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1 Characterization of magnesium silicate hydrate (M-S-H)

2 CCR

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12

13 Abstract (150 words max)

14 In this study, the structure of synthetic magnesium silicate hydrated phases (M-S-H) and the
15 distribution of water as a function of the Mg/Si ratio were investigated. Different analytical
16 techniques indicated that M-S-H phases are nano-crystallite hydrated phyllosilicates with
17 relatively short coherence length (1.2 nm) and small particle size (>200 m²/g). Zeta potential and
18 cations exchange capacity measurements showed a negative surface charge on M-S-H from the
19 deprotonation of the silanol groups. The negative surface charge is compensated by exchangeable
20 magnesium or others cations. Combined analyses were used to characterize the water distribution
21 in M-S-H revealing the following: i) *confined* water; its amount depends strongly on the relative
22 humidity ii) *very confined* water (or possibly water coordinated to magnesium), and iii) hydroxyl
23 groups bound to magnesium and to silicon.

24 Keywords:

25 Magnesium silicate hydrate (M-S-H), structure, water content, surface properties

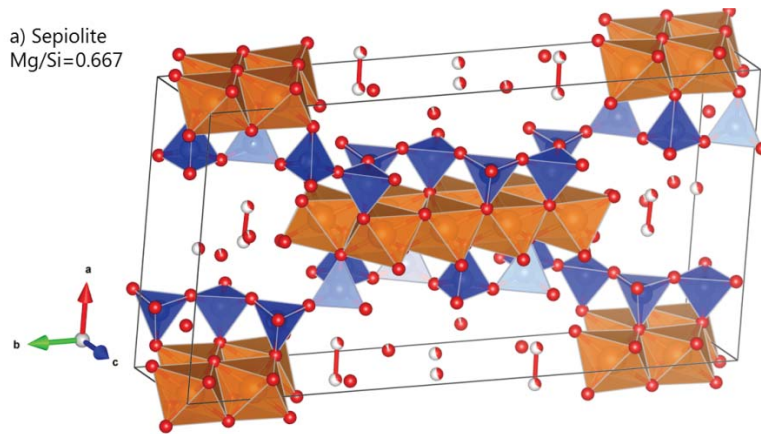
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27 1. Introduction

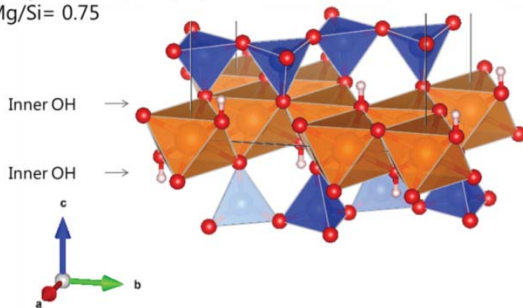
28 Magnesium silicate hydrate (M-S-H) phases are of interest as M-S-H may form i) as a main
29 reaction product in magnesia-silica binders which are under development as sustainable
30 alternatives to Portland cement [1-3], ii) at the interface of cement-based materials in contact with
31 clays [4-8] and/or iii) at the interface of cementitious materials with groundwater, seawater, and
32 MgSO₄ or MgCl₂ solutions [9-11]. In magnesia-silica binders, magnesia and silica dissolve and
33 react to form magnesium silicate hydrate gels. At the interface of Portland cement and blended
34 cements, leaching and carbonation of the C-S-H decrease pH at the surface of the cement sample,
35 resulting in the decalcification of C-S-H and the formation of amorphous silica which reacts with
36 magnesium to form M-S-H [12, 13].

37 The properties and solubility of M-S-H phases synthesized in the laboratory have been studied
38 previously [14-17]. In short term experiments (1 to 6 months), a Mg/Si of around 1.0 was
39 reported [14, 16-21], while in long term studies (1 year or longer) [15, 22], a wider range of
40 compositions (Mg/Si = 0.8-1.3) has been determined. For M-S-H formed at the interaction zone
41 of cement with seawater, Mg/Si ratios up to 2 were observed for Portland cement [11] or as low
42 as 0.5 for the interface between low-pH cement and clay rocks [5]. This wide range of
43 compositions might be related to changes in the structure, which is investigated in the present
44 paper.

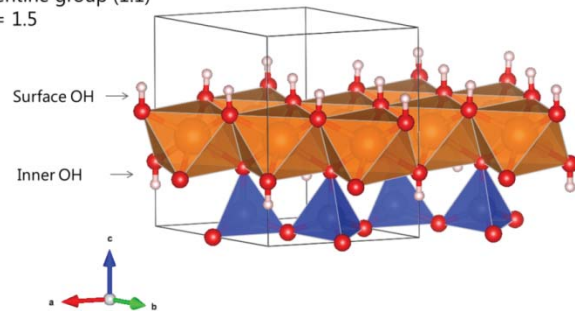
45 ^{29}Si MAS NMR studies showed that the silicates are arranged in tetrahedral layers and
46 magnesium in octahedral layers comparable to 2:1 or 1:1 phyllosilicates as shown schematically
47 in Figure 1. The structure of M-S-H is poorly ordered and has been related to sepiolite [14],
48 hydrated nanoparticles of talc [16], hydrated talc or hydrated antigorite [15], lizardite [17, 23],
49 stevensite [15] or saponite [7, 16].



b) Phyllosilicate/talc (2:1)
Mg/Si= 0.75

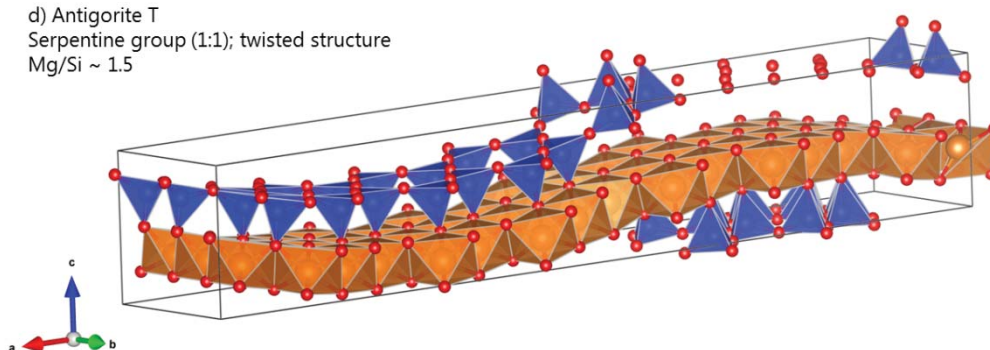


c) Serpentine group (1:1)
Mg/Si= 1.5



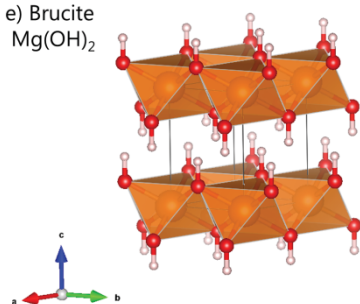
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d) Antigorite T
Serpentine group (1:1); twisted structure
Mg/Si ~ 1.5



52

e) Brucite
Mg(OH)₂



53

54 *Figure 1: Schematic sketches of the structure of a) sepiolite, T:O:T structure, b) 2:1 phyllosilicates with a T:O:T*
 55 *structure such as talc, c) 1:1 phyllosilicate (T:O structure) such as the serpentine group, d) brucite e)*
 56 *antigorite T (T:O structure phyllosilicate) (orange: octahedral magnesium site, blue: tetrahedral silicate site).*
 57 *The structures are from [24-28] using the VESTA software [29].*

58 The ²⁹Si MAS NMR spectra of M-S-H showed approximately 2/3 Q³ signals indicating silica
 59 sheets and 1/3 of Q² signals indicating either very small coherent areas of silica sheets and/or
 60 defects in the silicate sheets or even double chain silicate layers [15, 16]. The Q² resonance
 61 occurs at a chemical shift of -85.5 ppm, while the broad signal at -92 to -97 has been attributed to
 62 2 or 3 different Q³ silicate sites depending on the deconvolution [15, 17, 30]. Deconvolutions
 63 taking into account the presence of 3 different sites indicated chemical shifts at -92.7, -94.7 and -
 64 96.8 ppm: Q³_a, Q³_b, and Q³_c [15]. The “poorly-organized” character of M-S-H leads to
 65 significantly broader signals than those observed in crystalline phyllosilicates. The chemical shift
 66 at -92.7 ppm is characteristic for serpentine group minerals [15, 31] such as antigorite, chrysotile
 67 or lizardite with a T:O structure (see Figure 1), while the chemical shift of -96.8 ppm is
 68 characteristic for talc [15, 16, 32-34] with a T:O:T structure. Both classes of minerals exhibit a
 69 potentially infinite layer of silicate. The presence of a second silicate tetrahedral layer on the
 70 other side of the octahedral magnesium layer doubles the sheets of silicate (T:O:T) and results in
 71 a more negative chemical shift for silica in talc than in serpentine group minerals with a T:O
 72 structure. The intermediate ²⁹Si MAS NMR resonance at -94.7 ppm in the M-S-H spectra could
 73 not be attributed [15, 16, 33, 34]. This intermediate chemical shift could be related i) to the
 74 presence of an empty neighboring magnesium site as in stevensite, which has as talc a T:O:T
 75 structure, but is deficient in magnesium: (□O)-Si-(O-Si)₃ where □ is a vacant site [32, 33], ii) to
 76 a high content of surrounding water in M-S-H structure [23], which would result in a resonance at
 77 -95 ppm as in the case of saponite, hectorite or stevensite and/or iii) to the variability of the Si-
 78 O-Si angles in M-S-H [23].

79 M-S-H as a precursor of sepiolite has been suggested by [14]. The ^{29}Si MAS NMR spectra of M-
80 S-H shows similarities with sepiolite ($\text{Si}_6\text{O}_{15}\text{Mg}_4(\text{OH})_2(\text{OH}_2)_2 \cdot 4\text{H}_2\text{O}$) spectrum. Sepiolite has a
81 phyllosilicate chain-structure derived from talc T:O:T ribbons with alternate silica and
82 magnesium layers (Figure 1a) for which, similar silicate signals as for M-S-H have been reported:
83 one Q^2 (at -85.2 to -85.5 ppm) and three Q^3 signals (first at -92.3 to -92.7 ppm, second at -94.3 to
84 -94.5 ppm and last at -98.2 ppm) as shown e.g. in [35]. The Q^3_{a} signal was attributed to the near
85 edge of the silicate sheet in the blocks while the Q^3_{b} and Q^3_{c} signals were attributed to the center
86 or the edge of the silicate sheet [36-39]. Sepiolite is needle-like clay with a low charge density,
87 low cation exchange capacity, which is not swelling. The Mg/Si ratio of sepiolite is equal to
88 0.667, lower than that observed in pure M-S-H [15] synthesized from MgO and silica fume,
89 although some studies, using other raw materials, have reported such a low ratio [14, 21]. In fact,
90 Wollast and al. [40] have observed the formation of a very poorly crystalline sepiolite-like phase
91 from the reaction of aqueous silica with seawater comparable to M-S-H. Sepiolite contains
92 different types of water, i) zeolitic water which can be removed by thermal treatment below
93 150°C , ii) coordinated water (Mg-OH_2^+) which is lost above 150°C and probably below 450°C
94 and is bound to the terminal magnesium cations of the octahedral sheet and iii) structural water
95 which corresponds to the hydroxyl group linked either to tetrahedral or octahedral layers [37, 41,
96 42].

97 Roosz et al. [16] indicated based on the X-rays diffraction (XRD) patterns of M-S-H and the
98 presence of the Q^2 signal in the ^{29}Si MAS NMR spectra that the M-S-H had only nanometer-sized
99 coherent scattering domains which also caused the broad reflections in the XRD pattern. The size
100 of a coherent region of M-S-H was estimated at 1.5 nm in the ab plane, and 2.4 nm along c.
101 Similarly, Chiang et al. [43] suggested based on SAXS measurement a spherical structure for M-
102 S-H with an average radius of 1.7 ± 1 nm.

103 In this paper, the effect of the Mg/Si ratio (ranging from 0.7 to 1.4) on the M-S-H structure,
104 including the distribution of the water and the particle properties, were investigated by ^{29}Si MAS-
105 NMR, ^1H - ^{29}Si CP MAS-NMR and FT-IR spectroscopy and with X-rays diffraction and X-ray
106 pair distribution function analysis, the water and hydroxyl contents and their distribution by DVS,
107 TGA and ^1H -NMR relaxometry, the particle size and the porosity by N_2 physio-sorption
108 measurements and the surface properties by CEC and zeta potential measurements. This study
109 aimed to contribute to a better characterization of the structure of M-S-H phases and including
110 the different types of water in M-S-H. Two additional M-S-H samples (Mg/Si=0.8 and 1.2) were
111 exposed to hydrothermal conditions in an autoclave (180°C for 4 days) to obtain better crystalline
112 M-S-H phases.

113 2. Materials and methods

114 2.1. Synthesis

115 Magnesium oxide (Merck, pro analysis, 0.18 ± 0.02 mass% Na_2O) and silica fume (SiO_2 , Aerosil
116 200, 0.9 mass% HCl) were used as starting materials. Different quantities of MgO and SiO_2 were
117 directly mixed with ultrapure water as detailed in [22]. The syntheses were carried out to obtain
118 ~ 5 g of solid and a water-to-solid (W/S) ratio of 45 to ensure a homogeneous suspension and
119 sufficient solution for analysis. All the syntheses were performed in a glovebox under a nitrogen
120 atmosphere to minimize CO_2 contamination. After equilibration at 20°C during 2 or 3.3 years, the

121 solid and liquid phases were separated by filtration under pressure (4-5 bars N₂) using nylon
122 filters (0.45 μm). Following the filtration, the solids were washed with a 50/50 (volume) water-
123 ethanol mix and then with ethanol (94 mass % alcohol) to remove dissolved ions and to prevent
124 the precipitation of salts during drying [44]. The samples were freeze-dried with liquid nitrogen
125 (for approximately 20 min at -195°C) and kept at -40°C under vacuum (pressure of 0.28 mbar)
126 for 7 days. Additional samples stopped after 3.3 years were dried in desiccators over 30% relative
127 humidity (RH).

128 In addition two M-S-H (Mg/Si = 0.8 and 1.2) suspensions, which had been previously
129 equilibrated at 20°C, were treated hydrothermally. The two suspensions were heated in a stainless
130 steel autoclave at 180 °C for 4 days, followed by a slow cooling to room temperature during
131 approximately 12-24 hours. The filtration process and freeze drying process was similar as
132 described above.

133 The solid phases were analyzed after further equilibration in N₂-filled desiccators at a RH of ~
134 34% (saturated CaCl₂ solution) for a period of 14 days or longer. After drying, the samples were
135 gently ground by hand.

136 2.2. Analytical techniques

137 2.2.1. Ion chromatography and pH

138 The liquid phases were analysed by ion chromatography (IC) immediately after filtration. The
139 dissolved concentrations of Mg, Na, K, Cl, Si in undiluted solutions or in solutions diluted by a
140 factor 10, 100 or 1000 were quantified using a Dionex DP series ICS-3000 ion chromatography
141 system. All concentrations were determined as duplicates and the mean value is given in the
142 following, the measurement scatter was ≤ 10%. The pH values (±0.1) were measured at ambient
143 temperature (23±2°C) in an aliquot of unfiltered suspension and the results were corrected to
144 20°C as described in [22].

145 2.2.2. Solid state NMR

146 The ²⁹Si MAS NMR experiments were recorded on a Bruker Avance III NMR spectrometer
147 using a 7 mm CP/MAS probe at 79.5 MHz applying the following parameters for the single pulse
148 experiments: 4500 Hz sample rotation rate, minimum of 3072 scans, 30° ²⁹Si pulse of 2.5 μs, 20 s
149 relaxation delays, RF field strength of 33.3 kHz during SPINAL64 proton decoupling.

150 The ²⁹Si NMR chemical shifts of the spectra were referenced to the most intense resonance at -
151 2.3 ppm of an external sample of an octamethylsilsesquioxane (Aldrich No. 52,683-5) which was
152 referenced to tetramethylsilane (TMS, δ²⁹Si = 0.0 ppm). The observed ²⁹Si resonances were
153 analysed using the Qⁿ classification, where a Si tetrahedron is connected to n Si tetrahedra with n
154 varying from 0 to 4. The quantification was performed by non-linear least-square fits using the
155 “DMFIT” software developed by Massiot et al.[45]. Silica fume was quantified taking into
156 account the shift at -100.9 ppm (Q³ from the surface of the amorphous silica [15, 46]) and the Q⁴
157 shift at -110 ppm. However, the T₁ relaxation time of silica fume can be very long and the
158 amount of silica fume generally might be underestimated. The Q¹ and Q² environments in M-S-H
159 were deconvoluted using mainly Lorentzian functions while the Q³ environment was
160 deconvoluted using Gaussian functions following the procedure outlined in [22].

161 ^1H - ^{29}Si cross polarization MAS NMR spectra were recorded on the same equipment applying the
162 following parameters: 4500 Hz sample rotation rate; minimum of 1536 scans, 3 s relaxation
163 delays, RF field strengths of 33 kHz during the polarisation transfer (ramp from 100-50%) with
164 contact times varying from 0.5 to 5 ms using the above mentioned proton decoupling conditions.

165 2.2.3. X-ray diffraction (XRD) and X-ray pair distribution function (PDF)

166 XRD data were collected using a PANalytical X'Pert Pro MPD diffractometer equipped with a
167 rotating sample stage in a θ - 2θ configuration applying $\text{CuK}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) at 45mV
168 voltage and 40mA intensity with a fixed divergence slit size and an anti-scattering slit on the
169 incident beam of 0.5° and 1° . The samples were scanned between 5° and $75^\circ 2\theta$ with a
170 X'Celerator detector.

171 In addition to the standard XRD measurements, X-ray Pair Distribution Function (PDF) analyses
172 were performed. This analysis focusses on the entire signals including Bragg peaks and diffuse
173 scattering. PDF represents the distribution of interatomic distances in a compound, regardless of
174 its crystalline state, determined experimentally by a Fourier transform of the powder pattern. PDF
175 is thus an efficient technique for studying of short coherence lengths materials such as cements
176 [47] or geopolymers [48]. The reduced PDF, $G(r)$, was obtained by taking a sine Fourier
177 transform of the measured total scattering function $S(Q)$, as shown in equation (1), where Q is the
178 momentum transfer given in equation (2) with θ as the scattering angle and λ as the wavelength
179 of the incident radiation [48, 49].

$$180 \quad G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q [S(Q) - 1] \sin(Qr) dQ \quad (1)$$

$$181 \quad Q = \frac{4\pi \sin\theta}{\lambda} \quad (2)$$

182 It is crucial to obtain diffraction data with a high momentum transfer (Q) in order to maximize
183 the resolution after the Fourier transform. We therefore used an X'Celerator Panalytical
184 diffractometer equipped with a Mo source ($\lambda_{\text{K}\alpha} = 0.70926 \text{ \AA}$). The powder diffraction pattern was
185 scanned over the 6.004 - 153.932° angular range with a step size of 0.0083° . The total acquisition
186 was the average of 2 runs recorded over 24 hours. The PDF and standard corrections [49] were
187 calculated with PDFGetX2 [50]. The density number of atoms ρ_0 used to calculate the PDF was
188 $0.10 \text{ atoms \AA}^{-3}$. The use of a finite value of Q (17 \AA^{-1}) for the PDF analysis led to the addition of
189 spurious oscillations to $G(r)$ depending on the distance r . These oscillations were smoothed by the
190 use of a Lorch (1969) function. On the other hand, calculated PDF from a given structure was
191 obtained with PDFGui [51]. Due to limited Q resolution, a value of 0.05 Gaussian dampening
192 (Q_{damp}) envelope was introduced in the refinement.

193 2.2.4. BET and apparent density

194 Nitrogen sorption isotherms were measured at 77.35 K using a Coulter SA3100 equipment. The
195 specific surface area (SSA_{BET}) was obtained by using Brunauer-Emmett-Teller (BET) equation
196 [52], in the pressure range from 0.05 to 0.2 P/P_0 . The t-plot method [53] is used to find the non-
197 porous surface area (so-called "external area") in the second part of the t-plot at $P/P_0 > 0.8$. The
198 pore volume (micro and meso-pores) is then calculated by subtracting the $\text{SSA}_{\text{t-plot}}$ to the SSA_{BET} .
199 The calculation of those SSA and the pore volume were made with the Beckman Coulter
200 Sorption Analysis software. The IUPAC classification [54, 55] gave the definition: micro-pore \leq
201 $2 \text{ nm} \leq$ meso-pores $\leq 50 \text{ nm} \leq$ macro-pores. The measurements were performed on the samples

202 kept in N₂-desiccators equilibrated at 30% RH. Just before analysis the samples were freeze-dried
203 for 2 hours to remove any adsorbed water molecules. The apparent density was measured by
204 helium pycnometry with a PMI Hg-porosimeter.

205 2.2.5. FTIR

206 Attenuated total reflectance (ATR) Fourier Transformation-Infrared (FT-IR) spectra were
207 recorded in the mid-region on a Bruker Tensor 27 FT-IR spectrometer between 600 and 4000 cm⁻¹
208 with a resolution of 4 cm⁻¹ by transmittance on small amounts of powder. The focus is made on
209 2600-3800 cm⁻¹ where the stretchings of O-H vibrations are located.

210 2.2.6. Dynamic vapour sorption (DVS) and thermogravimetric analysis (TGA)

211 The water adsorption and desorption isotherms were determined with a VTI-SA Dynamic Vapour
212 Sorption Apparatus (DVS) manufactured by TA Inc. The DVS device allows continuous
213 monitoring of the mass of the samples exposed to changing RH by means of a high-precision
214 micro balance with an accuracy of 10 µg. The RH in the chamber was varied in the range 0-94%
215 by a controlled flow of a mixture of dry gas (N₂) and wet gas (saturated H₂O vapor) with
216 accuracy ±1% as determined by a dew point analyser. The isotherms were determined at
217 20.0±0.1°C; as controlled by means of Peltier elements. Approximately 15 mg of 2 year-old M-
218 S-H and 2mg of 3.3 year-old M-S-H, pre-dried in a desiccator at a 35%RH, were placed in a glass
219 sample holder in the measuring chamber of the DVS. Changes in mass were monitored
220 continuously and logged at 1-min intervals. Equilibrium criterion to be reached before proceeding
221 to each next RH step was set as 0.007% of a sample mass in 5 min and the maximum length of a
222 step was set as 12 h. At the end of the sequence of RH steps, the reference dry mass was
223 determined by drying a sample to constant mass at 105°C and 0% RH (in DVS) and at 980 °C (in
224 TGA). The loss of the strongly physically bound water and or very loosely bound hydroxyl
225 groups can occur around 105°C, therefore the water content is expressed relative to the mass
226 determined at 980 °C.

227 Thermogravimetric analyses (TGA) were carried out on ground powder (~30 mg) with a Mettler
228 Toledo TGA/SDTA 8513 instrument using a heating rate of 20°C/min from 30 to 980 °C. Traces
229 of brucite (Mg(OH)₂) which loses water at around 400-420°C was detected only in the samples
230 with Mg/Si = 1.3 and 1.4.

231 The total water bound in M-S-H was quantified from the total water loss between 30 and 980°C
232 and the water associated to hydroxyl groups in M-S-H was quantified from the water loss
233 between 250 and 800°C [15]. Both results were normalized to the dry mass at 980 °C and
234 corrected for the amount of brucite as detailed in [22]; the results are given per silica.

235 2.2.7. ¹H NMR relaxometry

236 ¹H NMR T₂ (spin-spin) relaxometry measurements were carried out on a Bruker Minispec NMR
237 spectrometer operating at 7.5 MHz. The 90° pulse length was 2.9 µs. The Carr–Purcell–
238 Meiboom–Gill (CPMG) and the quadrature echo (QE) pulse sequences were used for resolving
239 the mobile and solid water populations, respectively. The samples previously conditioned at
240 different RH were measured while sealed in miniature PCTFE containers, same as used in [56].
241 Mass measurements before and after the NMR tests were carried out to verify constant mass of
242 the samples.

243 The CPMG enables probing liquid water confined in different populations (sizes) of pores owing
244 to the property that shorter T₂ relaxation times correspond to stronger interactions with the solids.

245 This method was used for water and porosity of hydrates, e.g. calcium silicate hydrate (C-S-H)
246 [57, 58]. Three types of water confined in microstructure have been described in C-S-H with the
247 corresponding T_2 : the interlayer/adsorbed water (~ 0.1 ms), gel water (~ 0.3 ms), and bulk water
248 (comprising water in interhydrate spaces and bulk water in larger pores, 1-3 ms) [56-58].
249 Similarly, in swelling clays such as montmorillonite, $T_2 \leq 0.05$ ms have been assigned to
250 hydroxyl groups in the clays, while signals at ~ 0.05 -0.5 ms have been related to water in the
251 interlayer and/or adsorbed water; the T_2 time varies depending on the interlayer distance. Longer
252 relaxation times have been assigned to water present in interparticle (external) pore space [59].

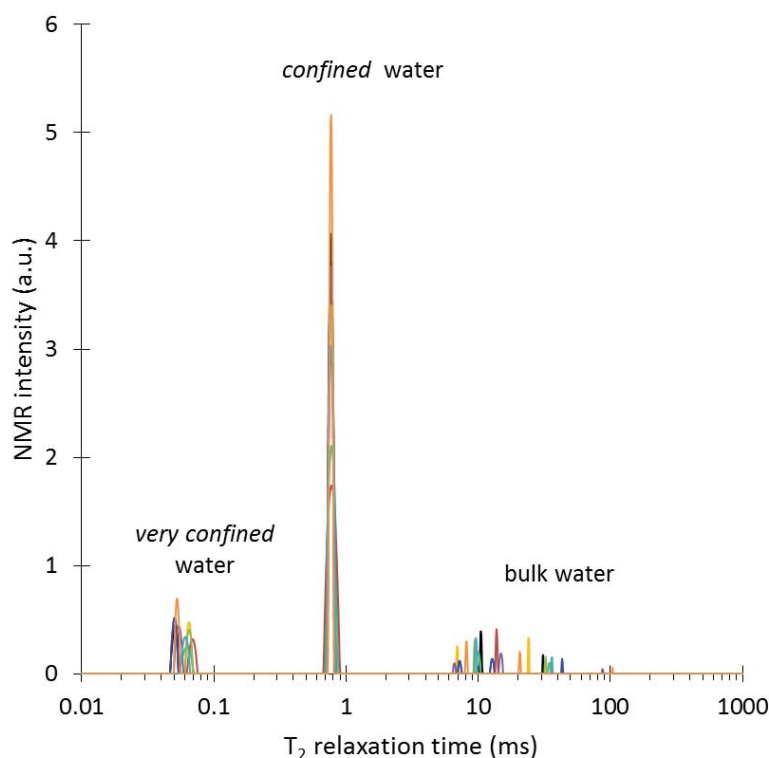
253 The relation between the transverse relaxation time and the size of the pore can be estimated, e.g.,
254 using the fast exchange model of relaxation (3):

$$255 \quad \frac{1}{T_2} \approx \frac{\lambda S}{V} \quad (3)$$

256 where λ is the surface relaxivity, S the surface area and V the pore volume [60].

257 The CPMG signal can be deconvoluted into the different exponential components using
258 numerical inversion. Applying the ILT requires relatively high signal-to-noise ratio (S/N), usually
259 in excess of 300-400/1; for the lower S/N the algorithm may often result in erroneous
260 deconvoluted data with artificial peaks at low T_2 . Typical CPMG recorded for M-S-H
261 (Mg/Si=0.9) equilibrated at 85% RH are shown in Figure 2, and three populations of water can be
262 found: the first at ~ 0.05 ms, a second at ~ 0.8 ms and the third above 6 ms. The structure of M-S-
263 H and the distribution of the water in M-S-H are less known than for C-S-H or clays. Based on
264 the assignments made for clays and C-S-H, the three different populations of water were assigned
265 to *very confined* water (interlayer and surface), *confined* water in the micro-pores and water in the
266 space between the M-S-H agglomerates, i.e., bulk water. The ILT was used to find the position of
267 the T_2 peaks corresponding to the different populations of water. However, as long as the position
268 of the peaks in the ILT-deconvoluted data was fairly constant between consecutive
269 measurements, the amounts of different water populations found with the ILT were prone to a
270 high scatter due to the aforementioned low S/N. Hence, a simple multi-exponential fitting with
271 the constrained number and positions of the T_2 peaks (as revealed by the ILT) was applied here to
272 get the repartition of the amounts of the different types of waters. The multi-exponential fitting
273 was carried out by minimizing the sum of squared errors.

274 Additionally, water with shorter T_2 times characteristic for stronger interaction with the solids
275 (chemically combiner water, also referred to as the *structural* or *solid* water corresponding to the
276 hydroxyl group signal was accessed using the QE pulse sequence. The QE signals were recorded
277 as a function of pulse gap in the range $\tau = 15$ –45 μ s. Those were deconvoluted into a Gaussian
278 (structural water) and an exponential (mobile water) decay parts [57, 58].



279
280 *Figure 2: 10 examples of CPMG T_2 results for the M-S-H 0.9 (85 %RH).*

281 2.2.8. Zeta potential measurements and cation exchange capacity (CEC)

282 The zeta potential was measured out directly in suspensions before filtration with 5 g of solid per
283 200 ml. The samples were stirred in a beaker with an overhead stirrer at 500 rpm during 10
284 minutes to ensure the homogeneity repartition of the particles and reach a stable value before the
285 measurement. During the measurements, they were stirred at 400 rpm and each measurement was
286 repeated 10 times. Zeta potential data were recorded with a ZetaProbe from Colloidal Dynamics
287 Inc., which is based on the frequency-dependent electroacoustic effect. Shortly, an alternating
288 voltage is applied to the suspension which causes charged particles to move back and forth at a
289 mobility that depends on their zeta potential. The software calculates the zeta potential from the
290 frequency-dependent mobility using the O'Brien equation [61]. Finally the values obtained were
291 background corrected with a measurement of the filtrated aqueous phase.

292 Cation exchange capacity (CEC) in the samples was measured on 100 mg of powder. The cations
293 on the surface and/or from the interlayer were exchanged with cobalt hexamine trichloride during
294 30 min at room temperature [4] using a solution/solid mass ratio of 30. The suspensions were
295 filtered and the concentrations of Na, K, Ca, Mg in solution were determined by ion
296 chromatography (IC) as detailed above. The sum of measured cations was compared to the total
297 CEC which was obtained from the difference in the cobalt hexamine concentration from the
298 original solution and from the leachate. Such concentrations were determined by colorimetry
299 (absorption band at 473 nm) using a UNI-CAM UV visible spectrometer. The excellent
300 agreement between the total CEC and the CEC calculated from the measured cations showed that
301 dissolution of M-S-H was negligible.

302 **3. Results and discussions**

303 **3.1. Insights on the M-S-H particles**

304 **3.1.1. Ageing of M-S-H**

305
 306 The formation of M-S-H proceeds in batch experiments very slowly such that after 1 year at
 307 room temperature thermodynamic equilibrium is generally not yet reached while after 2 years M-
 308 S-H seemed to have been near to equilibrium conditions as detailed in [22]. Thus, in addition to
 309 samples aged for 1 or 2 years [22], also well-aged samples with an equilibration time of 3.3 years
 310 were investigated. To verify that (near) equilibrium conditions have been reached, the
 311 composition of the aqueous and solid phase after 3.3 years were compared to M-S-H equilibrated
 312 for 1 and 2 years and to M-S-H which has been prepared at 180°C (hydrothermally prepared: “M-
 313 S-H HT”). Dissolved concentration and pH values measured in the aged samples (3.3 years) are
 314 presented in Table 1. The concentrations and pH measured after 3.3 years were comparable to the
 315 2-year old samples which indicated that 3.3 years samples, as well as the 2 years ones, were close
 316 to thermodynamic equilibrium.

317

318 *Table 1: Measured dissolved concentrations in the solutions and measured pH values in equilibrium with the*
 319 *synthesized M-S-H samples after 1, 2 [22] and 3.3 years of curing at 20°C and with the hydrothermally*
 320 *prepared M-S-H (0.8 and 1.2).*

	mmol /L	Mg	Si	Na	pH (20°C)
room temperature					
1 year	0.8	0.33	1.36	0.33	8.5
	0.9	0.32	0.66	0.38	8.7
	1.0	0.26	0.07	0.41	9.3
	1.1	0.13	0.02	0.43	9.9
	1.2	0.10	0.004	0.44	10.3
	1.3	0.10	0.003	0.47	10.4
2 years	1.4	0.13	0.004	0.49	10.4
	0.7	0.37	1.47	0.34	8.2
	0.8	0.38	1.44	0.38	8.3
	0.9	0.40	0.34	0.42	8.6
	1.0	0.35	0.06	0.46	9.2
	1.1	0.15	0.008	0.45	9.8
3.3 years	1.2	0.13	0.008	0.48	10.0
	1.3	0.09	0.003	0.50	10.3
	1.4	0.12	0.001	0.51	10.3
	0.7	0.39	1.49	0.34	8.3
	0.8	0.38	1.26	0.37	8.3
	0.9	0.41	0.46	0.42	8.5
	1.0	0.43	0.05	0.45	9.1
	1.1	0.25	0.009	0.47	9.7
	1.2	0.23	0.005	0.51	9.9

	1.3	0.18	<0.002	0.52	10.3
	1.4	0.15	<0.002	0.53	10.4

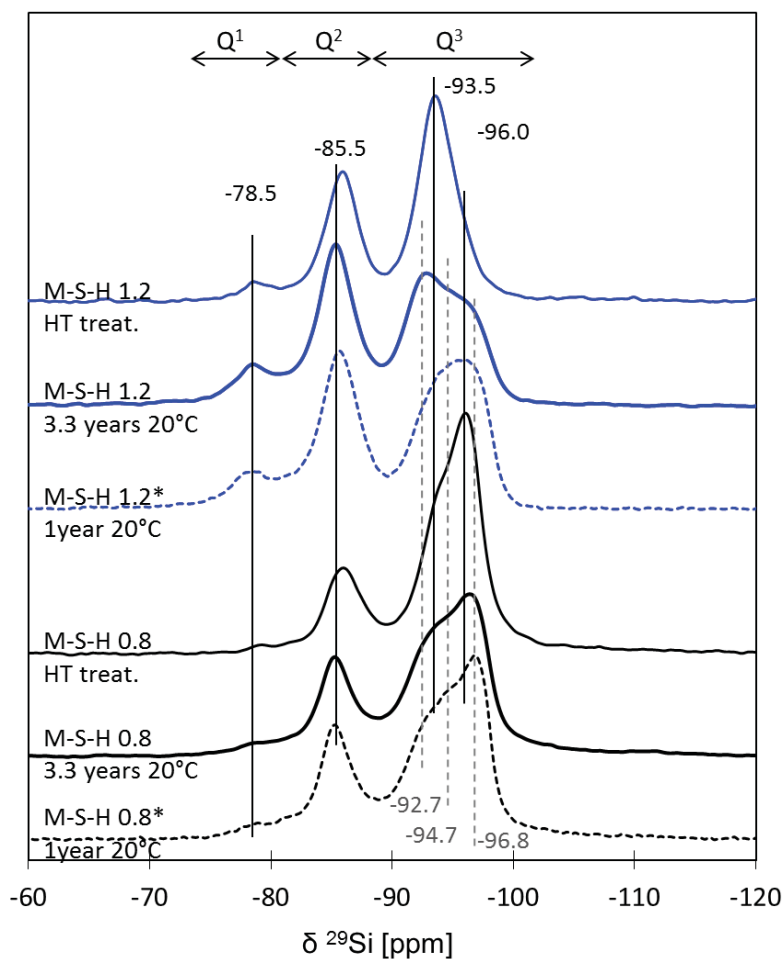
	M-S-H HT				
	0.8	0.24	1.821	0.38	8.1
	1.2	0.35	0.024	0.53	9.2

321

322 Also, the ^{29}Si MAS NMR spectra of M-S-H samples cured 3.3 years at room temperature were
 323 compared to the spectra of the 1 year-old samples and to the hydrothermally prepared M-S-H in
 324 Figure 3. The overall shapes of the spectra were similar between the 1 year and 3.3 years
 325 samples.

326 The deconvolutions of the spectra are detailed in Table 2. The M-S-H 0.8 aged for 3.3 years
 327 showed a lower content of Q^2 and higher content of Q^3_{tot} resulting in a reduced Q^2/Q^3 than the
 328 sample aged for 1 year. This more significant degree of polymerization in the old sample
 329 indicates that with time the structure of low Mg/Si M-S-H becomes more similar to talc, which
 330 shows a single, rather narrow Q^3 band at -97 ppm [32-34]. Also the hydrothermally prepared M-
 331 S-H showed a higher degree of ordering and a more distinct but still rather broad band -96.5 ppm.
 332 This trend of higher ordering at higher temperature agrees with other findings [62, 63], who
 333 observed a progressive better ordered structure for M-S-H formed at higher temperatures and the
 334 formation of talc at 600°C.

335 For the M-S-H 1.2 sample which contains more magnesium, the amount of Q^1 , Q^2 and Q^3_{tot} did
 336 not change significantly between 1 to 3.3 years. However, a higher intensity of the signal at -92.7
 337 ppm (Q^3_{a}) after 3.3 years indicated a somewhat greater degree of organization and a structure
 338 related to serpentine group minerals such as lizardite or antigorite (Mg/Si=1.5, T:O structure, see
 339 Figure 1). The hydrothermally prepared M-S-H 1.2 showed one only Q^3 band at -93 ppm which
 340 would be consistent with a 1:1 T:O well-ordered structure.



341
 342 *Figure 3: ^{29}Si MAS NMR spectra of the M-S-H hydrothermally prepared (0.8 and 1.2) compared to ^{29}Si MAS*
 343 *NMR spectra of M-S-H samples synthesized at 20°C after 1 year (*=from[22]) or 3.3 years of curing.*

344
 345 *Table 2: Chemical shifts and relative intensities of different silicon sites obtained from the deconvolution of*
 346 *the ^{29}Si MAS NMR spectra of M-S-H synthesized at room temperature and prepared hydrothermally (HT)*
 347 *presented in Figure 3.*

		M-S-H (room temperature)					
		Q ¹	Q ²	Q ³ _a	Q ³ _b	Q ³ _c	Q ² /Q ³
		-78.3	-85.5	-92.7	-94.7	-96.7	
		±0.3 ppm	±0.3 ppm	±0.3 ppm	±0.3 ppm	±0.3 ppm	
0.8	1 year	3	34	25	8	26	0.6
0.8	3.3 years	2	28	26	17	23	0.4
1.2	1 year	7	46	14	12	21	1.0
1.2	3.3 years	8	47	25	6	14	1.0

		M-S-H (HT. prepared)					
		Q ¹	Q ²	Q ³ _a	Q ³ _c	Q ² /Q ³	
		-79.0 ±0.5 ppm	-85.8 ±0.5 ppm	-93.7 ±0.5 ppm	-96.2 ±0.5 ppm		

0.8	HT	0	22	30	48	0.3
1.2	HT	5	32	63	0	0.5

348 *Quantification error* $\approx \pm 10\%$ of absolute amount of (%Si) +2.5%.

349 In summary, M-S-H synthesized at room temperature were similar after 1 or 3.3 years although
350 the longer reaction time resulted in slightly better-ordered structures. The M-S-H 0.8 HT
351 structure is comparable to a poorly ordered 2:1 phyllosilicate such as talc or stevensite while M-
352 S-H with a higher Mg/Si showed instead a structure similar to a 1:1 phyllosilicate such as
353 antigorite. In all cases, a significant amount of Q² was still present, also in the hydrothermally
354 prepared samples.

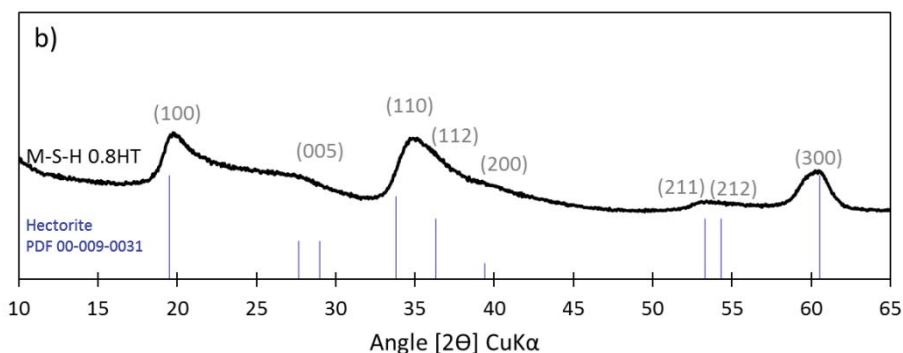
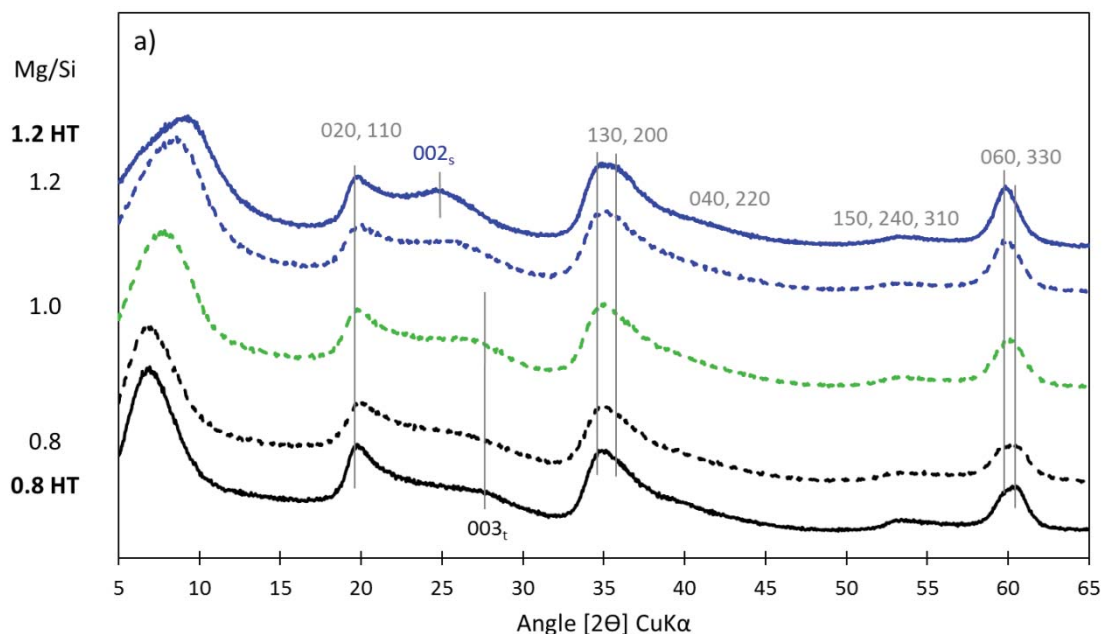
355 3.1.2. X-rays diffraction

356 3.1.2.1. X-ray diffraction patterns

357 The XRD patterns of the M-S-H phases with different Mg/Si ratios together with the
358 hydrothermally prepared M-S-H are shown in Figure 4a. XRD patterns showed very broad
359 reflections. The patterns were very similar with equal relative intensity and positions of the broad
360 reflections independent of the Mg/Si ratio. The humps have been indexed, in Figure 4a, following
361 the indexing of M-S-H based of talc, Mg₃Si₄O₁₀(OH)₂, from [16] and also based on the structure
362 of kerolite, Mg₃Si₄O₁₀(OH)₂.H₂O, a hydrated variety of talc from [64, 65] and of deweylite from
363 [66], a naturally occurring hydrous amorphous magnesium silicate with a composition between
364 Mg₃Si₄O₁₀(OH)₂ 0.3-0.7H₂O and Mg₃Si₂O₅(OH)₄0.3-0.7H₂O. Kerolite or deweylite had been
365 described by [64-66] as extremely fine-grained or disordered talc or stevensite minerals possibly
366 mixed with minerals from the serpentine group such as lizardite or antigorite. Similar to the
367 reflection profiles of M-S-H, the XRD patterns of these materials are broad indicating extremely
368 small crystallite size, disorder or both. Lin et al. [67] compared M-S-H-like phase to hectorite,
369 swelling clay, and indexed the broads reflections as detailed in Figure 4b.

370 The reflections at 59.9 °2θ are shifted to slightly lower angles at higher Mg/Si (both for
371 preparations at ambient and hydrothermal temperatures). These reflections are characteristic for
372 the main layer of trioctahedral phyllosilicates. This difference from M-S-H 0.8 to M-S-H 1.2 is
373 consistent with the slight increase of the 060 distance from 1.528 Å (60.5 °2θ) in 2:1
374 phyllosilicates (talc) to 1.54 Å (60.05 °2θ) in 1:1 phyllosilicates (serpentine). This indicates only
375 small changes in the large scale of the sheets arrangement.

376 The reflection at 27.2°2θ corresponds to the (003) distance of talc and is better defined in the M-
377 S-H 0.8HT sample. A reflection at 24.9°2θ can be observed in M-S-H 1.2HT, which could be
378 attributed to the (002) of the serpentine mineral. Those observations confirmed a high
379 resemblance of the hydrothermally prepared M-S-H with the two end-members talc (2:1) in the
380 case of M-S-H 0.8HT and serpentine (1:1) minerals in the case of M-S-H 1.2HT.



381

382

383

384 *Figure 4: a) XRD patterns of M-S-H samples (3.3 years, 20°C) and of hydrothermally treated M-S-H indexed*
 385 *following kerolite, $Mg_3Si_4O_{10}(OH)_2 \cdot H_2O$ (0.8: $(003)_t$ for talc and 1.2 $(002)_s$ for serpentine); b) XRD patterns of*
M-S-H 0.8 HT indexed following hectorite.

386

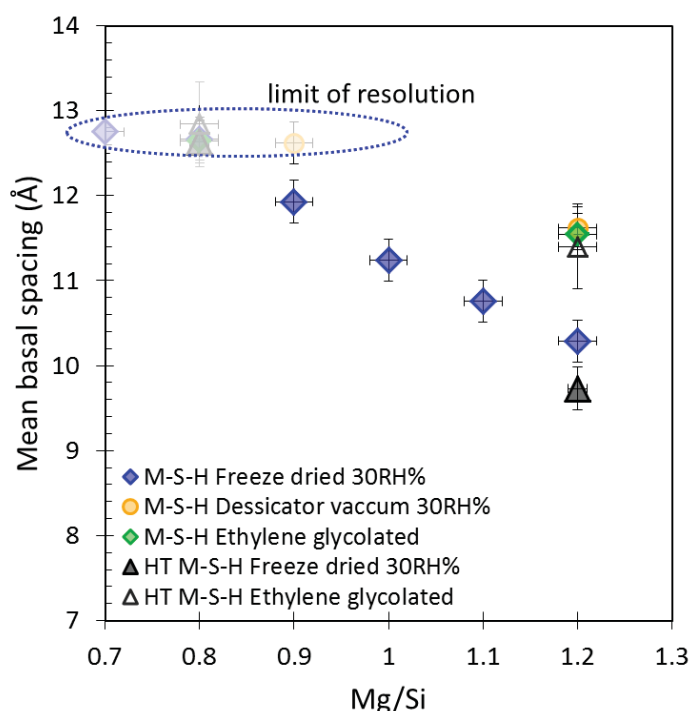
387 3.1.2.2. Basal spacing drying and swelling

388 The main difference between the patterns of M-S-H (Figure 4) was in the reflection at 7-9 °2θ
 389 which corresponds to layer-to-layer (001) distance as detailed in [16]. As discussed in [16], the
 390 minimal coherent regions in M-S-H phases can lead to shifts of the signals related to the 001
 391 distance which can result in an overestimation of this distance. The 001 distance of the M-S-H
 392 0.8 was at the detection limit and could be larger than the 12.7 Å indicated in Figure 5. The
 393 measured layer-to-layer distances of the M-S-H synthesized at room temperature and
 394 hydrothermally prepared are plotted in Figure 5 as a function of the Mg/Si.

395 An increase of Mg/Si ratio from 0.8 to 1.2 resulted in a shift of the first reflection from 7.0 to 8.6°
 396 2θ indicating a decrease of the mean basal spacing from at least 12.7 Å to 10.3 Å.

397 The drying procedure affected the measured (001) distance, as visible at high Mg/Si. The freeze
 398 dried samples re-equilibrated to 33 % RH always showed a lower layer-to-layer distance than
 399 samples which were dried directly to 33 % RH, without initial freeze drying as shown in Figure
 400 5, indicating that freeze drying resulted in a collapse of the interlayer which was not or only
 401 partially restored during rehydration.

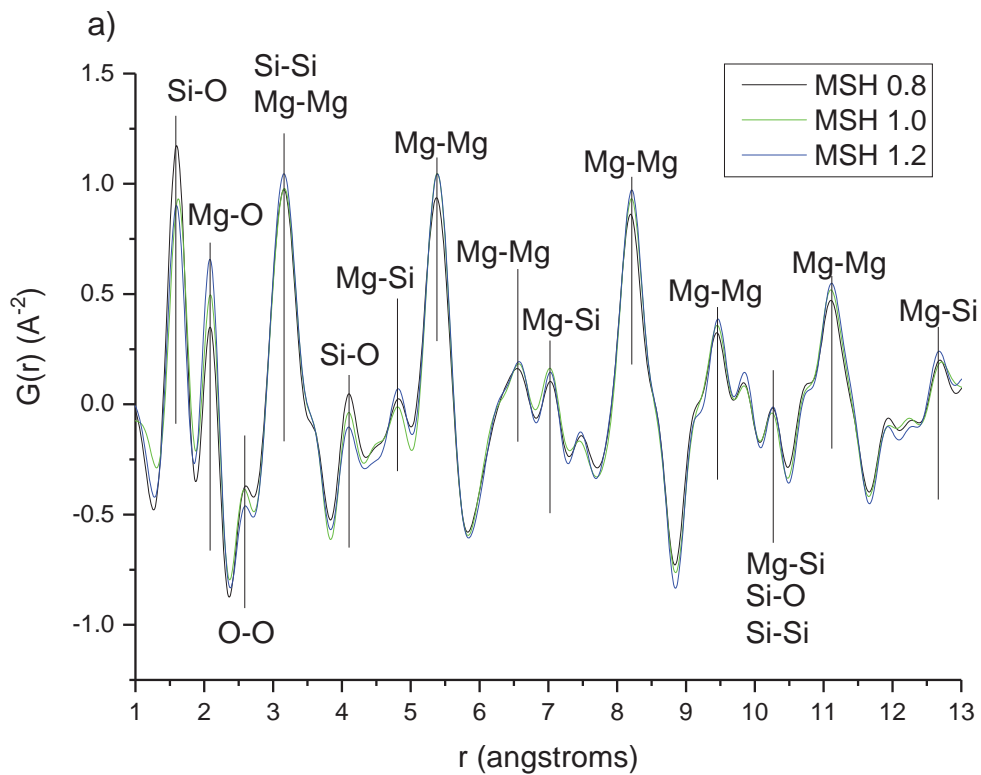
402 The addition of ethylene glycol to the freeze-dried samples resulted in an increase of their layer-
 403 to-layer distances indicating a swelling of the M-S-H as also characteristic for hydrated 2:1
 404 phyllosilicates with layer charge. At low Mg/Si, the (001) the distance was either too big to be
 405 measured (>12.7) or non-existing while at high Mg/Si the distance increased 10.3 to 11.6 Å.



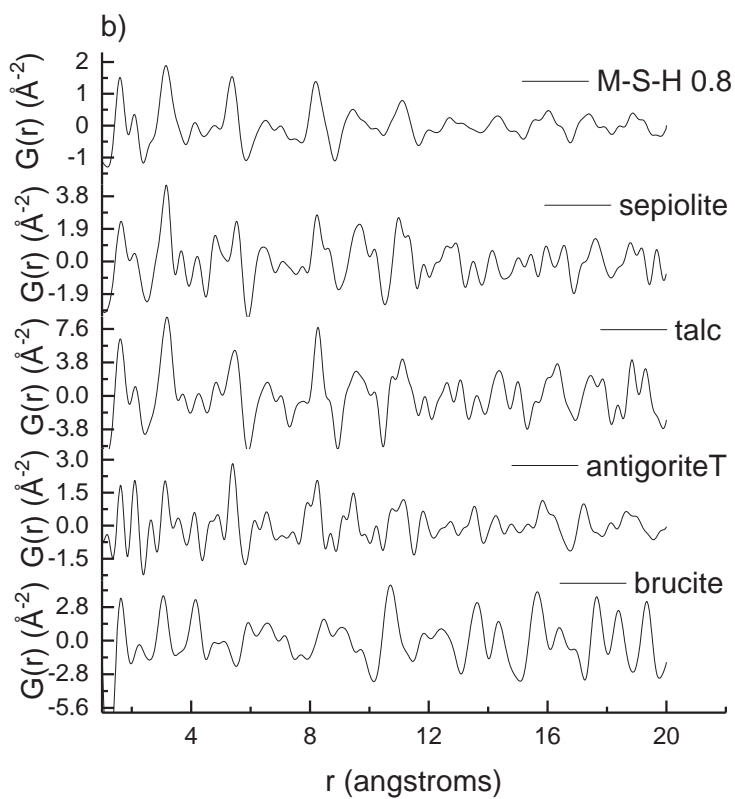
406
 407 *Figure 5: Mean basal spacing (layer-to-layer distance) measured from XRD patterns of the M-S-H samples*
 408 *(diamonds and circles) and for hydrothermally prepared M-S-H (triangles) as a function of Mg/Si in M-S-H.*
 409 *Freeze dried = freeze dried samples and re-equilibrated to 33RH% over CaCl₂, desiccator vacuum= directly*
 410 *dried over CaCl₂ 33RH% (*might be not completely equilibrated) in a vacuumed desiccator.*

411 3.1.2.3. X-ray pair distribution function (PDF)

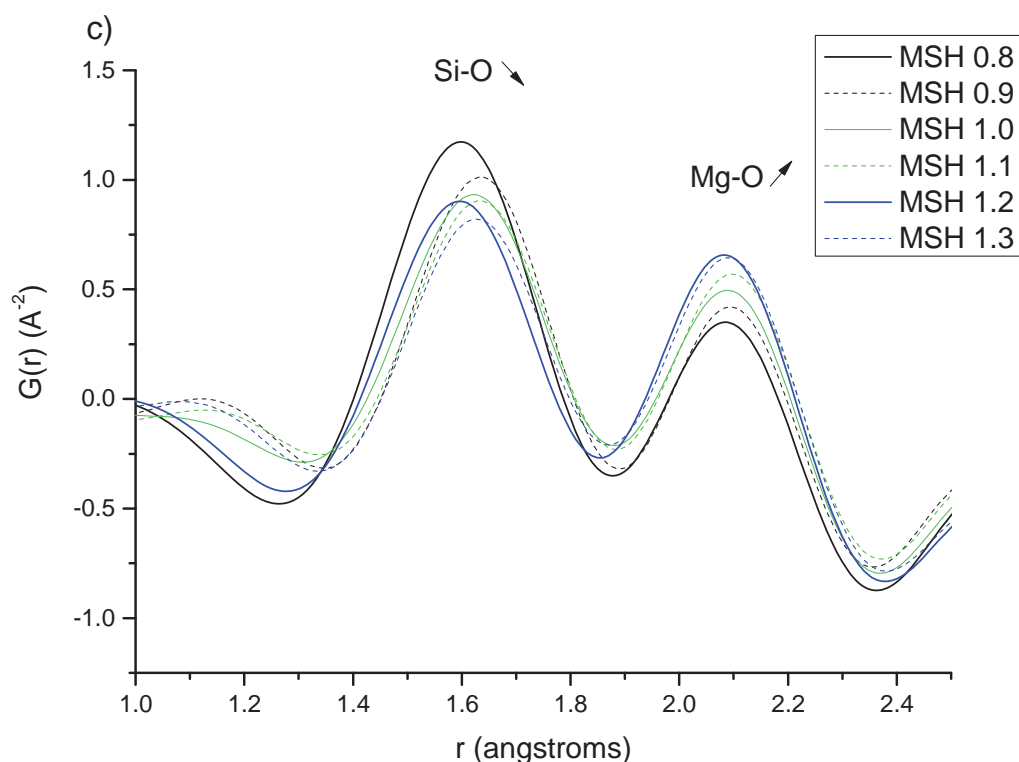
412 Additional characterizations of the M-S-H samples were performed using X-ray pair distribution
 413 function (PDF) analysis (Figure 6). The X-ray PDF analyses of the M-S-H samples were very
 414 similar regardless the Mg/Si ratio (Figure 6a). Figure 6b compares the pair distribution functions
 415 of M-S-H, sepiolite [24], talc [25], antigorite T [28] and brucite [26]. The structures of these
 416 minerals are schematically represented in Figure 1. Antigorite (Figure 1d) corresponds to a 1:1
 417 phyllosilicate (serpentine group) and differs from lizardite (Figure 1c) by a curved structure with
 418 alternated T:O blocks.



419
420



421



422
 423 *Figure 6: a) X-ray pair distribution function of M-S-H 0.8, 1.0 and 1.2, b) 2X-ray pair distribution function of M-*
 424 *S-H 0.8 compared to X-ray pair distribution functions of sepiolite, talc, antigorite T and brucite, c) Zoom on X-*
 425 *ray pair distribution functions of M-S-H 0.8 to 1.3.*

426

427 Compared to the crystalline minerals which showed a coherence length higher than 20 Å (Figure
 428 6b), M-S-H exhibited a rather short coherence length, close to 12 Å (Figure 6b) whatever the
 429 Mg/Si ratio, which is consistent with their poorly crystalline nature and the nano-sized particles
 430 [16, 43] as previously discussed.

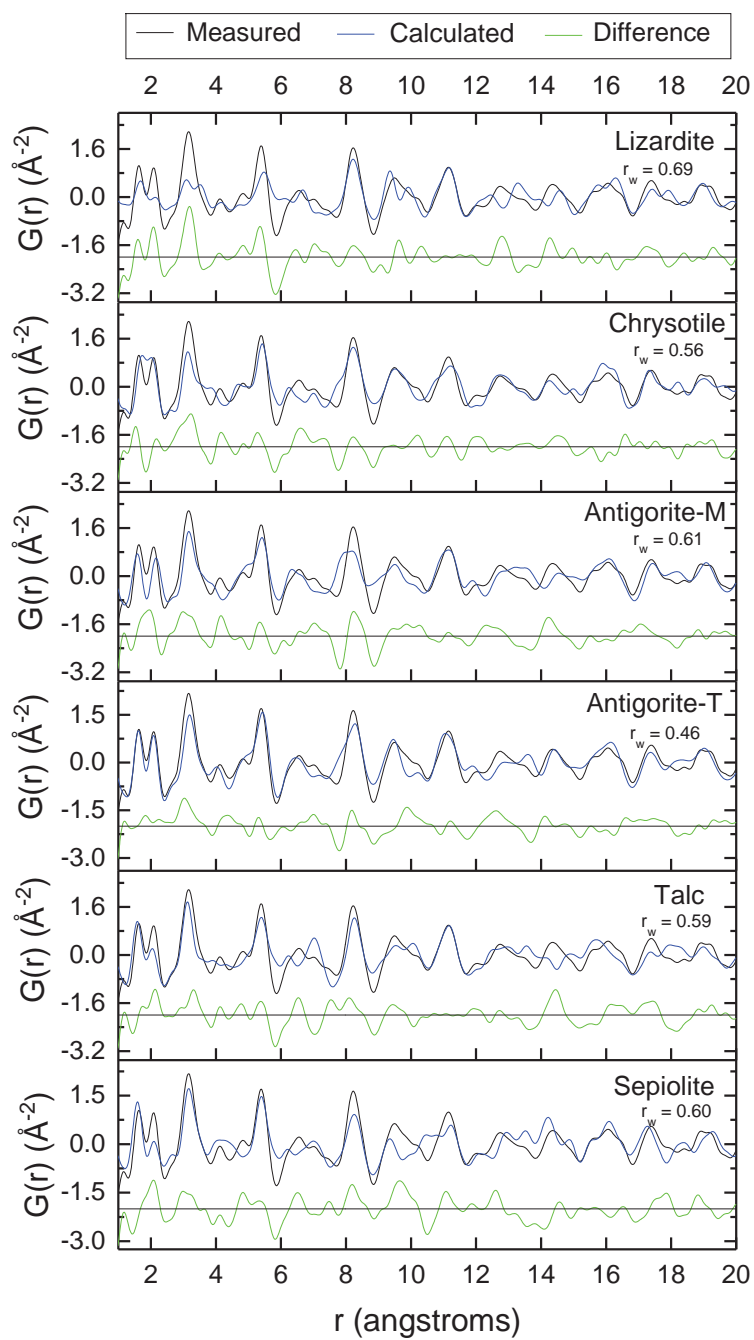
431 The peaks were tentatively assigned using the structures of talc and antigorite as references [25,
 432 28]: they mainly corresponded to Mg-Mg ($r = 3.13 \text{ \AA}$, 5.36 \AA , 8.21 \AA , 9.42 \AA , 11.06 \AA) and Mg-
 433 O (2.09 \AA) distances within the same layer as well as Si-Si (3.20 \AA) and Si-O distances in
 434 tetrahedral silicate layer ($r = 1.61 \text{ \AA}$). The X-ray PDF analysis of M-S-H confirmed a structure
 435 where magnesium is bound to oxygen in the surrounding of silicon and hydroxyl groups. The
 436 intensity of the Si-O peak at $r = 1.6 \text{ \AA}$ decreased whereas that of the Mg-O peak at $r = 2.1 \text{ \AA}$
 437 increased at high Mg/Si ratio, which was consistent with the depletion of SiO_2 and the
 438 enrichment in MgO (Figure 6c). The slight variations in the positions of the peak maxima were
 439 due to experimental uncertainties.

440 In a second stage we tried to fit the pair distribution functions of M-S-H by refining the structures
 441 of the different phyllosilicate minerals using the PDFgui software [51]. The refined parameters
 442 included the scale factor, the lattice parameters (a , b and c , the angles being kept constant), the
 443 isotropic displacement parameters of Mg, Si and O, and δ_1 , a coefficient for $(1/r)$ contribution to
 444 the peak sharpening (for small distances, the motion of two contributing atoms can be correlated).
 445 The instrumental resolution parameter was determined by refinement of a nickel reference
 446 sample as $Q_{\text{damp}} = 0.05$. The calculations were performed over the 1-20 Å range. Figure 7

447 compares the pdf function of M-S-H 1.3 with those resulting from the refinement of sepiolite
448 [24], talc [25], chrysotile [68], lizardite [27], antigorite M (monoclinic) and antigorite T (triclinic)
449 [28]. The fit parameters are detailed in the Appendix. The best fit, corresponding to the lowest
450 residuum r_w (quality weighted parameter characterizing the difference between observed and
451 simulated pdfs) was obtained for triclinic antigorite Tb [28]. Antigorite has an alternating-curved
452 structure slightly deficient in magnesium and hydroxyl groups. Antigorite Tb, described by [28],
453 shows one or more offsets in the octahedral sheet at the change of T:O. At this offset, the
454 coordination number of the magnesium atoms decreases and oxygen atoms in the vicinity form a
455 tetragonal pyramid around it. Chrysotile was the second best fit. This mineral is composed of
456 tubular fibers due to the rolls up of the sheets. The pdf results are consistent with the ^{29}Si MAS
457 NMR data showing a silicate structure of M-S-H 1.3 similar to that of the phyllosilicates of the
458 serpentine group. The better fits with chrysotile and antigorite T rather than with lizardite and
459 antigorite M would indicate that the stacking of sheets is wavy and the T:O-like blocs are
460 randomly repeated. The chemical composition and the nano-crystallinity of the M-S-H 1.3
461 sample would suggest a structure close to that of antigorite rather than chrysotile which has the
462 almost ideal chemical composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ($\text{Mg}/\text{Si} = 1.5$), causing the fibrous shape (as
463 the octahedral sheet is larger than the tetrahedral sheet).

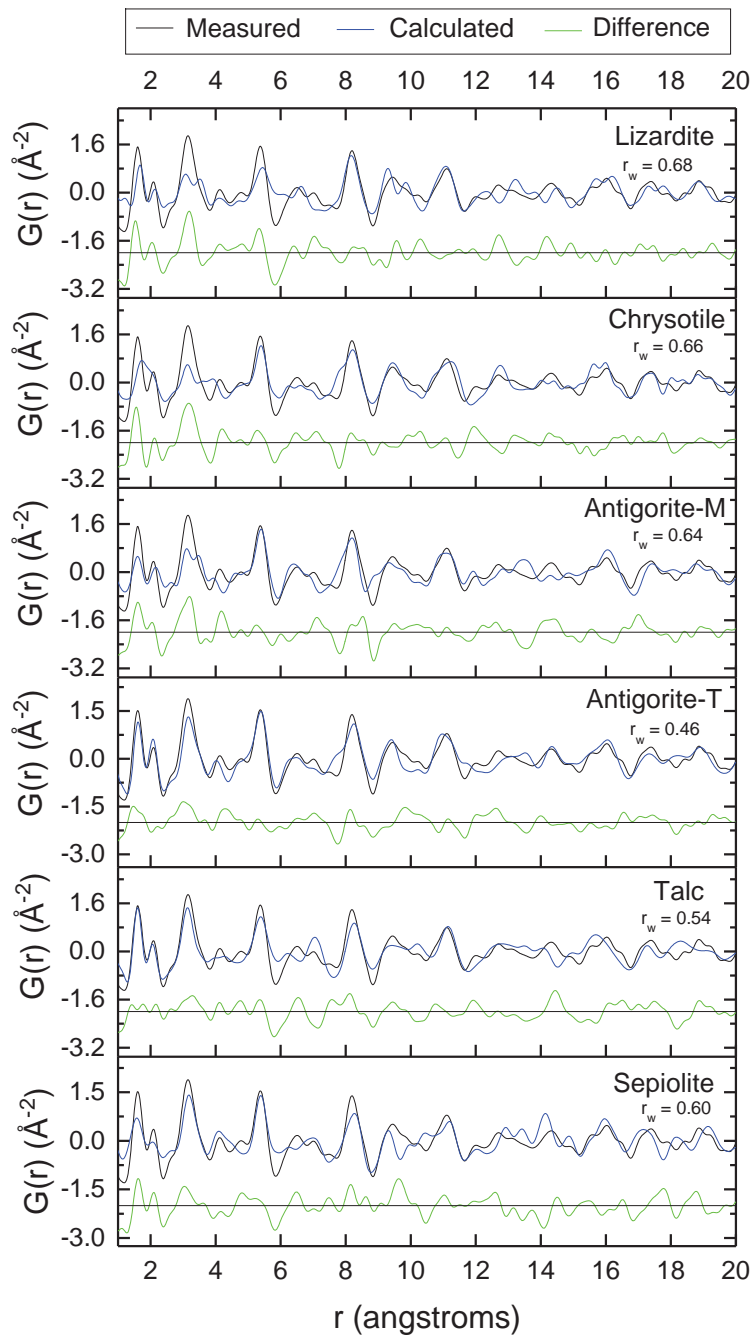
464 Similarly, the X-ray pair distribution function of M-S-H 0.8 was fitted by refining the structures
465 of lizardite, chrysotile, antigorite (monoclinic or triclinic) talc and sepiolite as shown in Figure 8.
466 The best fit was surprisingly achieved with triclinic antigorite Tb, followed by talc and sepiolite.
467 A structure close to that of triclinic antigorite, as for M-S-H 1.3, would be consistent with the fact
468 that these two samples exhibit similar XRD patterns and pair distribution functions. It would also
469 suggest a wavy structure at low Mg/Si ratio. However, the results obtained by other
470 characterization techniques rather indicate a talc-like structure: the Mg/Si ratio of M-S-H 0.8 is
471 close to that of a 2:1 phyllosilicate; M-S-H 0.8 HT and talc exhibit strong resemblance, as shown
472 by X-ray diffraction and ^{29}Si MAS-NMR.

473 Looking more closely at the fit obtained with the refined structure of talc, it can be seen that the
474 quality of the fit decreased for r distances above the coherence length of the M-S-H particles (12
475 Å). Restricting the fit calculations to the 1-12 Å range provided very good results (Figure 9), both
476 with talc and antigorite ($r_w = 0.42$ in both cases). Complementary techniques and/or a better
477 resolution (provided by a high energy synchrotron source) are thus necessary to discriminate
478 between the two structures.



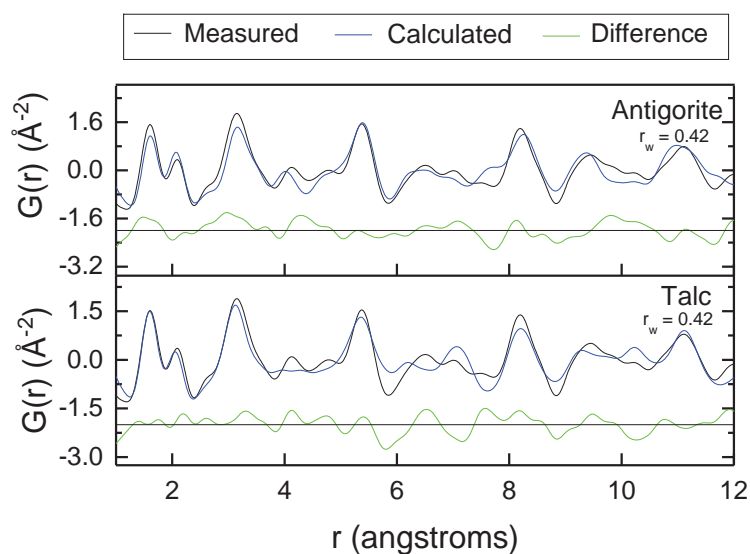
479

480 *Figure 7: Comparison of M-S-H 1.3 X-ray distribution function with those of the refined structures of lizardite,*
 481 *chrysotile, antigorite, talc and sepiolite over the range 1-20 Å (details of the fits in the Appendix).*



482

483 *Figure 8: Comparison of M-S-H 0.8 X-ray distribution function with those of the refined structures of lizardite,*
 484 *chrysotile, antigorite, talc and sepiolite over the range 1-20 Å (details of the fits in the Appendix).*



485

486 *Figure 9: Comparison of M-S-H 0.8 X-ray distribution function with those of the refined structure of triclinic*
 487 *antigorite (Tb) and talc over the range 1-12 Å (details of the fits in the Appendix A).*

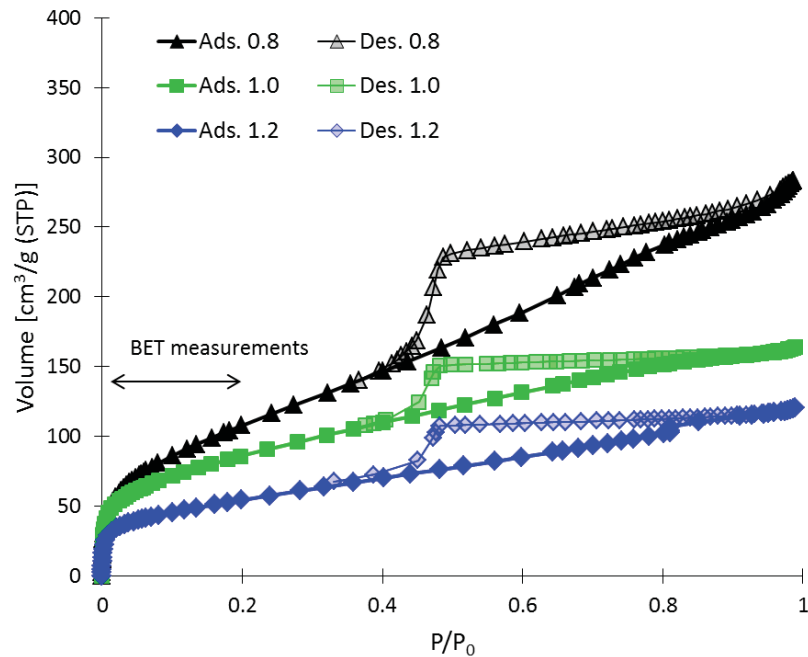
488

489 The X-ray PDF analyses of M-S-H showed similar atoms distances in M-S-H as in phyllosilicate
 490 minerals and thus agree with the ^{29}Si MAS NMR data: M-S-H phases are composed of silicate
 491 sheets with small coherent regions.

492 3.1.3. Particle size, porosity, and density

493 M-S-H samples of 3.3 years were characterized by N_2 physio-sorption measurements. The
 494 isotherms with the presence of hysteresis loops (Figure 10) were of the IV type according to the
 495 IUPAC classification [54]. The initial vertical slope is characteristic of the presence of
 496 microporosity (equivalent diameter between 0.4 nm and 2 nm). The adsorption part of the Type
 497 IV isotherm can be attributed to monolayer-multilayer adsorption. The hysteresis had been
 498 associated to capillary condensation taking place in meso-pores (diameter between 2 nm and 50
 499 nm). The general features of the N_2 -isotherm were similar to those observed for phyllosilicates
 500 synthesized at room temperature such as reported for synthetic clay-like hydrated heterite,
 501 stevensite or saponite [33, 69, 70] or talc [71].

502 The M-S-H samples synthesized at room temperature exhibited an H2 or H4 hysteresis
 503 characteristic of plate-like materials with meso-pores [54]. The H2 hysteresis is characteristic of
 504 less ordered material than H4. The micro-porosity (< 2 nm) in clay usually corresponds to the
 505 interlayer, and the meso-porosity corresponds to meso-pores formed between the particles
 506 (particularly during acid treatment) [72].



507
 508 *Figure 10: N₂ adsorption-desorption isotherms of the M-S-H samples 0.8, 1.0 and 1.2 (synthetized at room*
 509 *temperature during 3.3 years).*

510

511 The specific surface areas (SSA_{BET}) were calculated from the N₂ physio-sorption measurements
 512 by applying the BET equation in the P/P° range 0.05 to 0.2 [52]. An SSA_{BET} of 406, 315 and 194
 513 m²/g, respectively, was calculated for M-S-H 0.8, 1.0 and 1.2 after 3.3 years (Figure 11). The
 514 relatively high measured SSA_{BET} for M-S-H were similar to the large surface area reported for
 515 synthetic clayey materials [33, 69, 70], where macro and mesopores are present together with
 516 micro-pores, while the SSA of talc has been measured to be 20 m²/g [71]. The SSA_{BET} of
 517 synthetic clay has been observed to increase with the water to solid ratio used during the
 518 synthesis [70]. Thus, M-S-H formed in non-diluted systems or in field experiments might exhibit
 519 a smaller SSA.

520 Figure 11 shows the SSA_{BET} as a function of the Mg/Si in M-S-H and at different curing times
 521 and temperatures. The SSA_{BET} decreased with the Mg/Si in M-S-H. The curing temperature, 20
 522 or 50°C, did not influence the SSA_{BET} . The SSA_{BET} was lower for the older samples indicating
 523 the formation of slightly bigger particles with time. The SSA_{BET} for M-S-H 0.8 (~ 400 m²/g) was
 524 2 times higher than for M-S-H 1.2 (~ 200 m²/g).

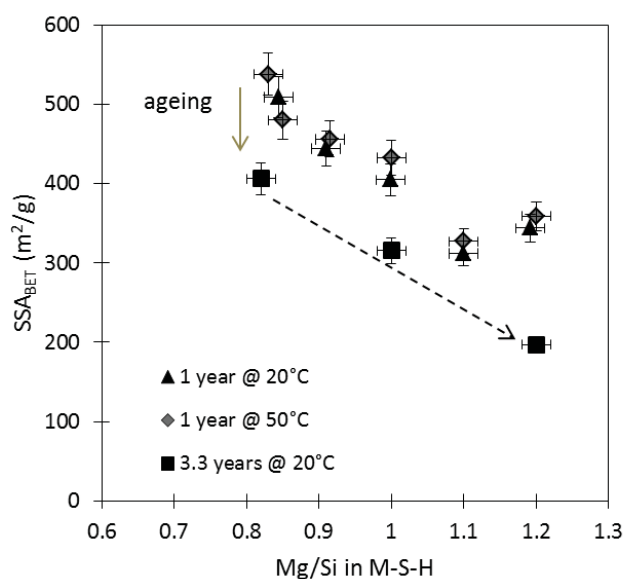


Figure 11: Specific surface area (SSA_{BET}) found in M-S-H as a function of the Mg/Si in M-S-H and of the curing time.

The t-plot method (detailed in section 2.2.4) quantifies the external surface *i.e.*, the surface without the micro/meso-porosity. The external surface variations follow the SSA_{BET} with a decrease with the increase in Mg/Si ratio, but much lower values (*e.g.*, 80 m²/g for the external surface compared to 400 m²/g for the SSA_{BET} for M-S-H 0.8). This denotes a high micro/meso-porosity in these samples as illustrated by the values of the pore volume in Table 3 (up to 0.113 cm³/g for M-S-H 0.8). However, this volume decreased with the increase of the Mg/Si in M-S-H and the reduction of the specific surface area. The grain density of M-S-H measured by helium pycnometry was relatively constant between 2 and 2.1 g/cm³ (Table 3) in M-S-H independently of the Mg/Si.

Table 3: Specific surface area (SSA) for M-S-H equilibrated for 3 years and hydrothermally prepared (HT) calculated by BET and t-plot methods from nitrogen isotherms and grain density (which has been measured on 3 months and 6 months samples).

	BET		t-plot			
	SSA ^a	C value ^b	SSA ^c (external surface)	Vads ^d	Pore volume ^e	Grain density ^f
	m ² /g		m ² /g	cm ³ /g STP	cm ³ /g STP	
0.8	406	46	80	73	0.113	2.1
1.0	315	74	21	68	0.105	2.0
1.2	194	112	17	41	0.063	2.1
0.8HT	378	62				
1.2HT	340	105				

^a Calculated with the BET equation for $0.05 < P/P^0 < 0.2$

^b BET C constant value

^c external surface calculated according to the t-plot method [52]

^d the volume adsorbed in the micro and meso pores

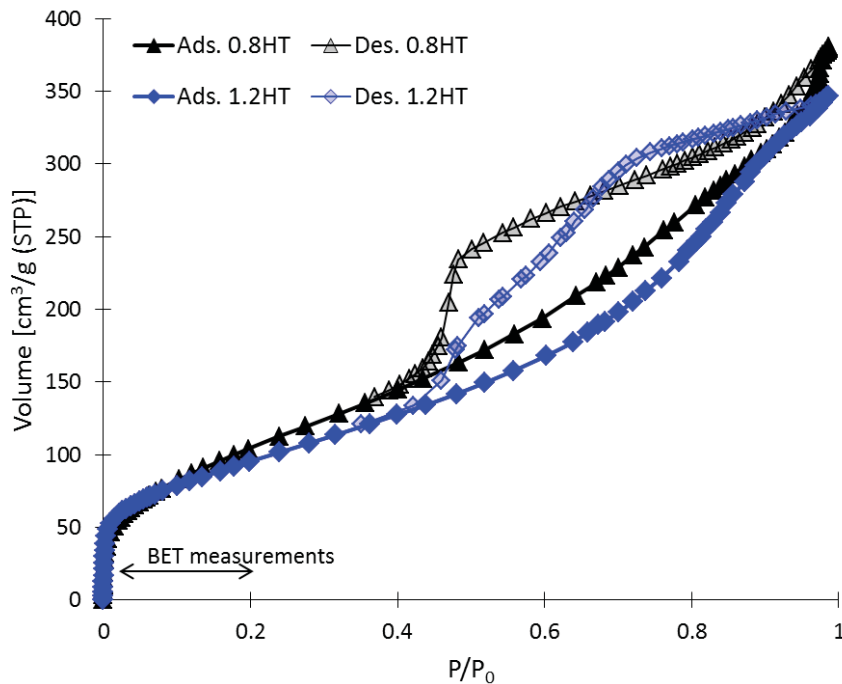
^e $V_{ads}/647$ (gas/liquid volume ratio ~ 647 for N₂ at 77 K)

^f averaged values of the measurements on the samples synthesized 1 year at 20°C and 3 months at 50°C (standard deviation ± 0.05).

548 N₂ physio-sorption measurements on the hydrothermally treated M-S-H indicated also type IV
549 isotherms according to the IUPAC classification, but an H3 hysteresis (Figure 31). The H3
550 hysteresis is related to aggregated materials with plate-like structure creating slit-shaped pores.
551 This confirms a better organization of the structure of the hydrothermal treatment of the M-S-H
552 and indicates the presence of a second porosity, which may be due to different packing. In these
553 two cases, the conditions were not recovered to apply the t-plot method for the calculation of the
554 external surface (probably due to the capillary condensation in macro-porosity).

555 An SSA_{BET} of 378 and 340 m²/g have been measured in the M-S-H 0.8HT and M-S-H 1.2HT
556 respectively. These values are relatively high and in the same range or even greater than the
557 SSA_{BET} measured for M-S-H synthesized at room temperature. The upper surface area and higher
558 volume adsorbed of M-S-H1.2HT compared to M-S-H 1.2 prepared at room temperature from
559 BET might be related to this observed 2nd porosity difference in packing. The M-S-H 0.8
560 equilibrated at room temperature and the hydrothermally prepared HT show a substantial
561 similarity in N₂ sorption (size and volume of the micro-pores) and in ²⁹Si-NMR indicating no or
562 little structural difference except the increased ordering in the sample treated at higher
563 temperature. The different micro porosity and silicate structure defined in the M-S-H 1.2HT
564 compared to M-S-H 1.2 seems to indicate a structural rearrangement during the hydrothermal
565 treatment.

566



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Figure 12: N₂ absorption-desorption isotherms of the hydrothermally treated M-S-H.

569

570 3.2. Water in M-S-H

571 Crystalline phyllosilicates, such as talc, which represents 2:1 structure, and serpentines (1:1
572 structure) are composed of theoretically infinite silicate layers and hydroxyl groups are only
573 linked to the magnesium, the so-called inner OH, and surface OH groups as detailed in Figure 1.

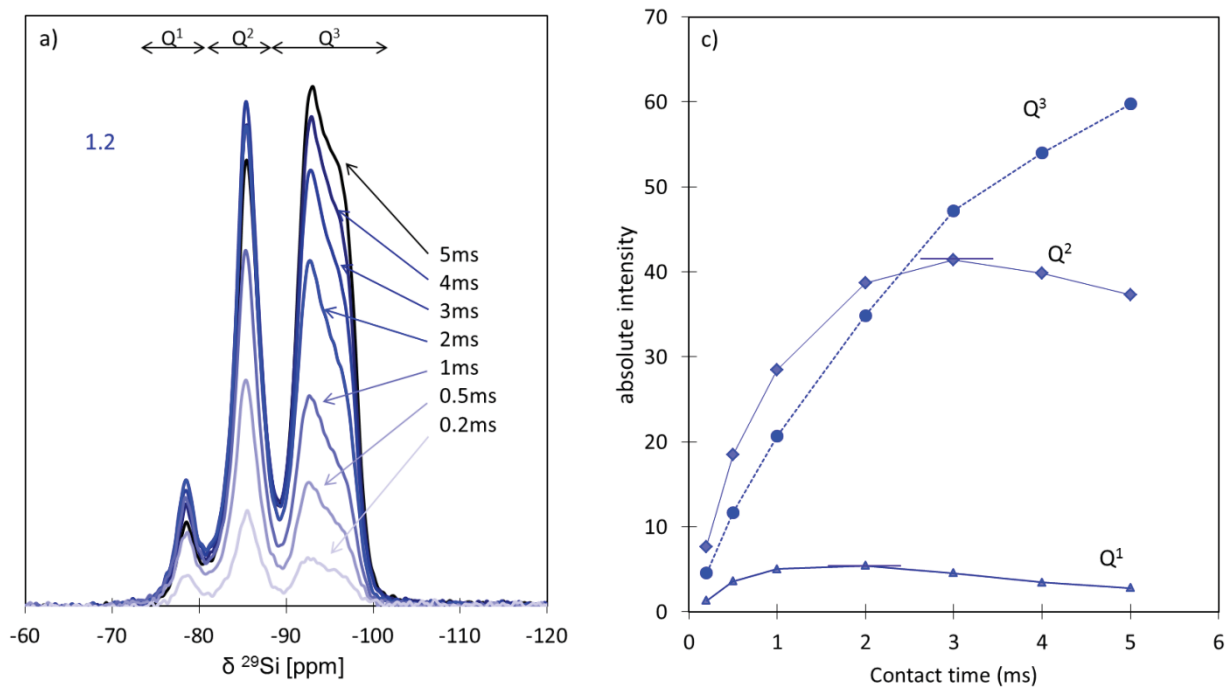
574 Some phyllosilicates such as sepiolite or amphibole also contain zeolitic water and water
 575 coordinated to charge balancing cations, water which is more confined than zeolitic water, while
 576 smectites contain water confined in the interlayer and at the surface. M-S-H contains between 1
 577 and 2.5 H₂O per silicon based on TGA measurements ([15, 16, 22]), thus significantly more
 578 water than talc, antigorite or clay minerals. Water in M-S-H was found to be present both as
 579 adsorbed water and within the structure as H₂O and hydroxyl groups ([15, 18]). In the following,
 580 the distribution of the water in the structure of M-S-H is investigated by different techniques.

581 3.2.1. ¹H-²⁹Si CP MAS-NMR spectroscopy

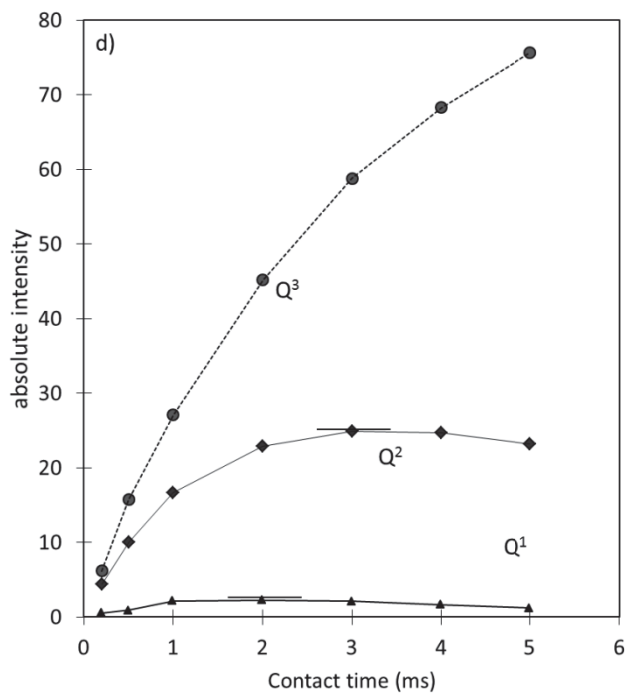
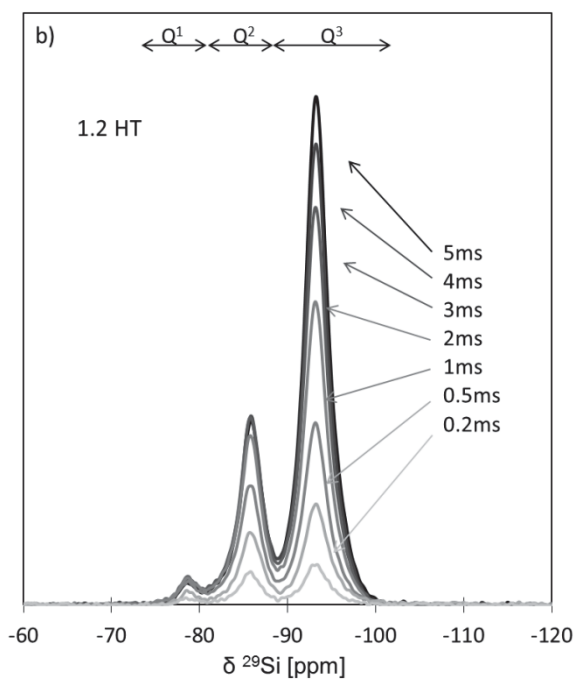
582 The variation of the contact time in ¹H-²⁹Si CP MAS-NMR (cross polarization magic angle
 583 spinning NMR) experiments allows investigating whether protons (from the hydroxide groups or
 584 water) are in the vicinity of silicate sites. The shorter the contact time, the closer a proton is.
 585 Therefore, the water adsorbed on the surface results in higher contact time than hydroxyl groups
 586 directly bound to silicon.

587 The ¹H-²⁹Si CP MAS-NMR spectra of M-S-H synthesized at room temperature, and
 588 hydrothermally prepared M-S-H recorded with varying contact times between 0 and 5 ms and the
 589 associated absolute intensities are shown in Figure 13 and Figure 14. The intensities of Q¹ and Q²
 590 site reached a maximum at a contact time between 2 and 4 ms, which indicated the presence of
 591 protons in the second or third coordination shell. From the geometry, the Q¹ and Q² silicate sites
 592 are present at the surface as Si-OH confirming the hydroxyl groups are linked to the Q¹ and Q²
 593 silicate sites as already observed by Nied et al. [15].

594 The Q³ sites showed a higher contact time of > 5 ms, which indicated that the Q³ silicate sites
 595 were not directly linked to hydroxyl groups but that the protons were in further distant
 596 coordination spheres such as hydroxyl groups bound to magnesium or sorbed water.
 597



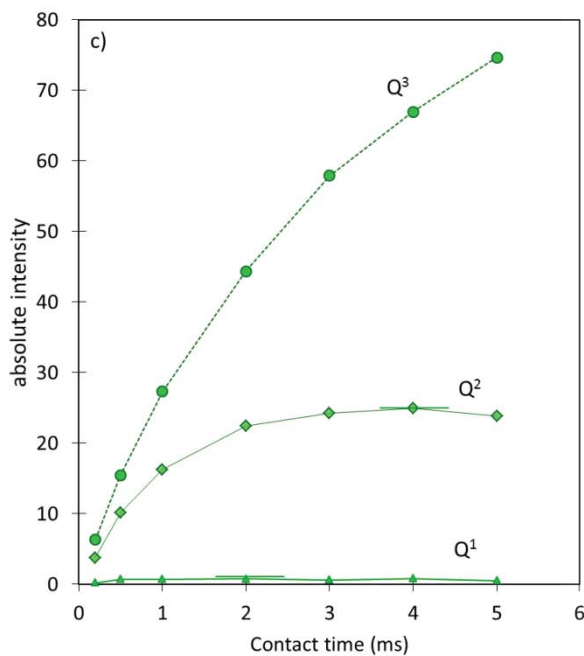
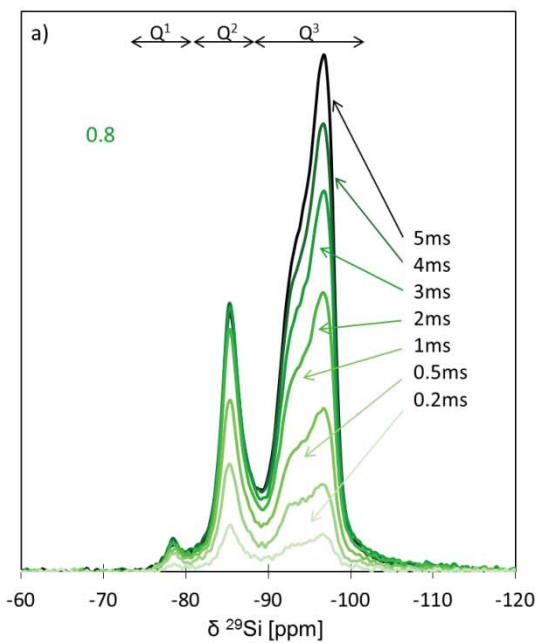
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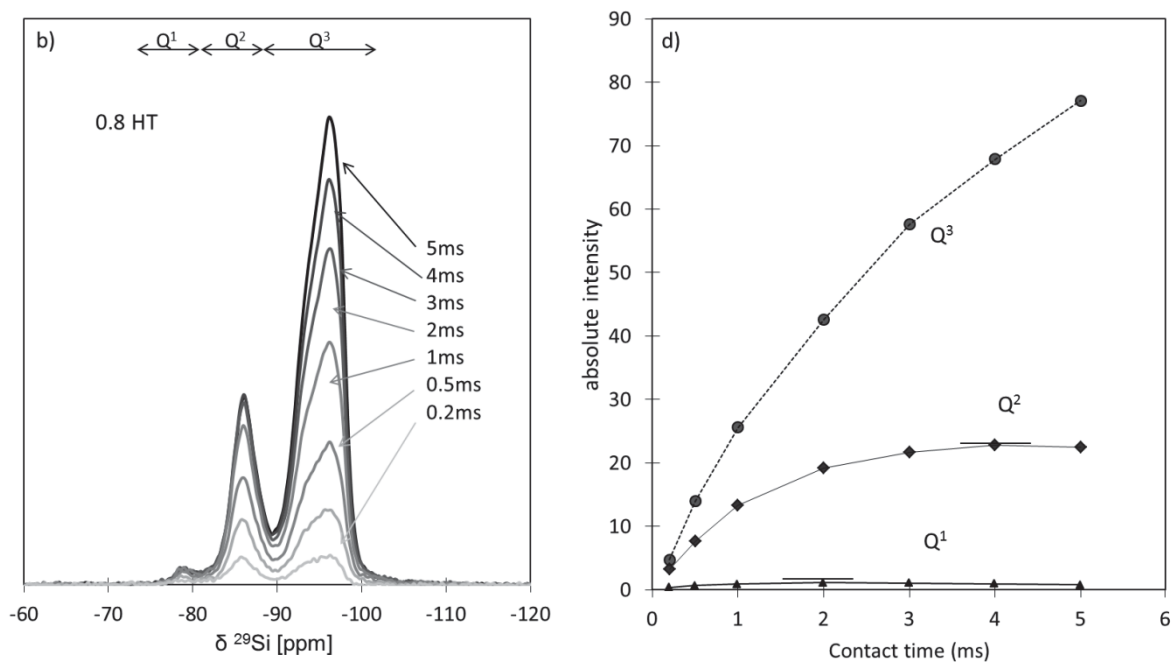
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Figure 13: ^1H - ^{29}Si CP MAS-NMR spectra at different contact time for a) the M-S-H 1.2 sample (3.3 years 20°C), b) the hydrothermally treated M-S-H 1.2 sample c) and d) absolute intensities associated as a function of the different contact times.

603



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605

606 *Figure 14: ^1H - ^{29}Si CP MAS-NMR spectra at different contact time for a) the M-S-H 0.8 sample (3.3 years 20°C),*
 607 *b) the hydrothermally treated M-S-H 0.8 sample c) and d) absolute intensities associated as a function of the*
 608 *different contact times.*

609

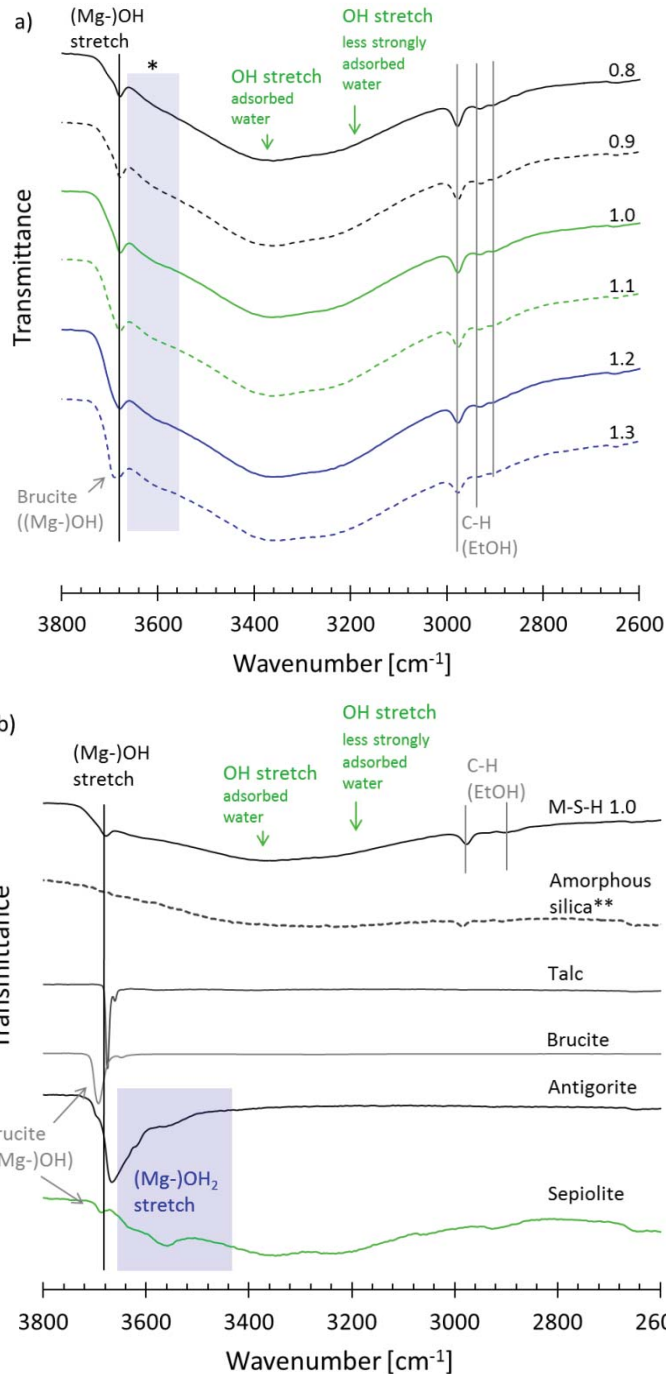
610 3.2.2. Infrared (FTIR) of hydroxyl vibrations

611 The FT-IR spectra recorded between 2600 and 3800 cm^{-1} on M-S-H with varying Mg/Si are
 612 presented in Figure 15a and compared with spectra of 2:1, 1:1 phyllosilicates, amorphous silica,
 613 and brucite in Figure 15b. The M-S-H 1.3 contained some residual brucite (~ 2 mass% of brucite
 614 normalized to 100 g dry mass, quantified by TGA), which can be seen by the presence of the
 615 band at 3698 cm^{-1} [73] and in comparison with the spectra in Figure 15b. The band (shoulder) at
 616 3680 cm^{-1} has been assigned to Mg-OH stretching vibrations in M-S-H [15, 67]. Else, little
 617 difference between the spectra recorded at different Mg/Si could be observed.

618 At lower wavenumbers, an overlapping of large bands corresponding to OH stretching vibrations
 619 of water molecules is found. The first band at ~ 3550-3600 cm^{-1} has been attributed in sepiolite to
 620 water coordinated to magnesium (Mg-OH_2^+), i.e., to water at the edges of the channels [74]; this
 621 kind of water is also observed in antigorite (Figure 15b). The presence of coordinated water is
 622 typical for well-crystalline minerals. Its observation in the poorly ordered M-S-H may be
 623 explained by the presence of very confined water molecules close to the octahedral layer in M-S-
 624 H. Indeed, Lin et al. [67] observed two types of water coordinated to magnesium in an M-S-H-
 625 like phase, the first one is described as adsorbed water on magnesium located at the edge of the
 626 layer (with a water loss at 90°C in TGA) and the second one adsorbed water on magnesium
 627 located in the silicates defects (with a water loss at 140°C). Furthermore, the similarities between
 628 M-S-H and antigorite observed by PDF analysis tend to confirm the presence of coordinated
 629 water in the M-S-H.

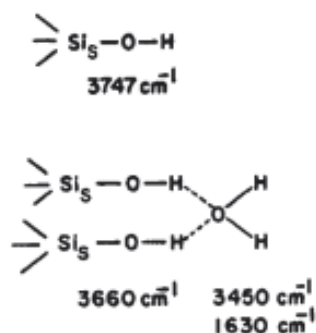
630 Hair [75] reported that OH stretching of dried silanol groups at 3747 cm^{-1} cannot be seen in the
 631 presence of adsorbed water and instead a “wet” silanol groups band is observed at 3660 cm^{-1} and

632 water sorbed on those hydroxyls at 3450 cm^{-1} (see Figure 35). The spectrum of the hydrated
 633 amorphous silica freeze dried and kept at 33% RH showed only the band at 3450 cm^{-1} and
 634 possibly a band at 3660 cm^{-1} (Figure 15b). Finally, the FT-IR spectra showed a trace of ethanol
 635 from the washing process.



636

637
 638 *Figure 15: a) FT-IR spectra of the M-S-H samples (3.3 years, 20°C); b) FT-IR spectra of minerals from [22] (the*
 639 *intensities of the spectra have been modified to fit the figure); both are zoomed between 2600 and 3800 cm⁻¹*
 640 *and the Assignments of the stretching bands according to minerals comparison [73, 76]; *vibrations between*
 641 *3600 and 3700 cm⁻¹ (Si-)OH · · OH₂ stretch [Amorphous silica [75]] or (Mg-)OH₂ stretch [Sepiolite [74] or M-S-*
 642 *H [67]]; **amorphous silica, hydrated, washed and freeze dried and kept at 33% RH.*



643
644 *Figure 16: Re-hydration of silica surface (reproduced from [75]).*

645

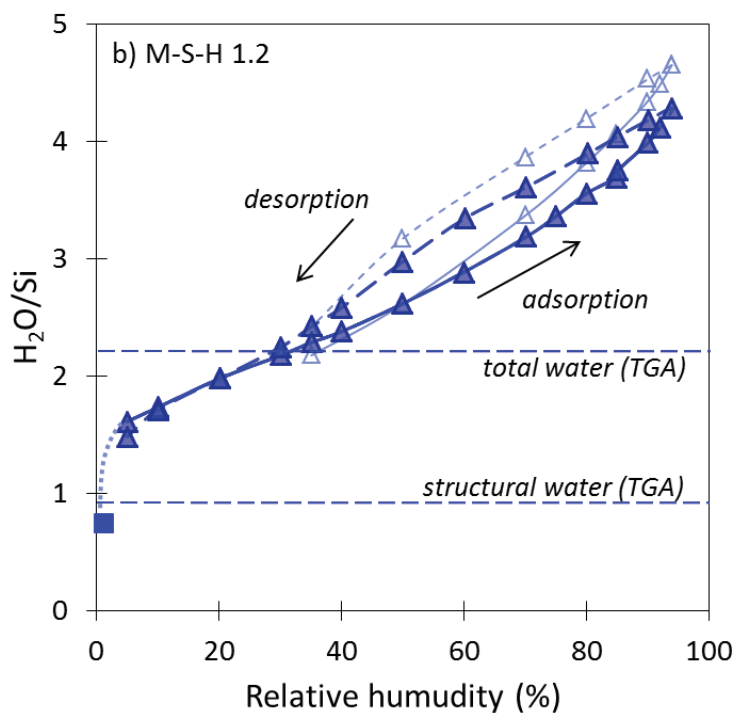
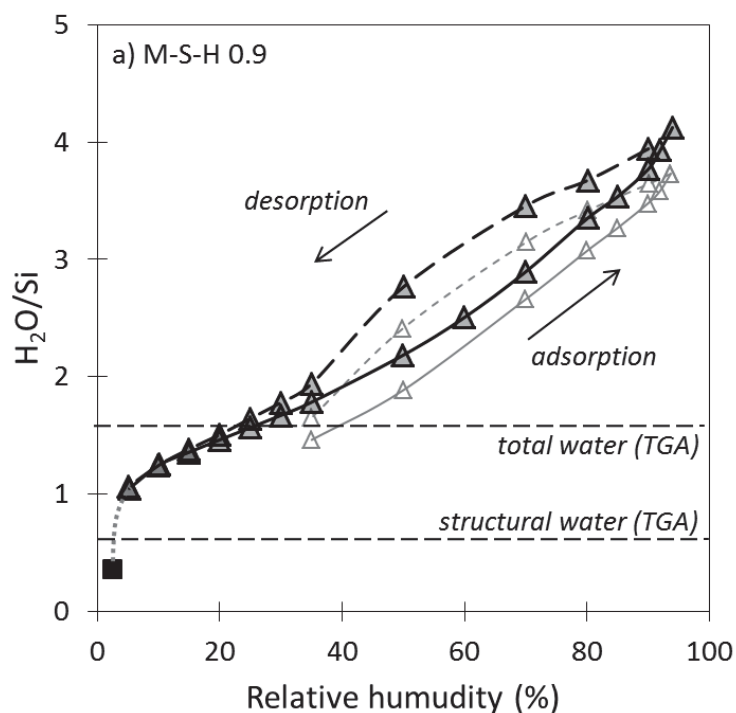
646 The FTIR data indicated that M-S-H phases contain hydroxyl groups bound directly to the silicon
647 and magnesium, but also a significant amount of physically bound and adsorbed water, in
648 agreement with ^1H MAS NMR (40kHz) data from literature [15] and our observations by ^1H - ^{29}Si
649 CP MAS NMR spectroscopy. The presence of coordinated water bound to magnesium might be
650 possible. The dependence of the number of water molecules on the RH is further probed by
651 dynamic vapor sorption (DVS) experiments and the different nature of the physically bound
652 water by ^1H NMR relaxometry measurements coupled to TGA.

653

654 3.2.3. Dynamic vapor sorption (DVS)

655 The results of the DVS measurements for M-S-H 0.9 and M-S-H 1.2 are shown in Figure 17. The
656 sorption curves show a hysteresis, as characteristic of microporous materials such as C-S-H [77]
657 or clay minerals [78] which confirms the presence of the micro-pores observed by the N_2 physio-
658 sorption measurements.

659 Compared to C-S-H, where the content of water is relatively constant between 20 and 70% RH
660 [77], the curve of M-S-H shows a gradual increase from 0 to 90% RH. This gradual increase of
661 water in M-S-H would be consistent with the dependence of the interlayer distances (and hence
662 water absorbed in them) on the RH as observed by XRD and with the behavior of swelling clays
663 such as saponite or montmorillonite [78].



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Figure 17: Water vapor isotherms (adsorption and desorption) of the a) M-S-H 0.9 and b) M-S-H 1.2 (20°C, 2 years: light and empty symbols; 3.3 years: dark symbols). The squares correspond to H_2O/Si in the sample at < 2.5 %RH measured by DVS (structural water), the horizontal dashed lines to the to the H_2O_{tot}/Si total water and to the H_2O_{OH}/Si structural water in M-S-H measured by TGA (see Table 6).

671 The mass at the end of the DVS experiment (drying to 0% RH at 105°C during 1 day) could be
672 expected to correspond to the dry mass of the M-S-H (M-S-H with structural hydroxyl groups,
673 but without hydroxyl groups or adsorbed water at the surface). In fact, the water content

674 quantified by DVS after drying to 0% RH at 105°C was lower than the content of hydroxyl
 675 groups found by TGA and ¹H-NMR relaxometry (as below). This is in agreement with the
 676 observation of weakly bound hydroxyl groups at the surface of the silicate layers, which are
 677 dehydroxylated at low temperatures [79] or coordinated water bound to magnesium [67].

678 3.2.4. Thermogravimetric analysis (TGA)

679 The TGA curves and the derivative weight losses of M-S-H aged at room temperature for 3.3
 680 years with Mg/Si = 0.8 and 1.2, and hydrothermally prepared M-S-H are shown in Figure 18.
 681 Three water loss regions characteristic for M-S-H can be seen.

682 The first water loss region between 30 °C and 250 °C observed for M-S-H synthesized at room
 683 temperature had been related to poorly (physically) bound water adsorbed on the surface
 684 (monolayer, multilayers and and/or in the interlayer) of the M-S-H [15, 18]. This water loss may
 685 also include the bulk water at high RH as TGA cannot distinguish clearly between the different
 686 types of physically bound water and the bulk water. The intensity of these low-temperature losses
 687 depends on the drying and the RH of the samples (Table 4) as also observed for C-S-H [77, 80].
 688 Two samples, M-S-H 0.9 and 1.2, had been freeze dried and re-equilibrated in a desiccator at ~85
 689 %RH for 4 months.

690 *Table 4: Total bound water and hydroxyl content (molar) per silica from TGA in M-S-H equilibrated at 33% RH*
 691 *and 85% RH (250-980°C: OH/Si hydroxyl groups, 30-980°C: H₂O_{total}/Si total bound water).*

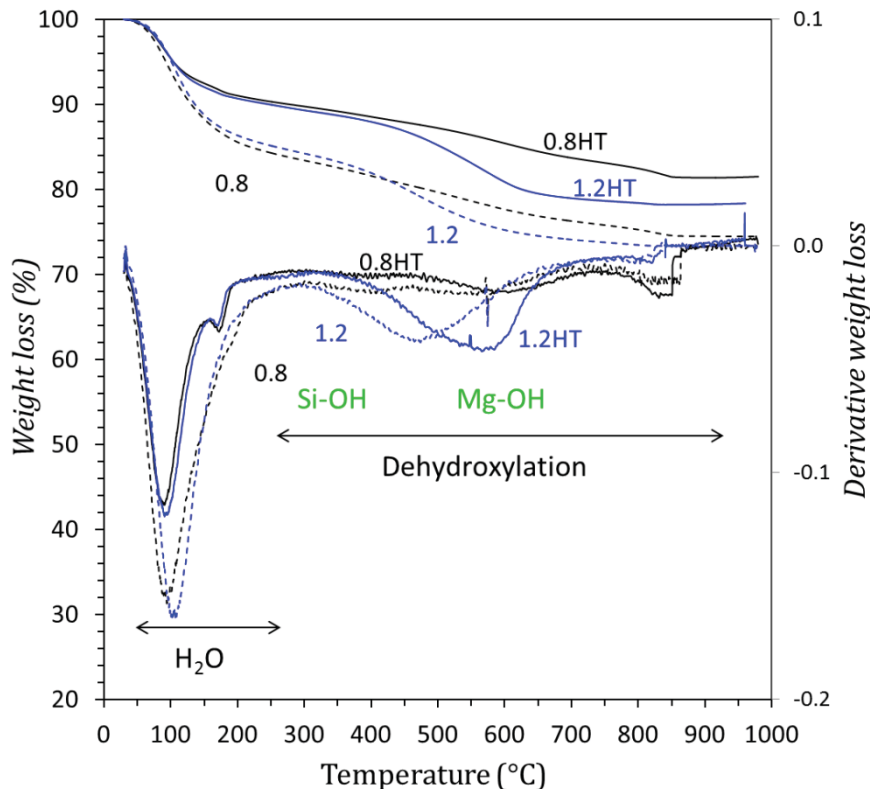
Samples equilibrated at		33% RH				85% RH	
Mg/Si		0.9	1.0	1.1	1.2	0.9	1.2
TGA	H ₂ O _{total} /Si	1.58	1.84	2.01	2.19	2.44	3.12
	OH/Si	1.29	1.52	1.69	1.88	1.31	1.85

692

693 The second and third water losses (>250°C) have been attributed to silanol and/or magnesium
 694 hydroxyl groups in M-S-H [15, 16, 18], but may also comprise water present as a monolayer on
 695 the M-S-H surface [15]. The second water loss in M-S-H 0.8 is centered at 390°C and relates
 696 mainly to the dehydroxylation of silanol (Si-OH) groups [79], while the third weight loss at
 697 500°C is related to the dehydroxylation of magnesium hydroxyl groups (Mg-OH). The M-S-H
 698 1.2 seems to show only one relatively significant water loss centered at 450°C which is due to the
 699 higher content of Mg-OH and the presence of more Si-OH. Zhuravlev [79] reported the
 700 dehydroxylation of bridged hydroxyl groups at the surface of amorphous silica between 180 to
 701 400°C, while the internal hydroxyl groups of the silica condensed only at around 900°C. The
 702 dehydroxylation of the minerals of the serpentine group (hydroxyl groups linked to the
 703 magnesium: inner OH and surface OH as detailed in Figure 1) has been observed by TGA at 670-
 704 900°C [81], while the inner OH groups linked to the magnesium in the talc structure
 705 dehydroxylates at 750-1000°C [34], in agreement with the weight loss observed for M-S-H at
 706 850 to 900°C.

707 The M-S-H synthesized at room temperature contained thus hydroxyl groups bound to silicon and
 708 magnesium, in inner and surface position. The gradual and almost continuous water loss
 709 compared to brucite with a sharp water loss of its hydroxyl groups at 410°C confirms the nano-
 710 crystalline character of M-S-H. Finally, the loss of the hydroxyl bound to magnesium at 450°C
 711 rather than at 700°C indicates less order in the octahedral layers of M-S-H than observed in
 712 serpentine minerals.

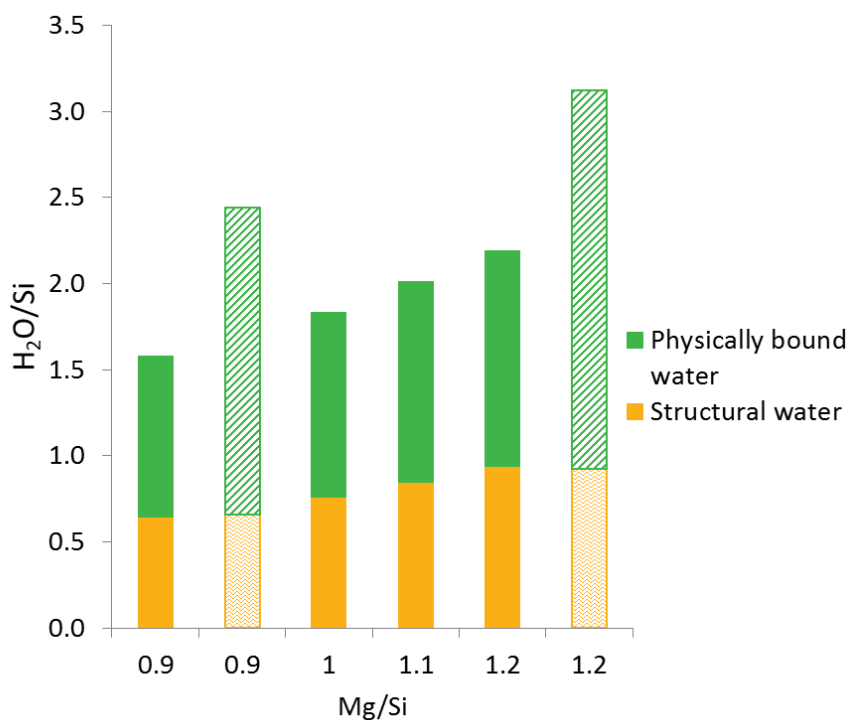
713 The TGA curves of the hydrothermally prepared M-S-H showed the same three water loss
 714 regions. The content of the physically bound water in the hydrothermally treated M-S-H seems
 715 more structured with a shoulder at 160°C. It is unclear whether this shoulder is associated to
 716 strongly physically bound water, i.e., very confined water, or whether this shoulder is already
 717 related to dehydroxylation of silanol groups. This shoulder might also be related to the loss of
 718 coordinated water as described for hydrated magnesium silicate gels [67] or sepiolite. The
 719 overlap of water losses from the dehydroxylation is centered at 550°C for the hydrothermally
 720 prepared M-S-H instead of the 450°C indicating a better structuring.



721
 722 *Figure 18: Thermogravimetric analysis (TGA) of hydrothermally prepared M-S-H samples compared to M-S-H*
 723 *samples with similar Mg/Si.*

724
 725 The repartition between physically bound water (30-250°C) and hydroxyl groups (250-900°C)
 726 quantified by TGA is shown in Figure 19 as H₂O/Si molar ratios. The samples equilibrated at
 727 higher RH showed a comparable amount of hydroxyl groups but much more physically bound
 728 water. Table 4 summarizes the content of the total water and hydroxyl per silicon. The total
 729 bound water and of hydroxyl groups increases with Mg/Si in M-S-H as previously reported [15,
 730 16].

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 732



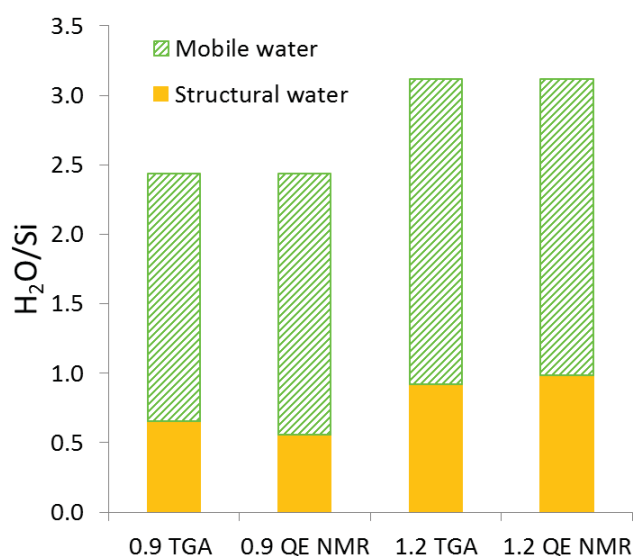
733
 734 *Figure 19: Repartition between water and hydroxyl groups in M-S-H as function of the Mg/Si quantified by*
 735 *TGA, physically bound water (30-250°C) and hydroxyl groups (250-900°C) (samples equilibrated at ~33% RH*
 736 *(plain columns) and ~85% RH (patterned columns)).*

737

738 3.2.5. ¹H NMR relaxometry

739 ¹H NMR relaxometry measurements were performed on the two M-S-H samples Mg/Si=0.9 and
 740 1.2 re-equilibrated at ~85% RH.

741 The fraction of structural water corresponding to hydroxyl groups can be accessed using the QE
 742 pulse sequence. The content of structural water and physically bound water obtained by QE is
 743 compared to the TGA results in Figure 20. The sum of QE (solid+mobile) has been normalized to
 744 the total bound water quantified by TGA. The results were in good agreement and showed that
 745 both QE and TGA could well differentiate the structural water from the physically bound water.



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Figure 20: Comparison of the repartition between water and hydroxyl groups in M-S-H as function of the Mg/Si quantified by TGA, physically bound water (30-250°C) and hydroxyl groups (250-900°C) and the deconvolutions of the QE-NMR recordings (samples equilibrated at 85% RH).

750

751 As shown in Figure 2, different T₂ relaxation times (~0.05 ms, ~0.8 ms, and > 6 ms) were
752 observed which are assigned to: *very confined* water, *confined* water (both physically bound
753 water) and bulk water. The average specific T₂ relaxation times obtained by inverse Laplace
754 transform (ILT) are given in Table 5. The results obtained at 33% RH showed similar first
755 relaxation time (*very confined* water), but a shorter relaxation time for the *confined* water. This
756 result, although prone to the error associated with the overall low signal at low RH, indicates a
757 more *confined* water at lower RH and is consistent with the XRD results where the basal spacing
758 was observed to decrease with the RH.

759 Table 5: Specific T₂ relaxation times obtained by ILT for the M-S-H samples equilibrated at 33 and 85% RH.

M-S-H	Very confined water ms	Confined water	Bulk water
0.9 85% RH	0.056 ±0.036	0.769 ±0.043	12.6 ±2.58
1.2 85% RH	0.049 ±0.015	0.821 ±0.014	6.80 ±3.84
0.9 33% RH	0.072 ±0.017	0.345 ±0.017	3.80 ±21.00
1.2 33% RH	0.048 ±0.034	0.342 ±0.053	2.04 ±1.11

760

± corresponds to the 95% confidence interval.

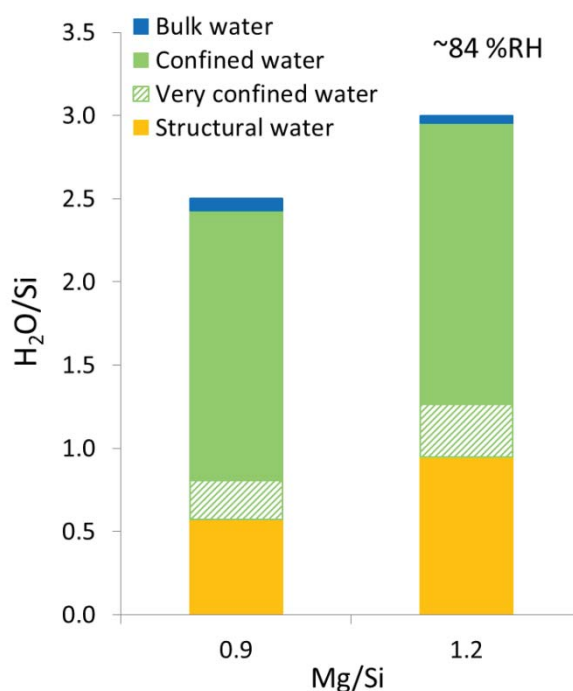
761

762 Figure 21 shows the repartition of water quantified by the QE (structural water) and multi-
763 exponential fitting of the CPMG (physically bound water and bulk water) normalized to the
764 mobile water found by the QE and the total bound water determined by TGA for the samples at
765 85% RH. The calculations gave similar results as the TGA (see Figure 19, patterned columns) for
766 the repartition between physically bound and structural water (hydroxyl groups). However, unlike
767 TGA or QE, CPMG can differentiate between the different populations of water such as *very*

768 *confined* water (probably the strongly adsorbed water), *confined* water and bulk water. The ¹H
 769 NMR relaxometry showed that the content of bulk water is low (<3% of the total water) which is
 770 in fact at the level of the background noise. The content of *confined* water, i.e. the water present
 771 in very fine pores, is about 65 and 56 % of the total water for the 0.9 and 1.2 M-S-H samples,
 772 while the amount of *very confined* water was around 10%. At higher Mg/Si the content of *very*
 773 *confined* water ($T_2 \sim 0.05$ ms) per silica increased (Table 6), however, if the water content is
 774 expressed per magnesium (Appendix B) the content of water remains relatively constant.

775 It should be however noted that due to the short T_2 (at ~ 0.05 ms) of this first peak of the CPMG
 776 assigned to *very confined* water, may not resolve all possible water, or artificially overestimate
 777 the position of the first peak. This is because the first echo was at 0.05 ms and consequently only
 778 part of the decay from the lowest peak could be resolved in the range of echoes of 0.05 -12 ms
 779 applied here.

780 The *very confined* water could include water in the interlayers (internal water) and water strongly
 781 adsorbed on the surface of the particle (external water), possibly also the coordinated water
 782 bound to magnesium as discussed previously. At both Mg/Si ratios investigated, the *very*
 783 *confined* water corresponded to approximately 10% of the signal, indicating the presence of more
 784 *very confined* water per Si at higher Mg/Si ratios.



785

786 *Figure 21: Repartition of the water in M-S-H normalized by the total bound water quantified by TGA as a*
 787 *function of the Mg/Si (structural water from the QE, mobile water from the CPMG).*

788

789 The samples equilibrated at 33%RH showed more of very confined water and less of confined
 790 water than the samples at 85% RH. The increase of the relative humidity of the sample fills the
 791 pore between particle and the first layers of water on the surface (very confined water) are shown

792 as less confined as soon as the pores are full (based on the assumed model of fast exchange of the
793 water molecules between the zone close to the solid surface and bulk of the pore [60].

794 It might be postulated that the slightly increasing *very confined* water content at higher Mg/Si is
795 due to: a) higher strongly adsorbed water content on the surfaces of silicates, b) higher
796 coordinated water content to magnesium i.e., to water coordinated at the edges and/or, c) more
797 *very confined* water in the smaller interlayer space. Indeed, the water of a nano-pore might be
798 described as only *very confined* water where the water of a slightly bigger pore might be
799 described in both *very confined* and *confined* water resulting with a higher content of *very*
800 *confined* water in smaller pores.

801 *Table 6: Total bound water and hydroxyl content (molar) per silica in M-S-H from DVS measurement, from*
802 *TGA and from the ¹H NMR relaxometry. The results are normalized to the total bound water quantified by TGA*
803 *(errors in TGA ± 12%; DVS ± 10 %; ¹H NMR ± 17%).*

samples equilibrated at		0.9			1	1.1	1.2		
		33%	85%	94%	33%	33%	33%	85%	94%
DVS	H ₂ O/Si (ads)	1.78	3.53 ^a	4.12			2.28	3.75 ^a	4.28
	H ₂ O/Si (des)	1.94	3.67 ^a				2.42	4.04 ^a	
	OH/Si (structural) ^b	0.72					1.48		
TGA	H ₂ O/Si	1.58	2.44		1.84	2.01	2.19	3.12	
	OH/Si (structural) ^c	1.29	1.31		1.52	1.69	1.88	1.85	
H NMR	bulk water/Si	0.07 ^d	0.07				0.06 ^d	0.05	
	confined water/Si	0.54 ^d	1.58				0.56 ^d	1.75	
	very confined water/Si	0.50 ^d	0.23				0.69 ^d	0.33	
	OH/Si (structural)	0.93 ^d	1.12				1.77 ^d	1.97	
CEC	Mg ²⁺ /Si	0.022			0.025	0.028	0.030		

804 ^a From the DVS measurements of the M-S-H equilibrated at 33% RH; ^b two times the H₂O/Si quantified in the
805 sample at <2.5 RH%; ^c structural water plus possibly strongly adsorbed water; ^d the results have been re-
806 normalized considering the signal due to bulk water with very large relaxation time (> 2 ms) as noise.
807
808

809 3.2.6. Discussion

810 The DVS measurements indicated that the amount of total water in M-S-H increased clearly with
811 the RH and fill the microporosity of the particles. TGA and DVS indicated the presence of more
812 physically bound water at higher RH. This physically bound was resolved by ¹H-NMR
813 relaxometry as *confined* water present in the micro-pores even at 85% RH, while hardly any bulk
814 water was found at this RH. DVS, TGA and ¹H-NMR relaxometry measurements indicated a
815 relatively similar amount of physically bound water per magnesium in M-S-H independent of
816 Mg/Si, which translated into a higher H₂O/Si at higher Mg/Si in M-S-H (Table 6).

817 A significant amount of hydroxyl groups (structural water) is also present in M-S-H, and the
818 number of hydroxyl groups quantified by DVS, TGA and ¹H-NMR relaxometry increased with
819 the Mg/Si in M-S-H (Table 6 and Appendix B). ¹H-NMR relaxometry data indicated that the
820 amount of OH/Si nearly duplicated from Mg/Si = 0.8 to 1.2 (Table 6), while the difference in the
821 amount quantified by TGA was less distinct, due to the substantial overlap of the different
822 signals. Also, the ²⁹Si MAS NMR data indicated the presence of more Q¹ and Q² silicates which
823 exhibit Si-OH groups (predominantly protonated, details in section 3.3) at higher Mg/Si (Table

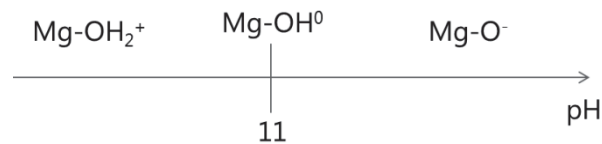
824 6). As also the content of hydroxyl groups per magnesium increased with the Mg/Si (Appendix
825 B), not only more hydroxyl groups are bound to the silicate at high Mg/Si but also more Mg-OH
826 groups are present.

827

828 3.3. Surface properties

829 Swelling phyllosilicates such as montmorillonite or saponite exhibit a negatively charged surface
830 due to the partial replacement of silicate by aluminate in the tetrahedral silicate layers. Cations
831 are present in the interlayers and/or external surface to compensate these negative charges. The
832 basal spacing depends on the nature of the counterion and its wettability.

833 Amorphous silica shows a negative zeta potential at pH values from 3 to 10 [82], due to the
834 deprotonation of surface silanol groups, while brucite exhibits positive zeta potential of
835 approximately 20 mV in the pH range 3-10 [82]. Pokrovsky and Schott [83] found, by studying
836 zeta potential of brucite as a function of the pH, a PZC (point of zero surface charge) of around
837 11, confirming that below this value, brucite has a positive effective surface charge (Figure 22).



838

839 *Figure 22: Schematic brucite surface charge in function of the pH (adapted from [83]).*

840

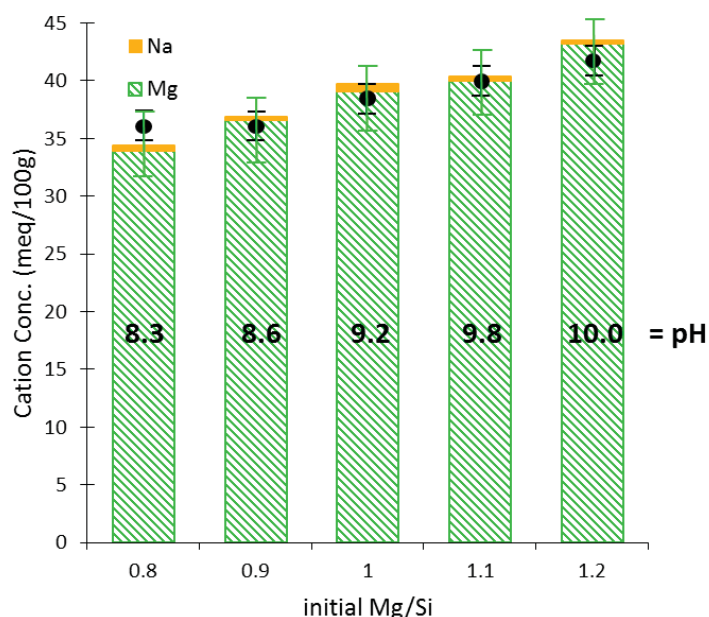
841 Antigorite exhibits an intermediate only slightly negative zeta potential, indicating a contribution
842 of both the positive magnesia-hydroxyl octahedral layers and the negative silica tetrahedral layers
843 [82]. In contrast, chrysotile with a comparable chemical composition exhibits a positive zeta
844 potential as its needle like structure exposes magnesium hydroxide on the exterior surface [82,
845 84].

846 3.3.1. CEC

847 The cation exchange capacity (CEC) is a measure of the amount of exchangeable cations present
848 either at the surface (in the Stern and diffuse layer) or interlayer of the solid particle. The CEC
849 quantifies the cations filtrated with the solid which charge-balance the surface charge of the solid
850 and corresponds thus to the surface charge density.

851 A positive CEC has been measured for M-S-H, as shown in Figure 23, which indicates the
852 presence of exchangeable cations in its structure and thus a negative surface charge of M-S-H as
853 in phyllosilicates. The measured CEC increased from ~ 35 meq/100g at pH from 8.3 (Mg/Si =
854 0.8) to ~ 40 meq/100g at pH 10 and Mg/Si = 1.2. This observation confirmed the presence of
855 hydroxyl surface groups like in amorphous silica and brucite that experience deprotonation upon
856 pH increase. As CEC measures the overall amount of exchangeable cations, it is well possible
857 that in addition to the negatively charged SiO^- also some Mg-OH_2^+ surface sites were present,
858 although less than the negatively charged silanol groups.

859 The kind and amount of cations present on the CEC sites were also measured; mainly magnesium
 860 was present plus 1 to 2 % sodium, which was present as an impurity in the starting materials. The
 861 presence of only 1 to 2% of Na⁺ on the CEC sites, although similar magnesium and sodium
 862 concentrations in solution were measured (Table 1), showed that the sorption of the bivalent
 863 Mg²⁺ is favored compared to the monovalent Na⁺, which is commonly observed on silica (see e.g.
 864 [85-87]). The CEC measured by the total of the cations released by the cobalt(III) replacement
 865 agreed well with the total CEC measured by colorimetry, indicating that the M-S-H phases did
 866 not dissolve significantly.



867 *Figure 23: Cation exchange capacity (CEC) measured by colorimetry (black circles) and concentrations of*
 868 *cations sorbed on M-S-H samples (2 years- at 20°C) measured by cobalt hexamine method as a function of the*
 869 *initial Mg/Si.*
 870

871 The amount of magnesium at the cation exchange sites was related to the total amount of
 872 magnesium present in Table 6. Only 2 to 3% of the total magnesium was present on the cation
 873 exchange sites of M-S-H.

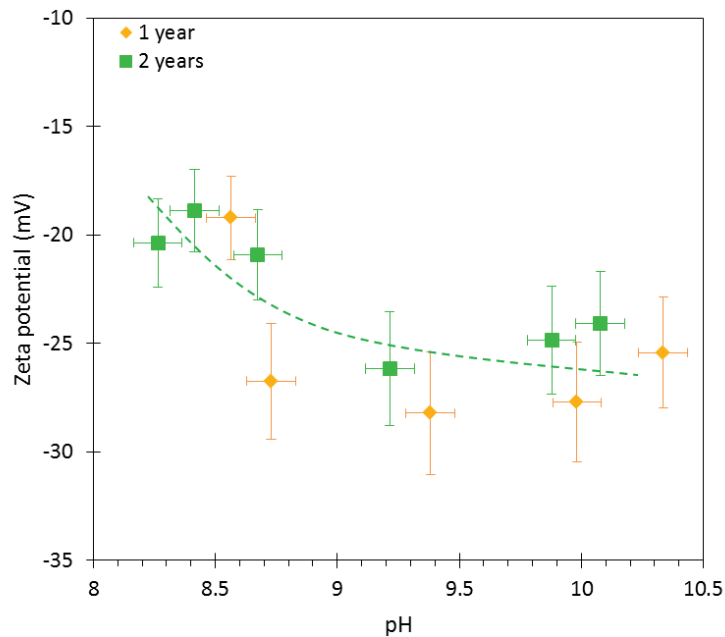
874 The total of exchangeable cations in M-S-H was higher than the CEC of sepiolite (~ 10
 875 meq/100g) [88] but lower than the CEC of e.g. saponite (~ 70-150 meq/100g) (e.g., [89, 90]),
 876 where Al and Fe replace a fraction of Mg and Si in the structure.

877

878 3.3.2. Zeta potential

879 The zeta potential measures the charge of a particle not directly at the surface but in some
 880 distance, such that (cat)ions near the surface in the Stern and even some in the diffuse layer,
 881 appear as part of the solid [61, 84, 91]. Thus the presence of more magnesium in the cation
 882 exchange sites of M-S-H can result in less negative zeta potential measurements. The zeta
 883 potential measurements on M-S-H particles, as shown in Figure 24, indicate a decrease from -19
 884 mV at pH 8.6 to -28 mV at pH 10.2. The zeta potential of hydrated amorphous silica was ~ -43
 885 mV at pH of 6.5 which corresponds well with literature data [82], while the zeta potential of
 886 brucite was positive ~ 2 mV at pH = 10.5 and is expected to be higher at lower pH values [83].

887 The negative effective charge of M-S-H confirms that the Si-OH groups on the Q¹ and Q²
 888 silicates are at least partially deprotonated: Si-O⁻ and that the low cation concentrations in
 889 solution did not fully balance these negative charges, i.e. not all the charge balancing cations are
 890 in the Stern layer but at least a part in the diffuse layer. The decrease in zeta potential from pH 8 to
 891 9 is probably related to the progressive deprotonation of silanol groups as the pH increases and
 892 magnesium concentrations decreases. The trend, more negative values at higher pH values and
 893 thus at higher Mg/Si agree well with the CEC measurements.



894
 895 *Figure 24: Zeta potential of M-S-H with Mg/Si=0.8-1.2 as a function of pH, M-S-H particles aged of 1 and 2*
 896 *years at 20°C, the line is only guide to eye.*

897 3.3.3. Effect of filtration on measured pH values

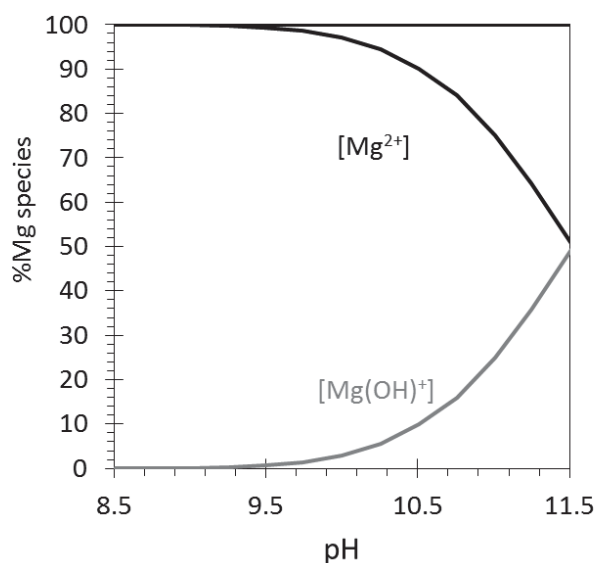
898 The presence of charged particle surfaces also affected the pH measurements; the pH of the
 899 filtrated liquid was systematically lower than the pH measured in the corresponding suspension
 900 as detailed in Table 7. The decrease of pH due to the filtration indicated that not only Mg²⁺ but
 901 also OH⁻, probably as MgOH⁺, was associated with the surface of M-S-H. In fact, in the pH range
 902 8-10, the fraction of MgOH⁺ becomes more important as the pH increases (Figure 25). The OH⁻
 903 /Si filtrated with the solid shown in Table 7 was calculated from the pH differences between the
 904 suspension and the corresponding filtrated supernatant. It indicates that the content of MgOH⁺
 905 counter-ions is very low (0.01 to 2% at pH 9.9) compared to the amount of Mg²⁺ found on the
 906 cation exchange sites (Table 6), which is in agreement with the fractions of MgOH⁺ and Mg²⁺ in
 907 the solution shown in Figure 25.

908 *Table 7: pH measured in the M-S-H samples after 3.3 years at 20°C.*

initial Mg/Si	pH measured in suspension	pH measured in filtrated solution	[OH ⁻] filtrated with the solid (mmol/l)	OH filtrated with the solid / Si*
0.7	8.3	8.0	0.0007	0.000003
0.8	8.3	7.9	0.0008	0.000003
0.9	8.5	8.2	0.0011	0.000005
1.0	9.1	8.8	0.0043	0.00002
1.1	9.7	9.1	0.0255	0.00012
1.2	9.9	9.6	0.0269	0.00013
1.3	10.3	10.0	0.0675	0.00034

909

* Mg on CEC: 0.02 to 0.03 Mg/Si (Table 6).



910

911 *Figure 25: Magnesium speciation ($Mg_{tot} = 100 \text{ mol/l}$) in solution at 20°C as a function of the pH.*

912

913

3.3.4. Discussion

914 The CEC measurements indicated the presence of exchangeable cations (mainly Mg^{2+}) at the
 915 surface of M-S-H. Its amount increased while the zeta potential decreased, when the pH raised,
 916 indicating an increase of the negative surface charge density of M-S-H with pH due to the
 917 deprotonation of the silanol groups of M-S-H.

918 The comparison of the CEC of 0.04 to 0.06 meq/Si (0.02 - 0.03 Mg_{exch}/Si) with the fraction of
 919 silanol groups of 0.3 to 0.6 per Si, indicated that only approximately 10% of the silanol groups
 920 were deprotonated in the pH range studied.

921 The zeta potentials measured in the M-S-H suspension were negative but decreased only
 922 moderately at higher pH values in contrast to the CEC measurements, in agreement with the
 923 presence of more Mg^{2+} at the surface at higher pH values. The presence of more magnesium on
 924 the cation exchange sites of M-S-H could also explain why the amount of *very confined* water
 925 quantified by ^1H NMR relaxometry increases with the Mg/Si, as Mg^{2+} in water is surrounded by
 926 6 to 18 water molecules $Mg[H_2O]_6^{2+}[H_2O]_{12}$ [92], such the amount of water should increase
 927 strongly with the amount of Mg^{2+} on the cation exchange sites. In addition, also the silanol
 928 groups are associated with additional water as observed by FTIR and ^1H - ^{29}Si CP MAS-NMR
 929 measurements. Thus the increase of the fraction of silanol groups (as observed by ^{29}Si MAS
 930 NMR spectroscopy) at high Mg/Si contributes also to the presence of more adsorbed water.

931

932

3. Conclusions

933 X-ray diffraction, X-ray pair distribution function results, and N_2 physio-sorption data confirmed
 934 that M-S-H phases were poorly ordered and nanosized phyllosilicates as already suggested in

935 [16]. The presence of 30% to 55% Q¹ and Q² sites at low and high Mg/Si, respectively, as
936 observed by ²⁹Si NMR, indicates a high fraction of silanol (Si-OH) groups present at edges sites
937 or defects in the silicates layers. Hydrothermal treatment resulted in M-S-H with a slightly better
938 ordered structure, as observed by ²⁹Si MAS NMR spectroscopy, X-ray diffraction data and TGA.
939 In all cases, M-S-H showed a small coherence length of about 1.2 nm, as measured by X-ray PDF
940 analyses, and a relatively high specific surface area of 300 to 500 m²/g and micro- and nano-
941 porosity similar to poorly ordered synthetic phyllosilicates.

942 The samples were observed to swell slightly in the presence of ethylene glycol and the water
943 content was highly dependent on the RH. ¹H NMR relaxometry performed on the samples
944 conditioned at 85%RH, combined with TGA measurement, showed that hardly any bulk water
945 was present, while large part of physically bound water was present in micro-pores. Also the
946 amounts of more confined water (either present at the surface or as water associated with Mg²⁺
947 cations) and hydroxyl groups were observed increasing at higher Mg/Si. This higher content of
948 hydroxyl groups at high Mg/Si was related to the higher content of magnesium and thus of Mg-
949 OH groups and to the increase of the density of silanol groups at higher Mg/Si.

950 M-S-H exhibited a negative surface charge indicating a partial deprotonation of the silanol
951 groups. The small negative surface charge also leads to the presence of a low amount of
952 magnesium on cation exchange sites (equal to 0.02 - 0.03 Mg/Si) compensating the negative
953 charge similar as has been observed for phyllosilicates. The negative surface of the M-S-H
954 particle might explain the weak cohesion and small particle size observed.

955 The different experimental techniques applied to characterize M-S-H showed a poorly order
956 structure related to phyllosilicate with a negative surface charge, exchangeable cations and both
957 structural and bound water types. The ill-defined and nano-sized structure of M-S-H with its large
958 number of silanol sites resulted in the presence of exchangeable cations. The strong resemblance
959 of M-S-H to hydrated 2:1 / 1:1 phyllosilicates could also indicate that an aluminum uptake in the
960 octahedral and tetrahedral layers of M-S-H could be possible similar to phyllosilicates. Further
961 investigations have been carried out to investigate the possible incorporation of aluminum in the
962 structure.

963 4. Acknowledgments

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965 Andreas Jenni for providing reference samples, Karen Scrivener for giving access to measuring
966 setups, and François Avet and Zhangli Hu, for help with the experiments. The solid state NMR
967 hardware was partially granted by the Swiss National Science Foundation (SNSF, grant no.
968 206021_150638/1).

969 5. Appendix

970 *Appendix A: Details of the X-ray PDF analysis fitting.*

971 ● *Minerals used:*

972 **Sepiolite fiche CIF:** 9014723

973 Formula : H₁₂ Mg_{3.592} O₂₂ Si₆

974 Calculated formula: Mg_{14.368} O₆₈ Si₂₄ W_{a20}

975 Groupe d'espace : P n c n

976 α=β=γ= 90° ; a=13.3067 Å ; b=26.9720 Å ; c=5.2664 Å

977 *Sanchez, M. , Garcia-Romero E. , Suarez, M. , Silva, I. , Fuentes-Montero L. , Martinez-Criado G. , Variability in*
978 *sepiolite: Diffraction studies Note: Sample BAT25 Note: T = 25 C, Journal of American Mineralogist, Vol. 96, pp.*
979 *1443 – 1454, (2011)*
980 **Talc fiche CIF:** 1011152
981 Formule : H₂ Mg₃ O₁₂ Si₄
982 Groupe d'espace : C 1 2/c 1
983 a=5.26 ; b=9.1 ; c=18.81 ; α=γ=90° ; β=100.08°
984 *Gruner, J. W. , The crystal structures of talc and pyrophyllite, Zeitschrift fuer Kristallographie, Kristallgeometrie,*
985 *Kristallphysik, Kristallchemie (-144,1977), Vol. 88, pp. 412-419, (1934)*
986 **Antigorite-Tb (n = 17) fiche CIF:** 19084
987 Formule : Mg₄₈ O₁₄₇ Si₃₄
988 Groupe d'espace : triclinique P 1 1
989 Dodony I, Posfai M, Buseck P R, Revised structure models for antigorite: An HRTEM study, American Mineralogist
990 87 (2002) 1443-1457
991 a=43.5 angstroms ; b=9.23 angstroms; c=7.27 angstroms; α= 90 ; β = 92°; γ=90°
992 **Antigorite-M fiche CIF:** 9014625
993 Formule : Mg₃₉ O₁₂₀ Si₂₈
994 Groupe d'espace : monoclinique P 1 m 1
995 a=35.02 ; b=9.23 ; c=7.27 ; α= β=γ=90°
996 Dodony, I.; Posfai, M.; Buseck, P. R., Revised structure models for antigorite: An HRTEM study Note: n = 14,
997 Journal of American Mineralogist, Vol. 87, pp. 1443 – 1457, (2002)
998 **Chrysotile fiche CIF:** 1010960
999 Formule : H₈ Mg₆ O₁₈ Si₄
1000 Groupe d'espace : C 1 2/m 1
1001 a=14.66; b=18.5 ; c=5.33 ; α=γ=90° β=93.27°
1002 Warren, B.E. ; Bragg, W.L., The crystal structure of chrysotile H₄ Mg₃ Si₂ O₉, Zeitschrift fuer Kristallographie,
1003 Kristallgeometrie, Kristallphysik, Kristallchemie (-144,1977), Vol. 76, pp. 201-210, (1931)
1004 **Lizardite fiche CIF:** 0005585
1005 Formule : Mg₃ Si₂ H₄ O₉
1006 Groupe d'espace : P 3 1 m
1007 a=b=5.332 ; c=7.332 ; α=β=90° ; γ=120°
1008 *Guggenheim S. and Zhan W. , Effect of temperature on the structures of lizardite-1T and lizardite-2H1, The*
1009 *Canadian Mineralogist, Vol. 36, pp. 1587-1594, (1998)*
1010

1011 ● **Fits:**

1012 For every fit, the Qdamp was set to 0.05 and Qmax was kept at 17, the fit range is detailed below.
1013

CIF file	Paramètre	Initial	1.3 (1-20 Å)	0.8 (1-20 Å)	0.8 (1-12 Å)
			<i>Figure 7</i> Ajusté	<i>Figure 8</i> Ajusté	<i>Figure 9</i> Ajusté
sepiolite	Scale factor	1	0.739	0.61	
	Delta1	0	1.128	0	
	a	13.4	13.125	13.038	
	b	26.8	27.281	27.065	
	c	5.28	5.415	5.418	
	α	90	90	90	
	β	90	90	90	
	γ	90	90	90	
	adp Mg	0	0.00549	0.0077	
	adp Si	0	0.0281	0.012	
	adp O	0	0.0356	0.0188	
	r _w			0.61	0.60

Talc	Scale factor	1	0.685	0.609	0.797
	Delta1	0	1.428	1.497	1.431
	a	5.26	5.39	5.352	5.356
	b	9.1	9.357	9.34	9.24
	c	18.81	18.019	18.266	18.39
	α	90	90	90	90
	β	100	100	100	100
	γ	90	90	90	90
	adp Mg		0.00931	0.018	0.0162
	adp Si		0.0619	0.045	0.0606
	adp O		0.0605	0.057	0.0564
	r_w		0.59	0.55	0.42
Antigorite Tb	Scale factor	1	0.849	0.793	0.865
	Delta1	0	1.047	1.141	1.058
	a	43.5	43.437	43.422	43.442
	b	9.23	9.455	9.401	9.395
	c	7.27	7.154	7.077	7.028
	α	90	90	90	90
	β	92	92	92	92
	γ	84.75	84.75	84.75	84.75
	adp Mg		0.0197	0.0312	0.0312
	adp Si		0.0144	0.00701	0.0081
	adp O		0.0244	0.0288	0.0269
	r_w		0.46	0.46	0.42
Antigorite M	Scale factor	1	0.769	0.546	
	Delta1	0	1.237	0	
	a	35.02	34.202	34.709	
	b	9.23	9.458	9.32	
	c	7.27	7.186	7.335	
	α	90	90	90	
	β	90	90	90	
	γ	90	90	90	
	adp Mg		0.0106	0.0274	
	adp Si		0.0352	0.0113	
	adp O		0.0441	0.0072	
	r_w		0.61	0.64	
Chrysotile	Scale factor	1	0.687	0.475	
	Delta1	0	1.535	0	
	a	5.34	5.339	5.468	
	b	9.241	9.497	9.196	
	c	14.689	15.067	14.823	
	α	90	90	90	
	β	93.66	93.66	93.66	
	γ	90	90	90	
	adp Mg		0.0049	0.025	
	adp Si		0.0355	0.0032	

	adp O		0.0915	0.0156
	r_w		0.56	0.66
Lizardite	Scale factor	1	0.123	0.128
	Delta1	0	0.639	1.379
	a	5.332	5.475	5.462
	b	5.332	5.281	5.232
	c	7.23	7.666	7.621
	α	90	90	90
	β	90	90	90
	γ	90	90	90
	adp Si		0.0103	0.0079
	adp Mg		0.00761	0.0196
	adp O		0.0175	0.0195
	adp H		0.000329	0.00033
	r_w		0.69	0.68

1014

1015 *Appendix B: Total bound water and hydroxyl content (molar) per magnesium in M-S-H from DVS*
1016 *measurement, from TGA and from the ^1H NMR relaxometry. The results are normalized to the total bound*
1017 *water quantified by TGA (errors in TGA $\pm 13\%$; DVS $\pm 11\%$; ^1H NMR $\pm 19\%$) (calculated from (Table 6)).*

		0.9		1	1.1	1.2			
samples equilibrated at		33%	85%	94%	33%	33%	33%	85%	94%
DVS	H ₂ O/Mg (ads)	1.98	3.92 ^a	4.58		1.90	3.13 ^a	3.57	
	H ₂ O/Mg (des)	2.16	4.08 ^a			2.02	3.37 ^a		
	OH/Mg (structural) ^b	0.80				1.23			
TGA	H ₂ O/Mg	1.76	2.71		1.84	1.83	1.83	2.60	
	OH/Mg (structural) ^c	1.43	1.46		1.52	1.54	1.57	1.54	
H NMR	bulk water/Mg	---	0.08			---	0.04		
	Confined water/Mg		1.76				1.46		
	Very confined water/Mg		0.26				0.28		
	OH/Mg (structural)		1.24				1.64		
CEC	Mg ²⁺ /Mg	0.025			0.025	0.025	0.025		

1018 ^a From the DVS measurements of the M-S-H equilibrated at 33% RH; ^b two times the H₂O/Si quantified in the
1019 sample at <2.5 RH%; ^c structural water plus possibly adsorbed water.
1020

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