about one order of magnitude. Also, for both types of films, we

435 observed a tremendous effect of relative humidity on the creep compliance: when increasing
 436 the humidity from about 60 % to about 95 %, their creep compliance increased by about
 437 two orders of magnitude.

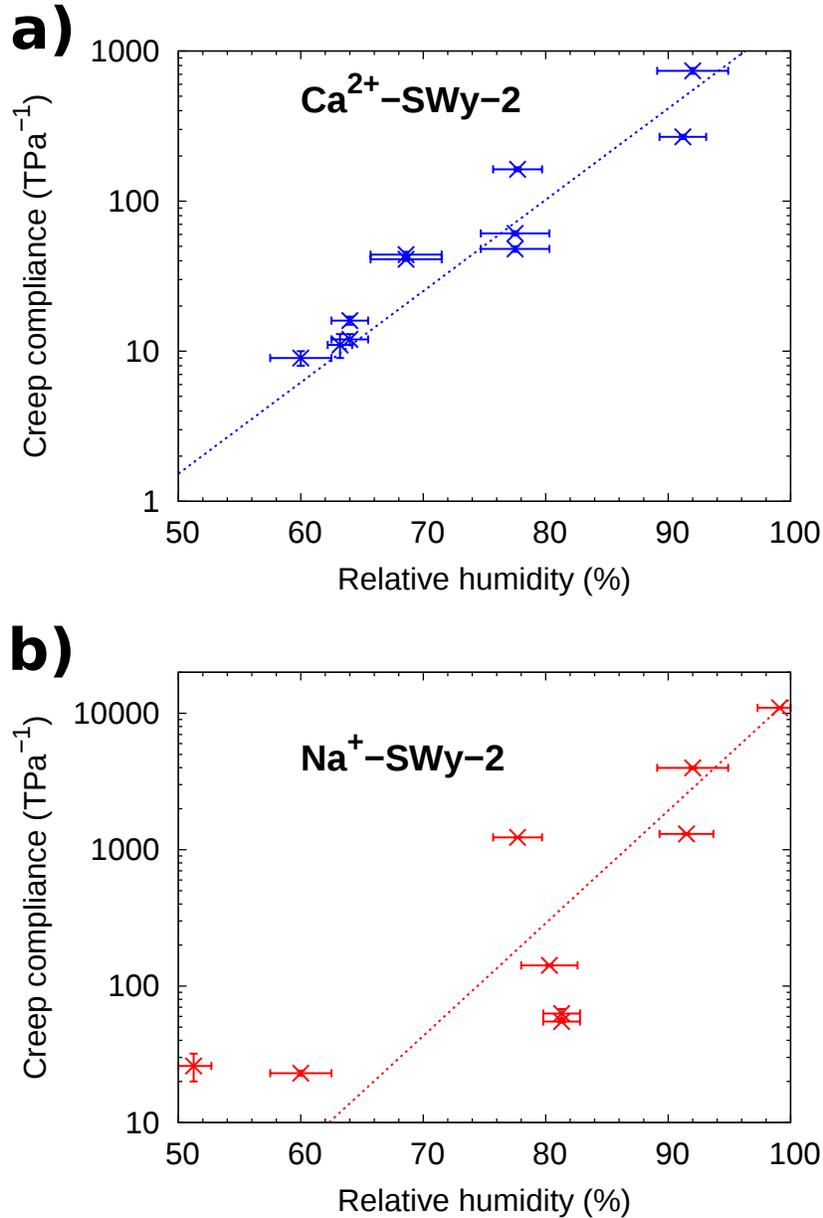


Figure 8: Creep compliance κ in function of relative humidity for (a) sample $\text{Ca}^{2+}\text{-SWy-2}$ and (b) $\text{Na}^{+}\text{-SWy-2}$. Dotted lines are visual guides.

438 We performed creep tests for relative humidities below 50 %, but we could observe no
 439 creep: the very low creep compliance at low relative humidities indeed required very long
 440 tests. Controlling the relative humidity with a high accuracy during such periods of several

441 days was impossible: the relative humidity and water content fluctuated slightly over time.
 442 The creep was therefore indistinguishable from the slight swelling and shrinkage of the film
 443 or the small variations of the elastic properties shown in Fig. 4.

444 Figure 9 displays the creep compliance as a function of water content. We performed a
 445 linear regression of the logarithm of the compliance versus water content (dashed lines in
 446 Figure 9) and obtained a correlation coefficient equal to 0.83 for the Ca^{2+} -SWy-2 films and
 447 to 0.78 for the Na^{+} -SWy-2 films. The compliance can therefore be well approximated by
 448 an exponential function of water content: creep is very much sensitive to the water content.
 449 The physical mechanism behind this strong dependency remains unclear.

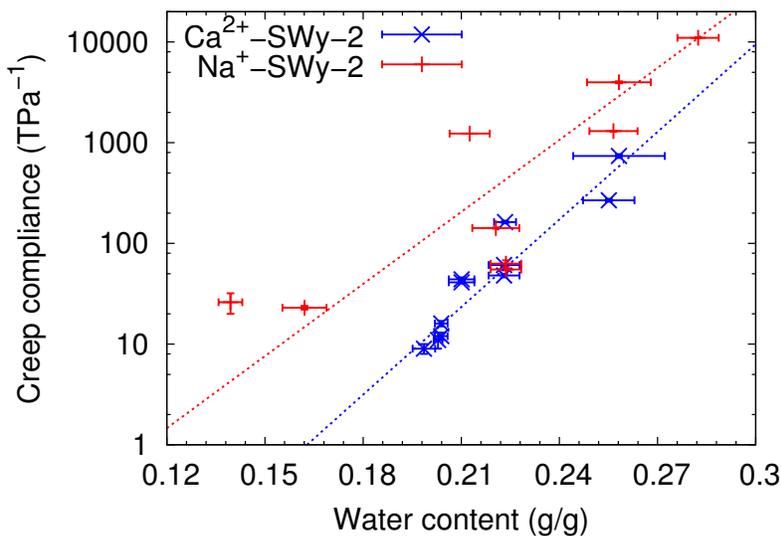


Figure 9: Creep compliance κ in function of water content for samples Ca^{2+} -SWy-2 and Na^{+} -SWy-2.

450 Conclusions

451 The conclusions of this work are:

- 452 • Whatever the interlayer cations are (here, sodium, calcium, or a mixture of sodium
 453 with calcium), the elastic and creep properties of clay films depended on relative hu-
 454 midity/water content. Increasing the water content made the clay films less stiff and

455 made them creep more.

456 • The nature of the interlayer cation had a significant effect on the elastic and creep
457 properties of the clay films and on the dependence of these properties on relative
458 humidity. Since the stiffness tensor of a clay layer at a given water content, as evaluated
459 by molecular simulations, does not depend on the nature of the interlayer cation,³⁰ the
460 reason why the elastic properties of the films depended on the interlayer cation must
461 originate from a scale greater than the scale of the clay layer: the structure of the
462 films at a mesoscale (e.g., the size and shape of the clay tactoids) must significantly
463 impact the elastic behavior of the film. It is likely that such structure at a mesoscale
464 also impacts the creep behavior of the films and at least partly explains why creep
465 depended on the nature of the interlayer cation.

466 • The Young's modulus exhibited a clear hysteresis when plotted versus relative humid-
467 ity, but no hysteresis when plotted versus water content. Therefore, the hysteresis
468 observed when plotting Young's modulus versus relative humidity mostly originates
469 from the hysteresis of the water adsorption isotherm. Such vanishing of hysteresis has
470 also been observed when focusing on the swelling properties of the same clay films.¹²
471 Therefore, the natural parameter on which elastic and swelling properties of the films
472 depend is the water content, not the relative humidity. Such observation is likely to
473 hold for other mechanical properties and should be recognized by any model of the
474 hydro-mechanical behavior of clay-based materials, at least at the scale of the clay
475 layers or of the clay particles.

476 • After a transient period, the creep of all tested films was a logarithmic function of
477 time. Since the films were loaded in tension, this logarithmic feature of creep cannot be
478 explained by free volume dynamics. The creep compliance could be well approximated
479 by an exponential function of water content.

480 In addition to these conclusions, the work here performed provides a complete set of data

481 on how the elastic and creep properties of films of montmorillonite with various interlayer
482 cations depend on water content and relative humidity. Moreover, the orientational order
483 of the films was characterized, as well as, elsewhere, their adsorption isotherms and swelling
484 properties.¹² Such set of data can serve as reference data for scientists working on bioinspired
485 clay-based hybrid materials. It can also be of value for modelers who aim at predicting the
486 mechanical behavior of clay-based materials (e.g., shales) at the macroscopic scale of the
487 engineer, from the behavior at the atomistic scale. Indeed, the results here presented make
488 it possible for them to confront the first steps of their upscaling scheme with experimental
489 data: such confrontation is necessary since, as we observed, the elastic properties of our films
490 depend significantly on the structure at a mesoscale (i.e., at a scale greater than the scale
491 of the clay layer). In particular, the dependence of the Young's modulus on the interlayer
492 cation must originate from this mesoscale. One can reasonably extrapolate that the mesoscale
493 structure is likely to play a significant role not only on the elastic properties of the pure clay
494 films here tested, but on the mechanical properties of all clay-based materials in general.

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618 Table of Contents Graphic

