



# Structure of Water Adsorbed on Nanocrystalline Calcium Silicate Hydrate Determined from Neutron Scattering and Molecular Dynamics Simulations

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# 1 **Structure of Water Adsorbed on Nanocrystalline Calcium Silicate** 2 **Hydrate Determined from Neutron Scattering and Molecular** 3 **Dynamics Simulations**

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## 41 **ABSTRACT**

42 Calcium silicate hydrate (C-S-H) is a disordered, nanocrystalline material that acts as a primary  
43 binding phase in Portland cement. Thin films of water are present on the surfaces and in nanopores of  
44 C-S-H, impacting many of its chemical and mechanical properties, such as ion transport, creep, or  
45 thermal behavior. Despite decades of research, a full understanding of the structural details of  
46 adsorbed, confined, and bulk water in C-S-H remains elusive. In this work, we applied a multi-  
47 technique study involving molecular dynamics (MD) simulations validated by neutron diffraction with  
48 an isotopic substitution (NDIS) and X-ray scattering methods to investigate the structure of water in C-  
49 S-H and C-A-S-H (an Al-bearing, low-CO<sub>2</sub> C-S-H substitute). Direct comparison of NDIS data with the  
50 MD results reveals that the structure of confined and interfacial water differs significantly from the  
51 bulk water and exhibits a larger degree of mesoscale ordering for more hydrated C-S-H structures.  
52 This observation suggests an important role of water as a stabilizer of the atomistic-level structure of  
53 C-S-H.

## 54 **1 INTRODUCTION**

55 Portland cement is one of the most important synthetic materials known to humans. In particular, it  
56 plays a critical role in infrastructure and contributes a significant portion of anthropogenic CO<sub>2</sub>  
57 emissions.<sup>1-4</sup> Although its formulation has remained remarkably constant for decades, the  
58 development of alternative formulations (low CO<sub>2</sub>, CO<sub>2</sub> resistant, fire resistant, resistant to sulfate  
59 attack, etc.) has emerged in recent years as an important research goal.<sup>3,5-7</sup> This new focus has  
60 generated a strong need for detailed insight into the fundamental origins of the structural, mechanical,  
61 and chemical properties of Portland cement. The task is challenging, however, because the structural  
62 complexity of the hydrated Portland cement phase remains incompletely understood.

### 63 ***The atomistic structure of C-S-H***

64 Calcium-silicate-hydrate (C-S-H), the main binding phase in Portland cement, is a nanocrystalline,  
65 partially disordered, hydrated phase with water present in C-S-H pores of all sizes, from micro- to  
66 meso- and macropores<sup>6,8-10</sup>. In addition to its structural disorder, C-S-H is also a complex material due  
67 to its significant chemical versatility, in particular its variable Ca/Si ratio.<sup>6,11,12</sup> Since Taylor established  
68 in 1950 the presence of two distinct phases with lower or higher Ca/Si ratios (C-S-H(I) and C-S-H(II),

69 respectively), there have been decades of debate about the structures of these phases.<sup>13</sup> It is now  
 70 generally accepted that the structure of C-S-H(I) resembles a defective tobermorite, and that C-S-H(II)  
 71 contains (nano)portlandite crystallites. Though questions remain regarding the spatial localization of  
 72 the portlandite, a relatively unified view has emerged with many atomistic models available.<sup>11,14–17</sup>  
 73 These different C-S-H models are consistently based on the structure of tobermorite, which consists of  
 74 layers of calcium oxide sandwiched between silica chains formed by groups of three tetrahedra  
 75 (dreierketten), with an interlayer space filled with water and ions.<sup>15</sup> These models differ primarily in  
 76 their assumptions about the types of defects that exist in the tobermorite structure, with some  
 77 common points regarding the substitution of  $\text{Ca}^{2+}$  ions by two hydroxyl groups and the presence of  
 78 silica defects mainly in the ‘bridging’ tetrahedra of the ‘dreierketten’ silica chains.

79 In the last decade, a significant advance towards a more comprehensive understanding of C-S-H  
 80 structure has been the application of atomistic simulation techniques to link C-S-H structural models  
 81 to measured physical properties.<sup>18</sup> A milestone in C-S-H atomistic modeling was reached by Pellenq  
 82 and coworkers with their development of a first C-S-H structural model with  $\text{Ca}/\text{Si} = 1.65$ , generated  
 83 by creating defects in a tobermorite structure and then populating it with water molecules, using a  
 84 Grand Canonical Monte Carlo (GCMC) approach.<sup>19</sup> Overall, the model reproduced several mechanical  
 85 properties of C-S-H, such as stiffness, strength, and hydrolytic shear response, while deviating from  
 86 measurements of certain structural features such as coordination numbers.<sup>20</sup> Qomi et al. later refined  
 87 this model by using a “reactive” interatomic potential model (ReaxFF) to generate more chemically  
 88 realistic structures and by creating a statistical ensemble of 150 atomic structures of C-S-H with  
 89 varying  $\text{Ca}/\text{Si}$  ratios.<sup>21</sup> A similar approach was used by Kovačević et al.,<sup>22</sup> who also used a statistical  
 90 approach to generate a large number of C-S-H structures with  $\text{Ca}/\text{Si} = 1.67$  and with random numbers  
 91 of silica oligomers for each model using both geometry optimizations and molecular dynamics (MD)  
 92 simulations carried out with the ReaxFF force field. They showed that from an energetic point of view  
 93 the model with  $\text{Ca}/\text{Si} = 1.67$ , achieved by randomly removing bridging silica tetrahedra and adding  
 94 calcium ions charge-balanced by hydroxide ions, was the most stable structure. This also involved the  
 95 breaking of silica chains into dimers and pentamers.<sup>22,23</sup>

96 More recently, an atomistic model that included a careful description and classification of different  
 97 types of defects within the C-S-H structure was developed by Kunhi-Mohamed et al.<sup>16</sup> The authors  
 98 created building blocks with varying defects to capture the disordered structure of C-S-H using a  
 99 combination of density functional theory (DFT) and MD simulations. Their model reproduced the  
 100 mean chain length (MCL) of C-S-H (based on experimental  $^{29}\text{Si}$  NMR data) and its mass density.  
 101 However, the authors reported that the predicted water content was significantly lower than expected  
 102 and the interlayer spacing was quite large (2.5 Å higher than the expected value) for  $\text{Ca}/\text{Si} = 1.67$ .<sup>16</sup>

103 Finally, another recent atomistic model was proposed by Androniuk et al.<sup>24</sup> based on the structure of  
104 tobermorite, where defects were introduced only at the external surfaces, keeping the tobermorite  
105 bulk structure unchanged.<sup>25</sup> This model was used to study gluconate and U(VI) adsorption on C-S-H.<sup>26</sup>  
106 Deprotonated surface oxygens (which were assigned a more negative charge than structural oxygen  
107 atoms) were found to be the most favorable adsorption sites on the C-S-H surface, with a strong  
108 affinity for both  $\text{Ca}^{2+}$  and uranyl cations,<sup>26</sup> in agreement with their previous observation that the  
109 structural defects act as potential sorption sites for interfacial species.<sup>25</sup>

110 A key challenge in testing the validity of the structural models outlined above is that the X-ray  
111 diffraction pattern of C-S-H is composed of both Bragg peaks and diffuse scattering. This is indicative  
112 of a nanostructure containing some periodicity and a high degree of disorder. The presence of diffuse  
113 scattering makes the comparisons between experiments and calculations particularly challenging,  
114 albeit not impossible.<sup>27</sup> In recent years, experimental studies using Pair Distribution Function (PDF)  
115 analyses of high-energy X-ray scattering data have allowed a direct comparison of experimental and  
116 calculated PDFs. Unlike Bragg analysis (i.e., 'conventional' XRD analysis), the PDF approach allows the  
117 analysis of both short and long-range order. To date, few studies have directly compared predicted  
118 PDFs of C-S-H to experimental ones. Qomi<sup>21</sup> and Bauchy et al.<sup>28</sup> calculated X-ray PDFs from their  
119 simulation predictions and compared them to previously reported experimental PDFs of synthetic C-S-  
120 H.<sup>29,30</sup> The results showed good agreement with regard to the major peaks up to 5 Å, though some peak  
121 shifts or broadenings were observed. The most recent direct comparison was done by Cuesta et al.,<sup>31</sup>  
122 who compared their experimental data with calculated PDFs based on the model of Kunhi-Mohamed  
123 et al.,<sup>32</sup> showing an overall good agreement with some discrepancies in the middle-range order.<sup>31,32</sup>

#### 124 ***Water in C-S-H***

125 The models described above have contributed significantly to the advancement of our understanding  
126 of the defective structure of C-S-H and to the development of structure-properties relationships at the  
127 molecular scale. However, few of these models have addressed the structural properties of water films  
128 present at the C-S-H surface. It is well known that thin films of water adsorbed on metal oxides exert a  
129 strong control on many physico-chemical properties of the adsorbent phase, such as wettability,  
130 rheology, mechanical strength, and chemical reactivity (e.g., reactivity towards ions present within the  
131 interfacial liquid phase).<sup>33-36</sup> Studies of these interfacial liquid layers are thus of importance in cement  
132 chemistry and engineering. Indeed, these water films have been shown to strongly influence  
133 carbonation reactions,<sup>37</sup> cohesion,<sup>38,39</sup> shear strength,<sup>40</sup> and the deformation,<sup>41</sup> shrinkage<sup>42</sup> and creep  
134 behavior<sup>43</sup> of cementitious materials.

135 Since the early studies by Powers and Brownyard in 1948, who identified the so-called evaporable and  
136 non-evaporable water in the cement phase,<sup>44</sup> extensive effort has focused on characterizing the

different types of water in cement paste, and more specifically in the C-S-H phase. Different experimental techniques, including neutron scattering, have been used to probe the water component of C-S-H. In particular, Allen et al.<sup>45</sup> used small angle X-ray and neutron scattering to study the mesoscale arrangement of C-S-H nanoparticles. They concluded that C-S-H consisted of roughly 5 nm-wide platelets composed of stacked C-S-H layers with an interlayer space filled with water, and they distinguished between adsorbed water located on the surface of the platelets and a bulk-liquid-like water component located in the pores between these platelets.<sup>45</sup> Pinson et al.<sup>46</sup> proposed a similar classification of water based on the results of water sorption isotherms (WSI): they identified water confined in the interlayer space ( $\leq 1$  nm), strongly bound to the C-S-H surfaces and removed only at relative humidities (RH)  $\leq 11\%$ ; a “gel pore water” component in 1 to 10 nm wide pores; and capillary water in pores larger than 10 nm. Finally, they reported the presence of a surface layer of adsorbed water, which remained present in gel and capillary pores after the pores had been drained of bulk-liquid-like water.<sup>46</sup> Nuclear Magnetic Resonance (NMR), and in particular  $^1\text{H}$  relaxometry experiments, have also provided detailed information on water dynamics in C-S-H and cement.<sup>47</sup> In particular,  $^1\text{H}$  NMR relaxometry experiments by McDonald et al.<sup>48</sup> allowed differentiating between the mobile intra-C-S-H sheet water and inter-C-S-H gel pore water.<sup>48</sup> A few years later, Muller et al.<sup>49</sup> and Valori et al.<sup>50</sup> showed the potential of  $^1\text{H}$  NMR relaxometry to distinguish between the dynamic characteristics of water in interlayer pores ( $< 1$  nm), gel pores (2-5 nm), interhydrate pores (roughly 10 nm), and capillary pores (about 1000 nm). This subdivision of water in different pores and surfaces of C-S-H was subsequently studied by Roosz et al.,<sup>51</sup> who showed how an initially dry synthetic C-S-H sample behaves when exposed to increasing humidity. The authors proposed a two-step process, with water being adsorbed on the surfaces when humidity increases from 0 to 75% RH, and subsequently filling the mesopores and interlayer spaces as RH increases up to 95%.<sup>51</sup> These authors also showed that the process is not readily reversible, with interlayer water being released at much lower RH during water desorption.

#### ***Molecular mechanisms controlling C-S-H wettability***

Even though, as shown above, the diffusive behavior of water in C-S-H has been the subject of multiple investigations, less information is available regarding the structural characteristics of the adsorbed water. Youssef et al.<sup>52</sup> used molecular modeling based on the structural C-S-H model of Pellenq et al.<sup>19</sup> to study water in confinement (interfacial/interlayer water). The authors showed with partial pair correlations of the water oxygen and hydrogen atoms that the local order of the confined water differed from that reported experimentally for bulk water.<sup>53</sup> The hydrophilic nature of C-S-H is explained by these authors as coming from the defective silicate chains, which act as hydrogen-bond (H-bond) acceptor sites, and from interlayer calcium ions, which coordinate water molecules.<sup>52,54</sup> This mechanism of surface hydrophilicity has been confirmed by studies on similar systems; for example,

172 Bonnaud et al.<sup>39</sup> showed using GCMC and MD methods that the hydrophilicity of  $\text{Ca}^{2+}$  ions physisorbed  
173 in silica nanopores (a simplified model of C-S-H) decelerates the water dynamics as compared to the  
174 hydroxylated silica surfaces without calcium ions. These authors also observed that the tetrahedral  
175 arrangement of bulk water is disturbed near the hydrophilic surface, and perturbed much more in the  
176 presence of calcium ions at the surface, due to water molecules being coordinated to  $\text{Ca}^{2+}$ .<sup>39</sup> As  
177 discussed by Bourg and Steefel,<sup>55</sup> water within silica nanopores can be split into two types depending  
178 on the pore size of the porous adsorbent: 2 to 20 nm wide pores contain significant amounts of surface  
179 water (located in the  $\sim 3$  first monolayers from the hydrophilic surface), which is highly structured and  
180 different from the bulk-like water found in the center of the pores, while pores narrower than about 2  
181 nm contain only confined water that is influenced by the two hydrophilic surfaces.<sup>55</sup> This simplified  
182 model is representative of water in the C-S-H phase: the first type would correspond to gel-pore water,  
183 with interfacial water (closest to the surface of C-S-H) having different structural characteristics than  
184 the bulk-liquid-like water. The second type corresponds to interlayer water confined between two C-S-  
185 H surfaces.<sup>46</sup> As a general trend, water near the surfaces of hydrophilic minerals tends to deviate more  
186 from bulk-liquid-like water, both in terms of translational and orientational dynamics, and its  
187 properties depend strongly on the nature of the substrate.<sup>55-59</sup> In the case of silica surfaces, the density  
188 of surface hydroxyl groups dictates the wetting behavior, with a hydrophilic to hydrophobic transition  
189 observed below 5 to 6 OH/nm<sup>2</sup>.<sup>21,60,61</sup>

190 In this paper, the structural properties of interfacial and interlayer water in C-S-H are probed using a  
191 combination of experimental and molecular modeling techniques. The technique of neutron diffraction  
192 with isotopic substitution (NDIS) is used to probe the short-range order of water adsorbed on C-S-H  
193 surfaces.<sup>62,63</sup> This method has previously been applied to systems showing structural similarities to C-  
194 S-H, such as clay minerals.<sup>64-66</sup> To perform the molecular modeling simulations, a simple model of C-S-  
195 H has been developed using a modified version of the CLAYFF force-field. Comparisons of the  
196 calculated and experimental X-ray PDFs of C-S-H in the literature demonstrate the challenges  
197 associated with creating an atomistic model that captures the complexity and disorder of the C-S-H  
198 phase. One particular challenge in comparing these models with experimental results is that most  
199 atomistic models developed for C-S-H (with very few exceptions)<sup>67</sup> share the similarity of being bulk  
200 models (i.e., they are based on C-S-H structures that are infinite in at least two directions), whereas  
201 experimental studies suggest that C-S-H is composed of nanocrystals with dimensions of only a few  
202 nanometers.<sup>30</sup> The C-S-H model that we present in this work consists of a single particle with  
203 dimensions of a few nanometers in every direction.

204 The paper is organized as follows: First, the stoichiometry of our experimental C-S-H samples and the  
205 distribution of water as a function of RH are discussed. Then, the development of the C-S-H model is  
206 described, including its validation by comparison to experimental scattering data. Finally, based on our

simulation and experimental results, we examine the structure and hydrogen-bonding (H-bonding) behavior of interfacial and interlayer water in C-S-H and calcium-aluminum-silicate-hydrate (C-A-S-H) samples conditioned at 55% and 98% of RH.

## 2 MATERIALS AND METHODS

### 2.1 Sample preparation

C-S-H samples with Ca/Si = 1 and 1.27 were synthesized by reacting calcium oxide and fumed silica in water inside a N<sub>2</sub> wet glove-box. Calcium oxide was obtained by calcination of CaCO<sub>3</sub> (Sigma-Aldrich, Fluka, Bioultra) at 1000 °C for 18 h and stored in a vacuum desiccator until usage. Fumed silica SiO<sub>2</sub> (Sigma-Aldrich, Aerosil 200) was placed in an oven at 40°C for 24 h to remove physisorbed water prior to each experiment. Deionized water was boiled and degassed with N<sub>2</sub> gas to remove all dissolved CO<sub>2</sub>. The quantities of calcium oxide and fumed silica required to prepare C-S-H of predetermined stoichiometry were calculated using the method reported by Haas and Nonat<sup>68</sup> (see Supporting Information Table S3). Samples were reacted under stirring conditions for 1 month in High Density Polyethylene (HDPE) bottles inside a wet N<sub>2</sub> glove-box, then filtered using Millipore® filter paper (0.22 µm, GSW1 UM), and wet C-S-H residue was left to dry inside the glove-box for 12 h. A part of these C-S-H samples was set aside for characterization of a fully-hydrated C-S-H. The remaining C-S-H was oven-dried at 40 °C in a vacuum oven for 24 h. After drying, samples were conditioned at controlled RH of 55 or 98 % using saturated salt solutions of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or K<sub>2</sub>SO<sub>4</sub>, respectively, in duplicate with normal and deuterated water for 1 week (described schematically in Supporting Information Figure S6). As samples are sensitive to atmospheric CO<sub>2</sub>, all synthesis and conditioning processes were performed under an inert gas atmosphere of N<sub>2</sub>. The C-A-S-H samples with Ca/Si = 0.9 and 1.1 and Al/Si = 0.1 were synthesized following a protocol that can be found elsewhere.<sup>17</sup> The conditioning time for the C-A-S-H samples was 1 month.

Following these protocols, we obtained C-S-H samples labeled CSH\_Ca/Si\_%RH\_h/d, where Ca/Si is the Ca/Si ratio of a sample, %RH is the relative humidity at which it was conditioned, and *h* or *d* signify conditioning with normal or deuterated water (Table 1). The C-A-S-H samples were labeled CASH\_Ca/Si\_%RH\_h/d. In the discussion of the results of neutron diffraction with isotopic substitution experiment (explained later), we refer to the difference between deuterated and hydrogenated samples as CSH\_Ca/Si\_%RH\_d-h, for example CSH\_1\_55RH\_d-h. If the properties of the C-S-H samples with a specific Ca/Si ratio are discussed in general, we refer to these as CSH\_Ca/Si.

### 2.2 Sample characterisation

#### Inductively coupled plasma - atomic emission spectrometry (ICP-AES)



239 Ca/Si ratios were determined using ICP-AES (Varian 720ES Agilent). The C-S-H particles (5-10 mg)  
240 were dissolved by adding concentrated 14M HNO<sub>3</sub> (distilled) and 28M HF (47-51%, Trace Metal™, for  
241 Trace Metal Analysis, Fisher Chemical) acids, followed by heating the solution for 24h at 80°C. The  
242 final step involved diluting with boric acid and ultrapure water prior to the measurement.

### 243 **Water adsorption volumetry**

244 Water adsorption isotherms were obtained at 25 °C using a Belsorp-Max instrument by BEL JAPAN  
245 Inc.III. A long acquisition time of at least 2 weeks was required due to the slow equilibrium kinetics.  
246 Prior to the measurements, all samples were outgassed at 40 °C for 24 h under a residual pressure of  
247  $4.652 \times 10^{-5}$  Pa. The classical Brunauer–Emmett–Teller (BET) theory and a generalized t-plot method  
248 were used to analyze the isotherms.<sup>69</sup> The BET theory was employed to obtain energetic C constants,  
249 which were used to plot t-curves based on the method discussed by Hagymassy<sup>70</sup> (Table 1).

### 250 **Thermogravimetric analysis**

251 Thermogravimetric analysis (TGA, Mettler-Toledo TGA-DSC3+) was used to examine the thermal  
252 decomposition and the water content of the C-S-H and C-A-S-H samples. The samples were analyzed at  
253 a heating rate of 10°C/min up to 600°C in a N<sub>2</sub> environment with a flow rate of 20 mL/min. The  
254 samples were loaded in aluminum crucibles and were hermetically sealed with aluminum caps inside  
255 a glove-box or a glove-bag filled with N<sub>2</sub> equilibrated at the same RH used to condition the sample. The  
256 sample masses used for TGA analyses varied between 8 and 31 mg (20±2 mg for C-S-H with Ca/Si=1,  
257 29±2 mg for C-S-H with Ca/Si=1.27, and 9±1 mg for C-A-S-H samples).

### 258 **Attenuated Total Reflection Fourier-transform infrared (ATR-FTIR) spectrometry**

259 FTIR spectra were acquired on an IS10 ThermoFischer spectrometer with high-performance diamond  
260 ATR Smart iTX™ Accessory (IRSTEA, Grenoble). The different vibrational bands were assigned using  
261 the OMNIC software.

### 262 **Synchrotron X-Ray diffraction**

263 Synchrotron XRD measurements for the C-S-H samples were performed at the ID31 and ID22  
264 beamlines of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Prior to  
265 analysis, C-(A)-S-H samples were loaded into 1.5 mm (ID31) or 2 mm (ID22) polyimide capillaries in  
266 glove-bags or a wet glove-box at the same RH values. The capillaries were closed on both ends using a  
267 two-parts epoxy adhesive.

268 At the ID31 beamline, a monochromatic X-ray beam of 78 keV ( $\lambda = 0.159$  Å) was used to obtain  
269 scattering patterns of C-S-H with Ca/Si = 1. The data sets were collected using a PilatusX 2M CdTe  
270 detector placed at a sample-to-detector distance of  $d_1 = 1.226$  m to obtain scattering patterns with a Q  
271 range of 0.1-6.2 Å<sup>-1</sup>, allowing the measurement of the Bragg peak corresponding to the interlayer

distance of C-S-H. A second set of experiments was performed with a shorter sample-to-detector distance of  $d_2 = 0.224$  m, yielding a  $Q$  range  $0.6$ - $27.6 \text{ \AA}^{-1}$ , for PDF analyses of the short- and medium-range order. C-S-H samples with  $\text{Ca/Si} = 1.27$  were measured at the ID22 beamline with a monochromatic X-ray beam of  $31 \text{ keV}$  ( $\lambda = 0.4 \text{ \AA}$ ). An angular range of  $0.001$ - $16^\circ$   $2\theta$  was used with a sample-to-detector distance of  $d = 1.4$  m, corresponding to a  $Q$  range of  $0.00027$ - $4.37 \text{ \AA}^{-1}$ .

Data were automatically corrected for internal dark current. Two-dimensional images of the scattered intensity were azimuthally integrated using the pyFAI software package.<sup>71</sup> The pattern from the empty capillary was subtracted as a background. PDFs were obtained using the PDFGetX3 software.<sup>72</sup>

The C-A-S-H samples were measured at the 11-ID-B beamline at the Advanced Photon Source, Argonne National Laboratory. The samples were analyzed with a monochromatic X-ray beam of  $58.6 \text{ keV}$  ( $\lambda = 0.2115 \text{ \AA}$ ). The data were collected with a Perkin Elmer XRD 1621 N ES detector and sample-to-detector distance of  $d = 0.799$  m to access a  $Q$  range of  $0.2$ - $10.4 \text{ \AA}^{-1}$ . Data were automatically corrected for internal dark current. Two-dimensional images of the scattered intensity were azimuthally integrated using the GSAS II software package.<sup>73</sup>

## 2.3 Neutron diffraction with isotopic substitution

Neutron diffraction with isotopic substitution (NDIS) analyses ([doi:10.5291/ILL-DATA.6-07-37](https://doi.org/10.5291/ILL-DATA.6-07-37), [doi:10.5291/ILL-DATA.6-07-32](https://doi.org/10.5291/ILL-DATA.6-07-32)) of C-S-H samples were performed at the D4 diffractometer<sup>74</sup> of the Institut Laue-Langevin (ILL), France. The incident wavelength of incoming neutrons was  $0.4963 \text{ \AA}$ , as determined using a Ni powder reference. The samples were loaded in cylindrical ( $6.05 \text{ mm}$  inner diameter,  $6.35 \text{ mm}$  outer diameter) vanadium containers sealed with a metallic O-ring under controlled atmospheres at the same RH values as the one used to condition the samples. The sample containers were weighed before and after each measurement to verify that no dehydration had occurred. Measurements were performed at ambient temperature ( $298 \text{ K}$ ). Results were corrected for inelasticity, multiple scattering, absorption, instrumental resolution, and background using the CORRECT program<sup>75</sup> and a custom-built Python code. Scattering and absorption cross sections were calculated using values from Sears' tables.<sup>76</sup> Scattering cross sections values for H and D were modified to account for  $0.4963 \text{ \AA}$  neutrons or adsorbed and bulk pore water that lies outside the neutron beam's coherence volume. After the above-mentioned experimental corrections, the neutron structure factor  $S(Q)$  was obtained, which contains information about the structural organization of the material at the atomic level. Subsequent Fourier transformation of the  $S(Q)$  yielded the density function  $G(r)$ , which is equivalent to the more commonly reported X-ray pair distribution function (PDF),<sup>63</sup> except for the difference in scattering lengths between neutrons and X-rays. Prior to calculation of the  $G(r)$ , the total  $S(Q)$  was multiplied by a window function selected to reduce the effects of the limited momentum transfer range.<sup>77</sup>

NDIS experiments for the C-A-S-H samples were performed at the SANDALS diffractometer at the ISIS pulsed neutron source, United Kingdom. Experiments were performed at ambient temperature (298 K). The C-A-S-H samples were loaded in flat plate containers made of a “null scattering” alloy of Ti and Zr (35 mm x 35 mm x 2 mm) under controlled atmospheres at the same RH values as the ones used to condition the samples. The sample containers were weighed before and after each measurement to verify that no dehydration had occurred. The measurements used a neutron beam with wavelengths ranging from 0.05 to 4.95 Å, with a resulting Q range of 0.13 to 50 Å<sup>-1</sup>. Results were corrected for inelasticity, multiple scattering, absorption, instrumental resolution, and background using the Gudrun package.<sup>78</sup>

Scattering patterns were obtained using samples conditioned with two different isotopes of H (<sup>1</sup>H and D). Results were analyzed using the so-called first order difference method, by which all partial structure factors not involving H are cancelled out to obtain a partial structure factor centered on H (i.e. reflecting only the contributions of interatomic pairs involving at least one H atom). After Fourier transformation, the resulting G(r) is a partial pair distribution function centered on the H atom.<sup>62,63</sup> Prior to G(r) calculation, the total S(Q) was multiplied by a window function selected to reduce the effects of the limited momentum transfer range.<sup>77</sup> Additional information on the NDIS method is provided in the Supporting Information.

## 2.4 Molecular dynamics simulation

Atomistic simulations were performed at the Cori supercomputer at the National Energy Research Scientific Computing Center (NERSC, USA) using the MD simulation code LAMMPS,<sup>79</sup> which solves Newton’s equations of motion for many-particle systems interacting through pairwise potentials. Interatomic interactions were described using the SPC water model<sup>80</sup> and the CLAYFF model of mineral-water interactions.<sup>81</sup> The CLAYFF force field was chosen because of its versatility and successful descriptions of various systems including clay minerals,<sup>55,56,82–84</sup> zeolites,<sup>85</sup> and other phases<sup>86–88</sup> validated against the results of X-ray and neutron scattering experiments<sup>82,89</sup> and a variety of other experimental techniques.<sup>90,91</sup>

A variety of force fields has been applied to simulate C-S-H and its crystalline analogues. These include the CLAYFF model, successfully applied to simulate a periodic C-S-H structure by Kalinichev and co-workers,<sup>24,92</sup> as well as a number of specialized force fields for cementitious systems, such as CSH-FF,<sup>93</sup> as summarized by Mishra et al.<sup>94</sup> One versatile option is the reactive force field ReaxFF<sup>95</sup>, applied to C-S-H by several authors,<sup>21,22,28,40</sup> which can predict covalent bond dissociation and formation reactions. Unfortunately, comparison of ReaxFF simulation predictions with experimental microstructural data is complicated by its tendency to overestimate unit cell sizes, dissociation of the silica chains,<sup>22</sup> and the formation of silanol groups.<sup>21,40</sup> Finally, various studies have complemented the force field based

approaches outlined above using DFT methods, an approach that provides powerful fundamental insight but remains computationally costly for disordered systems such as C-S-H.<sup>32,40</sup>

In the present study, we have applied the CLAYFF force field to model, for the first time, a nanoparticle of C-S-H, including non-satisfied bonds at the edges in *x* and *y* directions. The modifications to the CLAYFF force field required to model the edge surfaces of C-S-H nanoparticles were performed based on the algorithms described in Lammers et al.<sup>96</sup>

Newton's equations of motion were solved using the Verlet algorithm with a 1 fs step. Electrostatic and dispersion interactions beyond a cut-off length of 15 Å were computed by Ewald summation. Water molecules were kept rigid using the SHAKE algorithm. The silica chains were kept semi-rigid by applying equilibrium bond angles  $\Theta_0$  taken from the X-ray crystal structure of tobermorite,<sup>97</sup> with angle bending force constant *K* adapted from the INTERFACE force field of Heinz et al.<sup>98</sup> The C-S-H nanoparticle was fixed for the first 15 ps, during which only water molecules were allowed to move, after which all atoms were allowed to move. The system was equilibrated for 1.5 ns and, then, simulated for 3.5 ns production runs in the NVT ensemble at *T* = 298 K. Analyses of the MD simulation trajectories were performed using custom-made Python codes. Atomic structures were converted to PDFs using the DiffPy-CMI package<sup>71</sup> and averaged over multiple frames using a custom-made Python code. For the analysis of H-bonding structure, for simplicity, an H-bond was considered to exist if the intermolecular O-H distance was less than < 2.375 Å.<sup>99</sup>

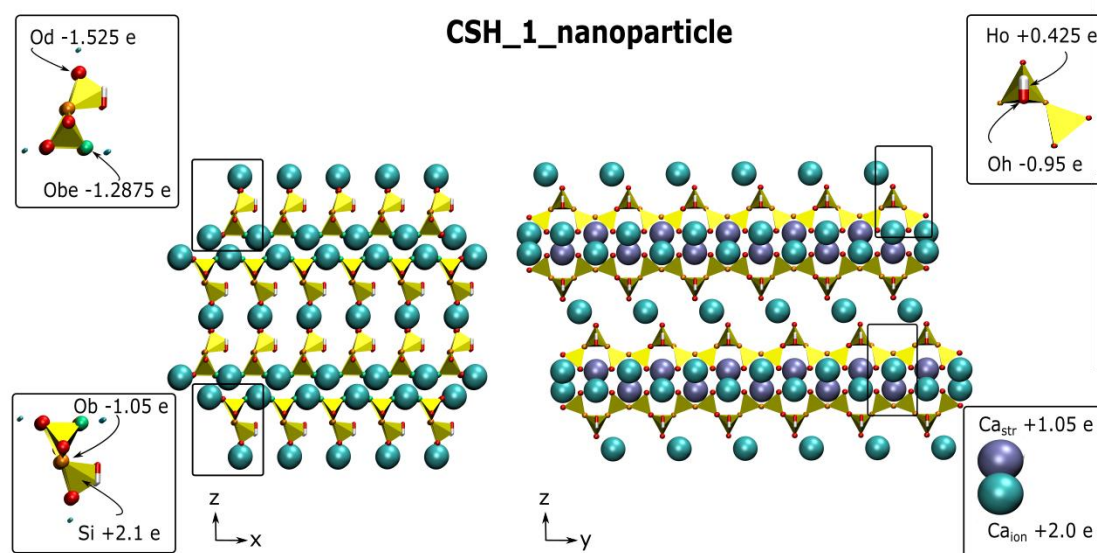
## 2.5 C-S-H nanoparticle model construction

As a starting structure to build a C-S-H nanoparticle model we used the unit cell parameters and the atomic coordinates of the 14 Å tobermorite model by Bonaccorsi et al.<sup>97</sup> A supercell model was obtained by multiplication of the tobermorite unit cell in the *x*, *y*, and *z* directions. The bulk tobermorite supercell was then cleaved in the *z* direction along the plane of interlayer Ca ions (removing half of the exposed surface Ca ions), which created an uncharged basal surface identical to that examined in previous studies.<sup>24</sup> To construct a nanoparticle, the tobermorite structure was then cleaved in the *x* and *y* directions, which created surfaces referred to hereafter as the *x* and *y* edge surfaces (Figure 1).

To construct these *x* and *y* edge surfaces, Ca-O bonds were broken in the *x* direction and Si-O bonds were ruptured in the *y* direction. In order to ensure that the edges carried no under-coordinated metals (Si or Ca), in agreement with Pauling's bond-valence theory and with the original CLAYFF model, we used the algorithm developed by Lammers et al.<sup>96</sup> (The full list of parameters is reported in Table S2 in the Supporting Information.) This approach resulted in the definition of two oxygens types not listed in the CLAYFF model. The first is a *deprotonated* silanol ( $>\text{SiO}^-$ ) oxygen (Od, with charge *q* = -1.525 *e*), which has been previously used by authors to simulate clay edge surfaces and silica

surfaces.<sup>100,101</sup> The second is a *bridging edge* oxygen (Obe, with  $q=-1.2875$  e), which is coordinated to one structural Si and one structural Ca atom. This bridging edge oxygen is found on the y edges and is under-coordinated by one structural Ca atom compared to CLAYFF bridging oxygen (Ob with  $q = -1.05$  e).

A structure with a ratio of  $\text{Ca}/\text{Si} = 1$  was then obtained by randomly removing bridging silica tetrahedra from our model tobermorite nanoparticle.<sup>15</sup> To maintain a charge-balanced structure, one of the bridging oxygens previously coordinated to the removed Si atom was replaced by a hydroxyl group, while the other was converted to a deprotonated silanol oxygen (See Supporting Information Figure S5). The resulting structure consists of silicate dimers and pentamers, which were shown to give energetically the most stable structures.<sup>22,23</sup> The lengths of these chains can be calculated using the  $Q^n$  definition describing different silicon environments identified by NMR:  $Q^1$  are the species with one Si neighbour, and  $Q^2$  have two Si neighbours. For this model, the ratio  $Q^1/(Q^1+Q^2)$  is higher than generally reported for C-S-H with  $\text{Ca}/\text{Si} = 1$  and closer to the value expected of  $\text{Ca}/\text{Si} = 1.2$ .<sup>102,103</sup> The reason for this too high number of  $Q^1$  species may be the limited size of the nanoparticle, in which to achieve the  $\text{Ca}/\text{Si} = 1$  the majority of bridging silica tetrahedra had to be removed. Overall, we note that the precise structure of C-S-H remains unknown; therefore, we have tried to use the simplest C-S-H structure that was consistent with available information.



**Figure 1.** Idealized C-S-H nanoparticle structure (after the cleaving and healing of the external surfaces, but prior to the random removal of bridging silica tetrahedra) in x direction (left) and y direction (right) showing all the atom types: ionic calcium  $\text{Ca}_{\text{ion}}$  (turquoise spheres), structural calcium  $\text{Ca}_{\text{str}}$  (violet spheres), tetrahedral silica Si (yellow polyhedra), bridging oxygens Ob (orange dots), hydroxyl oxygens and hydrogens Oh and Ho (red and white licorice), bridging edge oxygens Obe (green dots), and deprotonated oxygens Od (red dots).

398 In this work, we simulated two models with two different hydration states. A high hydration state in  
399 which the 1892-atom C-S-H nanoparticle is suspended in a water droplet containing 12705 water  
400 molecules, which we named CSH\_1\_98RH, and a low hydration state where the particle is hydrated  
401 with only 448 water molecules, CSH\_1\_55RH. Thus, CSH\_1\_55RH model contains one monolayer of  
402 water, i.e. water within 3 Å from the C-S-H surface. In order to understand better the properties of the  
403 adsorbed interfacial water, we compared the first monolayer of water in CSH\_1\_98RH (referred later  
404 to as CSH\_1\_98RH\_monolayer), with the water in CSH\_1\_55RH. The CSH\_1\_98RH\_monolayer  
405 comprises about 1000 water molecules, which is roughly 2.2 times more than in CSH\_1\_55RH. These  
406 hydration states were selected to mimic the CSH\_1\_98RH\_h (presence of bulk-liquid-like water, water  
407 to solid ratio 0.32 g/g) and CSH\_1\_55RH\_h experimental systems (presence of only interfacial and  
408 interlayer water, water to solid ratio of 0.24 g/g). We emphasize that we refer to our simulated  
409 systems as 55RH or 98RH by analogy with the absence or presence of bulk-liquid-like water in our  
410 experimental conditions at these RH values, and that we did not quantify the activity of water in our  
411 simulations.

## 412 **2.6 Stoichiometry of water in C-S-H**

413 A precise determination of the stoichiometry and the types of water within the experimental samples  
414 is needed to analyze the NDIS data. Both bound water (i.e., water chemically incorporated into the  
415 structure of C-S-H) and so-called free water (i.e., water adsorbed on the surfaces and found in the  
416 capillary pores of C-S-H) are present in the samples and scatter neutrons differently. Therefore, a  
417 precise quantification of the abundance of structural hydroxyls, interlayer water, adsorbed interfacial,  
418 and bulk-like water in the capillary pores is paramount.

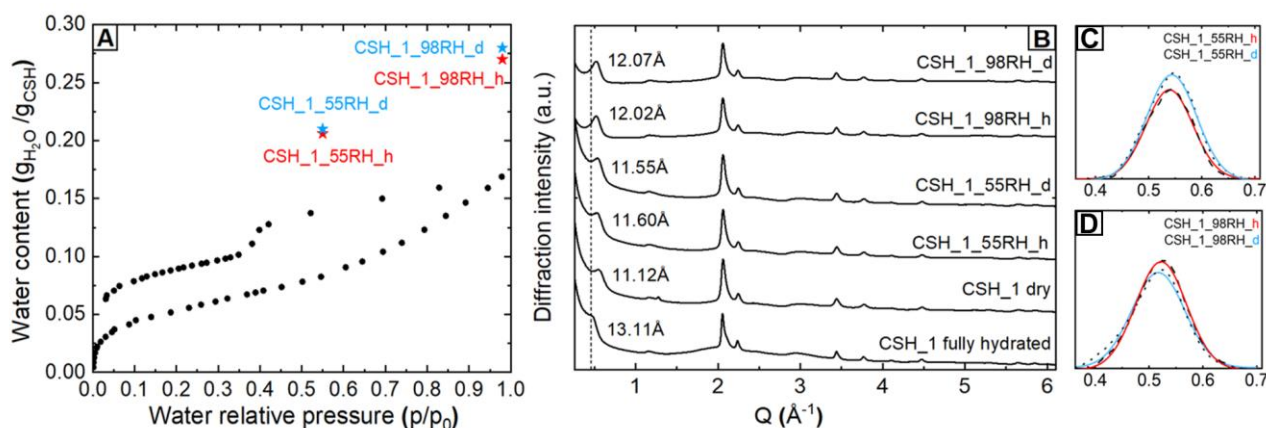
419 Calcium-silicate-hydrate has a highly variable stoichiometry, which mainly depends on the Ca/Si ratio  
420 and hydration state of the sample and is directly related to the abundance of defects in the C-S-H  
421 structure.<sup>51,104–106</sup> In our case, a key challenge was the estimation of the relative abundance of  
422 hydroxyls, interlayer water, interfacial water, and bulk pore water at varying RH values. Moreover, for  
423 a subset of our samples an additional complication arose from the incomplete deuteration of the  
424 deuterated C-S-H samples. To overcome this problem we applied the method described by Roosz et  
425 al.<sup>51</sup> and adapted it to the various RH values and deuteration levels of our samples.<sup>51</sup> The degrees of  
426 deuteration were obtained from ATR-FTIR spectra by comparing the relative areas under the O-H and  
427 O-D stretching frequencies at 3500 cm<sup>-1</sup> and 2600 cm<sup>-1</sup>, respectively (see Figure S3 in the Supporting  
428 Information). The total mass of water was obtained from the TGA measurements by assuming that at  
429 300°C all the water in C-S-H had evaporated. Roosz et al.<sup>51</sup> used 150°C as a threshold value judging  
430 from the complete collapse of the interlayer spacing at this temperature by XRD. However, careful  
431 inspection of our data for C-S-H with various Ca/Si ratios and RH values revealed that 300°C is a more

appropriate threshold value to ensure that all bound water has evaporated. This value lies in the range of temperatures (260-600°C) in which a phase transition between tobermorite 14 Å and tobermorite 9.6 Å is observed, indicating the loss of highly bound water.<sup>107</sup> The remaining weight loss from 300°C-600°C was assumed to be due to the loss of hydroxyl groups, as portlandite dehydroxylation occurs around 450°C.<sup>108</sup> The maximum temperature was 600°C due to melting temperature of aluminum crucibles used. Roos et al. noted that the temperature ranges used here are approximate and are sensitive to drying method and temperature.<sup>51</sup>

Adsorbed interfacial water content was quantified using the t-plot method, i.e., by plotting the volume of water adsorbed vs. the number of monolayers adsorbed at a certain value of RH. The specific surface area (SSA) and the volume of the monolayer  $V_{\text{monolayer}}$  were derived from the BET equation. Then, the volume of water at a corresponding RH level was calculated by multiplying the statistical number of layers by  $V_{\text{monolayer}}$ . Interlayer water content was estimated by combining the values of the basal spacing (i.e., the  $d_{001}$  reflection) from the XRD data and the hysteresis observed by WSI (Table 1). Capillary bulk pore water content was calculated by subtracting the interlayer and adsorbed water masses from the total water mass. The same procedure was applied to the deuterated samples, taking into account the corresponding degrees of deuteration. The results of the above-described experiments and the stoichiometry for the C-(A)-S-H nanoparticles and the corresponding distribution of water are shown in Tables 1-2.

### 3 RESULTS AND DISCUSSION

#### 3.1 Types of water and water content in C-S-H



**Figure 2.** (A) Water adsorption/desorption isotherm of CSH<sub>1</sub>. Black circles show WSI results. Red and blue stars indicate the water content deduced from the TGA data for hydrogenated and deuterated samples at 55 and 98% RH. (B) XRD patterns of CSH<sub>1</sub> fully hydrated (dried overnight in the glove-box), CSH<sub>1</sub> dry (oven dried at 40°C in vacuum), and hydrogenated and deuterated CSH<sub>1</sub> at 55 and 98% RH (conditioned for 1 week). The vertical dashed line shows the  $Q$  value associated with the  $d_{001}$  reflection of CSH<sub>1</sub> fully hydrated. (C,D) Examples of Pseudo-Voigt fits to the  $d_{001}$  reflection.

459 Adsorption/desorption isotherm for CSH<sub>1</sub> is shown in Figure 2 (other isotherms for C-(A)-S-H are  
460 shown in Figure S4 in the Supporting Information). In accordance with findings of Roos et al.<sup>51</sup> and  
461 the IUPAC classification of Sing et al.<sup>109</sup> the isotherms belong to the type-II with H3 hysteresis loop  
462 behavior, signaling the presence of mesopores. The calculated BET SSA decreases with increasing  
463 Ca/Si ratios, from 187 m<sup>2</sup>/g for CSH<sub>1</sub> to 132 m<sup>2</sup>/g for CSH<sub>1.27</sub> (data for other Ca/Si ratios not shown  
464 here). The C-A-S-H samples follow a similar trend, with SSA values generally higher for C-A-S-H than  
465 for C-S-H (Table 1). The total amount of water derived from the TGA curves for CSH<sub>1</sub> samples is  
466 shown in Figure 2. Our TGA results for ~12 Ca/Si ratios at five different hydration levels (see Figure S8  
467 in the Supporting Information) were compared to the data of Cong and Kirkpatrick<sup>102</sup> (and other  
468 authors<sup>45,51,110-114</sup>) and showed good agreement with the overall trend of increasing total H<sub>2</sub>O/Si ratio  
469 with increasing Ca/Si ratio.

470 Both deuterated and hydrogenated C-(A)-S-H samples hold larger amounts of water as quantified by  
471 TGA than by WSI at the same RH values. One possible explanation is the limited equilibration time. The  
472 TGA samples were equilibrated in specific RH atmospheres by storing the C-S-H samples in desiccators  
473 over the saturated salt solutions for 1 week, and C-A-S-H samples for 1 month. The C-(A)-S-H samples  
474 measured with WSI were equilibrated for a few hours at each corresponding value of RH (done  
475 automatically by the instrument). Therefore, consistent with conclusions of Odler,<sup>115</sup> the amount of  
476 adsorbed water in the samples equilibrated for longer times (TGA experiment) is larger than in  
477 samples with shorter equilibration times (WSI experiment). Another potential difference is the  
478 normalization of the WSI points: Roos et al.<sup>51</sup> normalized adsorbed water amounts by the mass of C-S-  
479 H dried at 150°C, estimated to correspond to fully dehydrated C-S-H, whereas we used the mass of C-S-  
480 H dried at 50°C, which is an optimal pre-measurement sample degassing temperature.

481 As expected, the total mass of water is higher for the 98% RH samples than for the 55% RH samples, as  
482 the former contain capillary bulk water as well as interfacial and interlayer water. At 55% RH, samples  
483 contain 0.22 to 0.26 g water per g of dry C-S-H, as determined upon heating to 300°C, with the total  
484 mass of water decreasing slightly with increasing Ca/Si ratio. The abundance of hydroxyls is similar  
485 for all samples of same Ca/Si ratio (Table 2), and the difference in water content is due to varying RH  
486 levels.

487 Water release occurs at lower temperatures in the 98% RH samples, indicating the presence of more  
488 labile, bulk-liquid-like water. In TGA experiments the bulk-like water desorbs first, but the evaporation  
489 process can cause some partial migration/re-arrangement of the interfacial water, leading to shifts in  
490 the inflection points and to different shapes of dTG curves for 55% RH and 98% RH samples (Figure S2  
491 in the Supporting Information).



**Table 1.** Results of ICP, XRD, TGA, WSI, and ATR FT-IR experiments used to determine the stoichiometry of C-(A)-S-H samples used in NDIS experiment.

Sample name	ICP	XRD	Thermogravimetric analysis			Water sorption isotherms (BET method)			ATR FT-IR
	Ca/Si ratio	d <sub>001</sub> (Å)	Mass loss (25-300 °C) (g/g <sub>dryCSH</sub> )	Mass loss (300-600°C) (g/g <sub>dryCSH</sub> )	Total mass loss (25-600°C) (g/g <sub>dryCSH</sub> )	BET c-value (-)	V <sub>monolayer</sub> (cm <sup>3</sup> /g)	SSA <sub>BET</sub> (m <sup>2</sup> /g)	D/H ratio
CSH_1_55RH_h	1.04	11.6(1)	0.206	0.039	0.245	69	55	187	0.44
CSH_1_55RH_d		11.5(1)	0.21	0.047	0.257				
CSH_1_98RH_h		12.0(2)	0.27	0.05	0.32				
CSH_1_98RH_d		12.1(2)	0.32	0.06	0.38				
CSH_1.27_55RH_h	1.27	10.3(1)	0.169	0.059	0.225	87	40	132	~0.5
CSH_1.27_55RH_d		10.3(1)	0.175	0.064	0.238				
CASH_0.9_55RH_h	0.9	12.4(2)	0.22	0.04	0.261	55	108	353	0.52
CASH_0.9_55RH_d		12.3(2)	0.24	0.045	0.285				
CASH_1.1_55RH_h	1.1	12.4(2)	0.207	0.039	0.246	67	90	291	~0.5
CASH_1.1_55RH_d		12.2(2)	0.216	0.05	0.266				

XRD patterns of C-S-H samples with varying water contents are shown in Figure 2. Results indicate that the d<sub>001</sub> spacing varies with Ca/Si ratio and RH level. The fully hydrated C-S-H has a full interlayer space with d<sub>001</sub> around 13.1(1) Å. Upon drying at 40°C in vacuum, the interlayer water evaporates and the d<sub>001</sub> value decreases to 11.1(1) Å. When these oven-dried samples were subjected to humid atmospheres, interlayer water was partially reincorporated as reflected in the d<sub>001</sub> values shown in Table 1. The d<sub>001</sub> reflection value and the total water contents derived from the TGA data were similar for hydrogenated and deuterated samples at the same RH values, with slight differences possibly due to the fitting errors of the XRD data and to the choice of temperature range (25 to 300 °C) used to quantify water content from the TGA results. Moreover, the d<sub>001</sub> reflection does not always uniquely reflect the interlayer spacing, as d<sub>001</sub> can be modulated by variations in scattering domain size<sup>27</sup> and

interstratification phenomena.<sup>27,116</sup> Nonetheless, previous studies have evidenced a trend towards decreasing d-spacing with increasing Ca/Si ratio,<sup>15,27</sup> with significant scatter hypothesized to result from differences in drying conditions, hydration levels, and sample handling.<sup>51,116</sup>

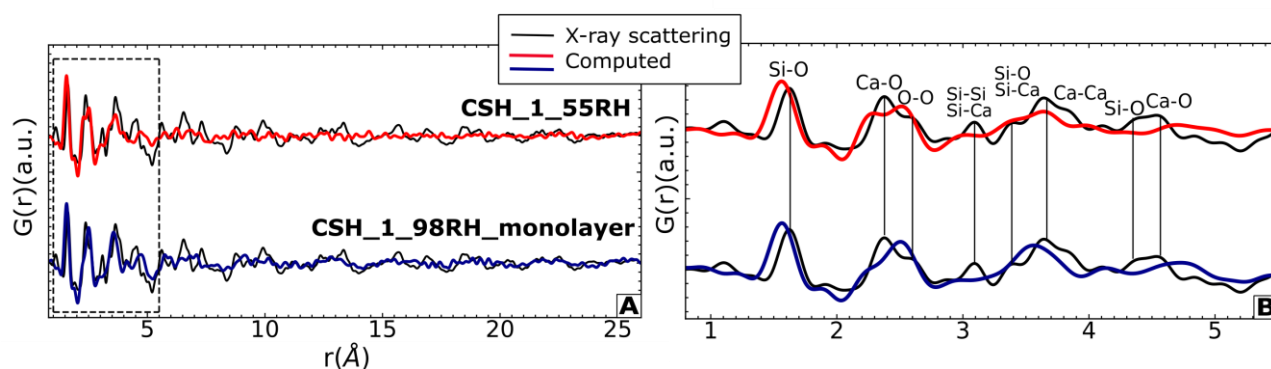
We note, in passing that the assigned stoichiometry of water in our samples may be, at least to some extent, unique to our dataset as the stoichiometry of water in C-(A)-S-H samples is sensitive to defect density (i.e., Ca/Si and Al/Si ratios),<sup>6,106,117</sup> drying method,<sup>51,116</sup> hydration level,<sup>51,105</sup> and sample handling (notably exposure to CO<sub>2</sub>) in ways that remain incompletely understood.

**Table 2.** Water stoichiometry in hydrogenated and deuterated C-(A)-S-H samples conditioned at 55% RH and 98% RH (more detailed stoichiometry in Supporting Information Table S1)

Stoichiometry	Name	H <sub>2</sub> O	D <sub>2</sub> O
Ca <sub>1</sub> Si <sub>1</sub> O <sub>2.8</sub> (OH) <sub>0.4</sub>	CSH_1_55RH_h	1.32	
	CSH_1_55RH_d	0.99	0.42
	CSH_1_98RH_h	3.2	
	CSH_1_98RH_d		3.43
Ca <sub>1</sub> Si <sub>0.8</sub> O <sub>2.43</sub> (OH) <sub>0.59</sub>	CSH_1.27_55RH_h	0.93	
	CSH_1.27_55RH_d	0.58	0.47
Ca <sub>1</sub> Si <sub>1.1</sub> Al <sub>0.11</sub> O <sub>2.8</sub> (OH) <sub>0.4</sub>	CASH_0.9_55RH_h	1.39	
	CASH_0.9_55RH_d	0.85	0.81
Ca <sub>1</sub> Si <sub>0.9</sub> Al <sub>0.09</sub> O <sub>2.63</sub> (OH) <sub>0.45</sub>	CASH_1.1_55RH_h	1.45	
	CASH_1.1_55RH_d	0.55	0.71

### 3.2 C-S-H structure

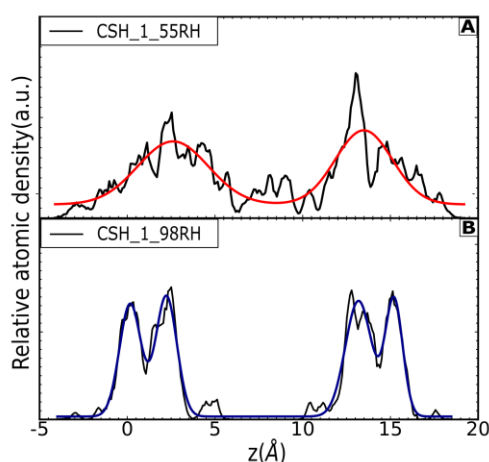
In this section we present the C-S-H models and compare the results of the structural analysis with the experimental X-ray and neutron scattering data. The starting point of our model validation was to compare the experimental X-ray PDF data with the calculated PDFs derived from our MD simulation results (Figure 3).



**Figure 3.** (A) Experimental X-ray PDF of CSH\_1\_55RH (black lines) compared to the computed X-ray PDF for CSH\_1\_55RH (red line, top) and CSH\_1\_98RH\_monolayer (darkblue line, bottom); (B) An enlarged region between 1-5.5 Å.

The first observation after comparing the two calculated PDFs is that the CSH\_1\_98RH\_monolayer is less disordered than the CSH\_1\_55RH structure. The calculated CSH\_1\_98RH\_monolayer PDF broadly reproduces the overall shape of the peaks up to 30 Å, though the intensities of the predicted correlations are generally lower than those observed in the experimental data. The level of discrepancy with the experimental PDFs remains at an acceptable level, with the main peak distances reproduced (though with some shifts) as also reported by previous authors.<sup>21,31,118</sup>

A significantly lower degree of long-range structure is observed in the predicted PDF of the CSH\_1\_55RH sample, with no obvious correlations beyond 5.5-6 Å. This difference can be explained by the presence of an ordered interlayer space in CSH\_1\_98RH containing a full monolayer of water, which stabilizes the structure and prevents the C-S-H layers from collapsing into each other. This effect is clearly demonstrated by the difference between the atomic density profiles of structural calcium atoms of the two structures in the direction normal to the basal surface (Figure 4), where the results for CSH\_1\_55RH (Figure 4A) show that the layers are highly distorted. A possible explanation of this distortion may reside in the simplifications of the CLAYFF force field,<sup>81</sup> notably its reliance on fixed partial charges and its non-bonded representation of interatomic interactions within minerals. Our results suggest that reactive force fields, such as ReaxFF, where atomic charges are calculated at each simulation timestep, may enable a more realistic description of the transition from hydrated to dehydrated C-S-H interlayers.<sup>95,119</sup>

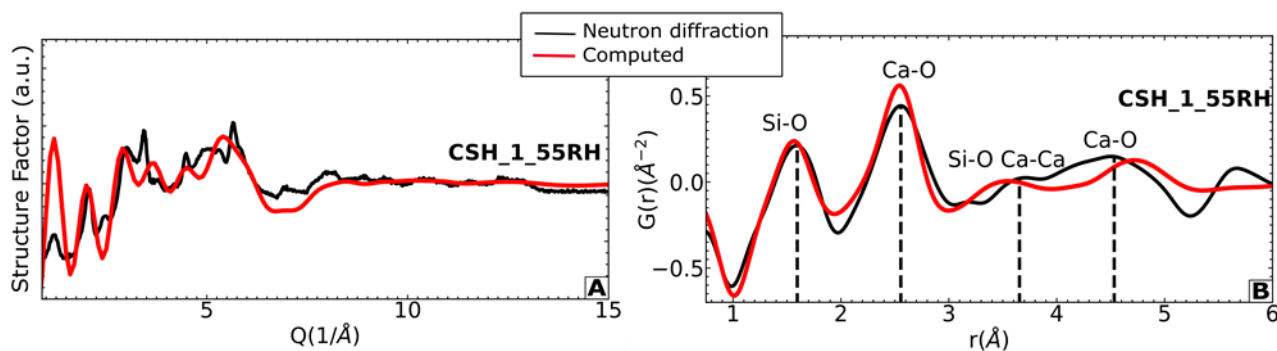


551

552 **Figure 4.** Computed atomic density profiles of structural calcium atoms along the  $z$  direction for  
 553 CSH\_1\_55RH (A) and CSH\_1\_98RH (B), with corresponding Gaussian fits in red and blue.

554 Beyond the unexpectedly high structural distortion in the CSH\_1\_55RH system highlighted in Figure  
 555 4A, the interlayer distance calculated by fitting a Gaussian function through the structural calcium  
 556 density profile yields a predicted basal spacing  $d_{001\text{-MD}} = 11.0(2)$  Å, relatively close to the measured  
 557 value of  $d_{001\text{-XRD}} = 11.6(1)$  Å derived from the XRD measurements. In CSH\_1\_98RH (Figure 4B), the  
 558 higher degree of interlayer hydration yields a larger basal spacing with excellent agreement between  
 559 simulations and experiments ( $d_{001\text{-MD}} = 13.0(2)$  Å vs.  $d_{001\text{-XRD}} = 13.1(2)$ , as reported in Table 1).

560 Comparison of X-ray PDF results over shorter distances (Figure 3B) shows that the two structures  
 561 display similar short-range order. Experimentally, clear peaks are observed at 1.6 Å and 2.4 Å  
 562 corresponding to Si-O and Ca-O correlations, respectively, followed by peaks at 3.1 Å (Si-Si and Si-Ca),  
 563 3.6 Å (Si-O and Si-Ca), 3.8 Å (Ca-Ca), and 4.3 Å (Si-O).<sup>29</sup> The calculated X-ray PDF data reproduce these  
 564 correlations, with a slight shift for some of the peaks in both CSH\_1\_55RH and  
 565 CSH\_1\_98RH\_monolayer. The shifts in the first two peaks, corresponding to Si-O and Ca-O distances,  
 566 can be directly attributed to a limitation of the CLAYFF potentials, as these distances derive directly  
 567 from the force-field parameters. Another explanation for the Si-O distances differing from the  
 568 experimental values could be the Si-O and Si-O-Si bond and angle parameters, which were adapted  
 569 from the INTERFACE force field.<sup>120</sup>



**Figure 5.** (A) Total neutron structure factor and (B) total neutron  $G(r)$  of CSH\_1\_55RH\_h showing the peaks corresponding to the atom pair correlations. Experimental data in black, computed data in red.

The shifts in other peaks are likely due to the limitations of the C-S-H model: the size of the modeled nanoparticle is 44 Å at its longest side and the model clearly lacks crystallinity due to the high concentration of defects. Nonetheless, the main correlations up to 5 Å and their corresponding intensities are reasonably reproduced by the model.

The next step in the model validation was to calculate the neutron scattering patterns, i.e., the total and partial  $S(Q)$  and  $G(r)$  functions (Figure 5). The calculated total structure factor of CSH\_1\_55RH (Figure 5A) reproduces the overall shape of the experimental  $S(Q)$ , but the experimental C-S-H sample presents sharper Bragg peaks, a feature not captured by the calculated  $S(Q)$ .

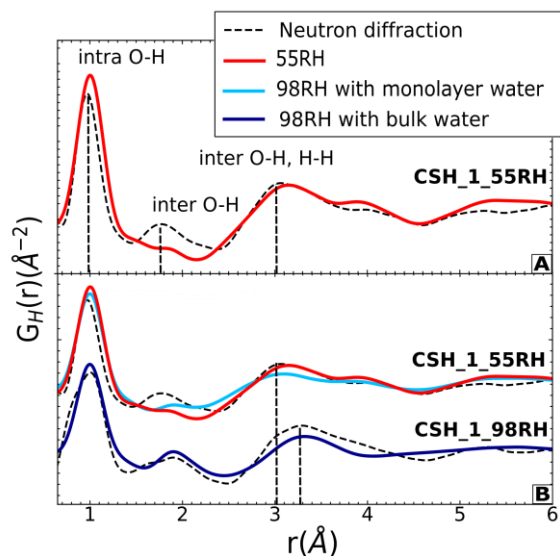
As stated above, this is probably due to the limited size of the coherent domain of our nanoparticle, which does not capture the long-range order that is present in some parts of the C-S-H samples. Still, the model reproduces satisfactorily the background oscillations from the diffuse scattering arising from the presence of water and the inherent disorder of the structure (Figure 5A).

Consideration of the total neutron  $G(r)$  confirms the broad consistency between experimental and computational results (Figure 5B). We note in passing that the experimental  $G(r)$ , derived by a Fourier transformation of the structure factor, becomes unreliable at real-space correlation distances below 0.7 Å, as the scattered intensity was measured only up to a  $Q$ -range of 23.5 Å<sup>-1</sup>.

### 3.3 Water structure

The Fourier transform of the first order difference  $S(Q)$  functions results in a partial  $G_H(r)$ , or partial PDF (Figure 6). The difference function represents the weighted sum of all the correlations functions involving hydrogen atoms. It is, therefore, much more sensitive to the structure of water than the results presented in the previous section. The neutron PDF functions in Figure 6 show overall similarities in the peak intensities and positions of the bulk capillary water in experimental

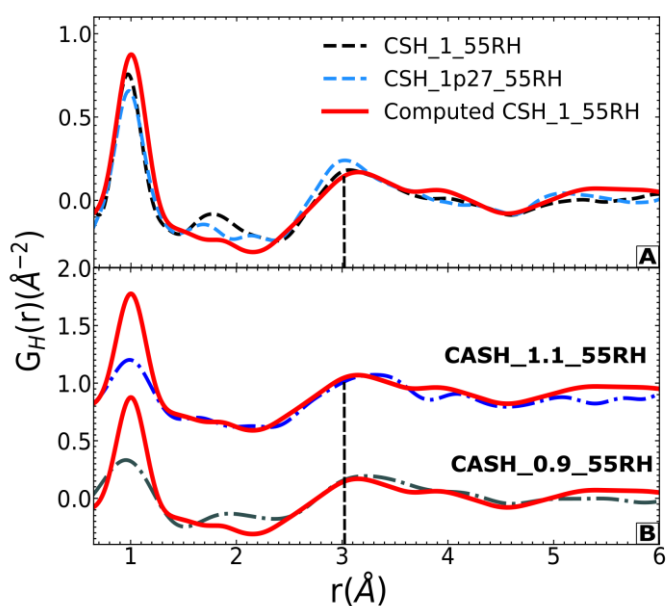
CSH\_1\_98RH\_d-h and in the calculated PDF of CSH\_1\_98RH containing bulk water, shown in dark blue (Figure 6B).



**Figure 6.** (A) Partial neutron PDF of CSH\_1\_55RH\_d-h and computed PDF CSH\_1\_55RH, showing the most significant atom correlations. (B) Partial neutron PDF of experimental (dashed black line) vs calculated CSH\_1\_55RH (red line) and CSH\_1\_98RH with a monolayer of water (light blue line); experimental (dashed black line) vs calculated CSH\_1\_98RH with bulk water (dark blue line)

The first peak at about 1  $\text{\AA}$  corresponds to the intra-molecular O-H distance. The second peak at 1.8  $\text{\AA}$  corresponds to the intermolecular H-bonding. It is clear from Figure 6B that the position and intensity of the intermolecular H-bonding peak is reproduced by the CSH\_1\_98RH model containing bulk water. The red and light blue curves compare the short-range order of interfacial/interlayer water calculated for the CSH\_1\_55RH system and for the CSH\_1\_98RH\_monolayer (i.e., system CSH\_1\_98H considering only interlayer water and the first monolayer of water on the external surfaces) against experimental results obtained for CSH\_1\_55RH (dashed black line). The main difference between these curves is that the intensity of the measured H-bonding peak of the CSH\_1\_55RH\_d-h sample is underestimated by the CSH\_1\_55RH model. Possible explanations for this discrepancy include model limitations as well as potential differences in water content (i.e., the real 55RH sample may contain more water) and NDIS data treatment artefacts associated with the Fourier transformation of the  $S(Q)$  to derive  $G_H(r)$ . A key point of agreement of these curves, however, is in the peak at 3  $\text{\AA}$ . This peak results from intermolecular correlations of the O-H and H-H atoms beyond the second nearest neighbor; therefore, it reflects the structure of the H-bonded water network, rather than that of individual H-bonds recorded by the peak at 1.8  $\text{\AA}$ . At this 3  $\text{\AA}$  peak, our results evidence a significant difference between interfacial/interlayer and bulk-like water, with a shift in peak position from 3.3  $\text{\AA}$  (for bulk-liquid-like water) to 3  $\text{\AA}$  (for interfacial/interlayer water) captured by both experimental and computational results. In particular, the computed PDF of CSH\_1\_55RH captures both the intensity and the peak

position at 3 Å of experimental CSH<sub>1.55</sub>RH<sub>d-h</sub>, thus confirming that the 55% RH results probe interfacial/interlayer water. Further comparison with computed PDF of CSH<sub>1.98</sub>RH<sub>monolayer</sub> reveals that although the position and broadening of the H-bonding peak deviate somewhat from the CSH<sub>1.55</sub>RH data, the position of the intermolecular O-H/H-H peak is within the 3 Å value. A comparison with the bulk-liquid-like water in CSH<sub>1.98</sub>RH reveals a shift of this peak position to a value of 0.2 Å longer than for CSH<sub>1.55</sub>RH. From this we can conclude that the local environment of the first monolayer of water on the surface of C-S-H is very similar to C-S-H containing only interfacial water. Likewise, the structure of water further than 1 monolayer from the surface resembles that of bulk liquid water.



**Figure 7.** (A) Partial neutron PDFs of the experimental CSH<sub>1.27</sub><sub>55RH</sub><sub>d-h</sub> (dashed blue line) compared to experimental and computed CSH<sub>1.55</sub>RH (red line). (B) Partial neutron PDFs of experimental CASH<sub>0.9</sub><sub>55RH</sub><sub>d-h</sub> (dash dotted gray line) and CASH<sub>1.1</sub><sub>55RH</sub><sub>d-h</sub> (dash dotted blue line) compared to the computed CSH<sub>1.55</sub>RH.

Comparison with NDIS results obtained for other samples reveals that the same features of the short-range order of water are found for the CSH<sub>1.27</sub> sample (Figure 7A) as well as for the C-A-S-H samples with Ca/Si = 0.9 and 1.1. The experimental C-A-S-H PDFs have lower peak intensities and broader peaks than the corresponding C-S-H PDFs (Figure 7B), likely because a smoothing window was required to compensate for the higher signal-to-noise ratio of the C-A-S-H data (particularly when extracting the difference signal between the deuterated and hydrogenated samples).

The similar local structure of interfacial/interlayer water in our C-A-S-H and C-S-H samples is consistent with a first-order approximation according to which the structure of C-A-S-H is similar to that obtained by substituting bridging Si by Al in C-S-H.<sup>15</sup> In our samples, one tenth of Si atoms were

643 substituted by Al, apparently with only limited effect on the structure of interfacial/interlayer water.  
644 At higher Al/Si ratios, however, the structure of water in C-A-S-H may be different due to the increased  
645 density of surface Ca ions required to charge balance structural Al.

646 Grangeon et al.<sup>11</sup> showed that the maximum Ca/Si ratio achievable by removing bridging silica  
647 tetrahedra without precipitating portlandite is around 1.25.<sup>11</sup> Therefore, we suggest that the local  
648 environment of water is dictated by the manner in which defects are introduced. Considering that in  
649 CSH\_1\_55RH and CSH\_1.27\_55RH defects can be created by removing the bridging silica tetrahedra,  
650 we presume that the structure of interfacial/interlayer water is similar for samples with these two  
651 Ca/Si values. To achieve higher Ca/Si ratios it would be necessary to introduce calcium ions in the  
652 interlayer or in the larger pores, leading to portlandite precipitation and, thus, probably creating a  
653 different water environment.

654 Finally, deviations in interfacial/interlayer water structure relative to bulk water are shown by  
655 comparing the Ow-Ow, Ow-Hw, and Hw-Hw pairs partial radial distribution functions of the calculated  
656 bulk water, CSH\_1\_55RH, and CSH\_1\_98RH\_monolayer structures (Figure S7 in Supporting  
657 Information). Overall, there are clear differences between the partial RDFs of bulk water and  
658 interfacial/interlayer water in our C-S-H models. The distance of the first Ow-Ow correlation of  
659 interfacial/interlayer water is clearly shifted by  $\sim 0.2$  Å with respect to that of the bulk water. The first  
660 minima and the second peak are shifted from the bulk water by  $\sim 0.9$  Å for CSH\_1\_98RH\_monolayer  
661 and by  $\sim 1$  Å for CSH\_1\_55RH. In the Ow-Hw correlations the H-bonding peak at  $\sim 1.67$  Å is lower than  
662 in bulk water for CSH\_1\_55RH, and almost absent in CSH\_1\_98RH\_monolayer. The Hw-Hw correlations  
663 show the greatest deviations from bulk water, with the second peak almost absent and a much  
664 broader and weaker third peak.

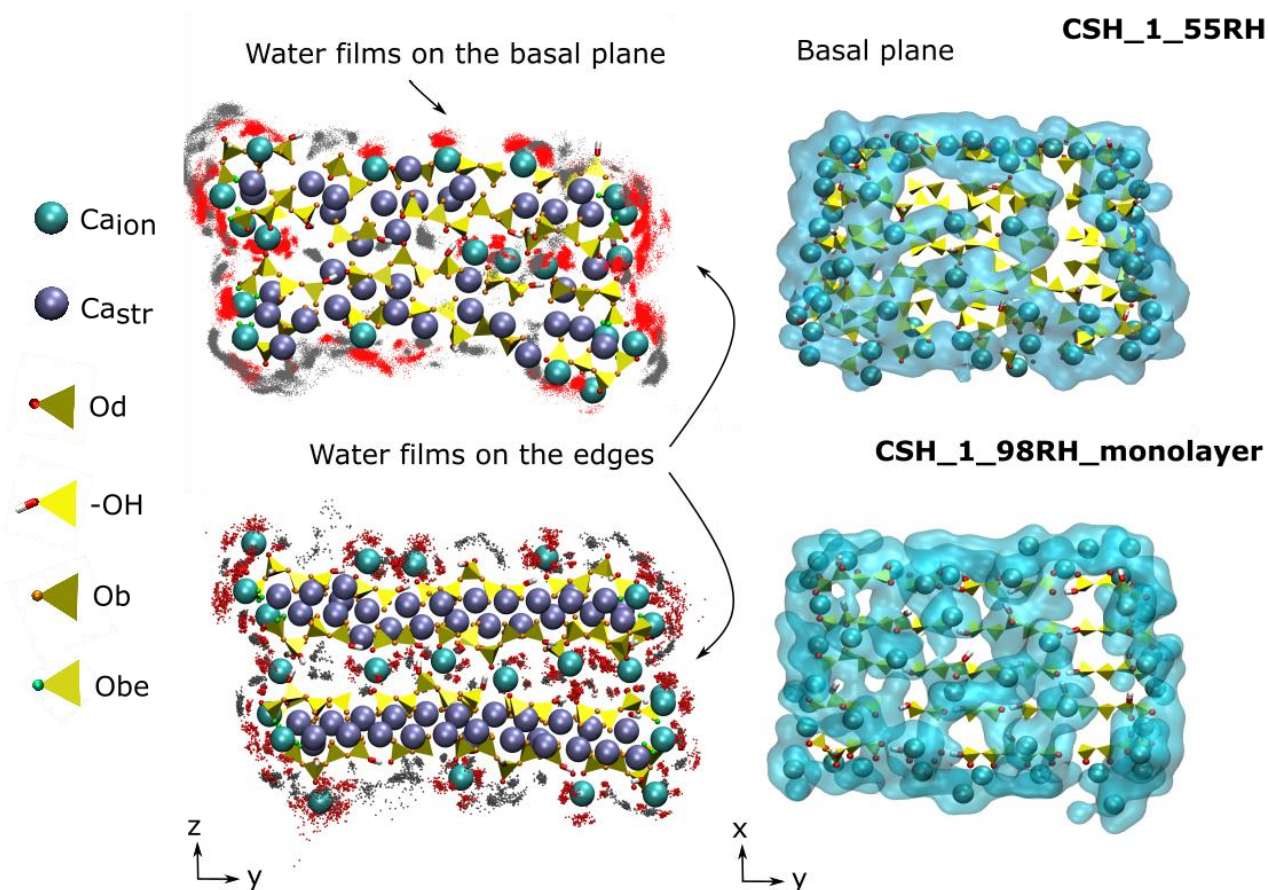
665 These findings are in agreement with the results of Youssef et al.<sup>52</sup>, who showed that confined water  
666 (interlayer and interfacial water) shows signs of distortion from the tetrahedral arrangement of bulk  
667 water when confined between C-S-H layers. They proposed that the extended Ow-Ow correlations are  
668 due to disordered hydrophilic C-S-H surfaces, with strong solvation effects of Ca ions and a quasi-two-  
669 dimensional confining geometry of C-S-H surfaces.<sup>52</sup> Our results support this notion that the very  
670 hydrophilic nature of C-S-H surfaces promotes a highly structured distribution of interfacial water.

### 671 **3.4 Distribution of interfacial and interlayer water on a C-S-H nanoparticle**

672 Predicted water distribution within our two C-S-H nanoparticulate systems, CSH\_1\_55RH and  
673 CSH\_1\_98RH\_monolayer, is shown in Figure 8. As mentioned above, a first qualitative assessment  
674 reveals that the structure of the CSH\_1\_98RH model is less distorted than that of CSH\_1\_55RH. This  
675 difference in crystallinity is observed at distances greater than 6 Å in the experimental PDFs (see  
676 Figure 3). This is likely due to the fact that the interlayer space of CSH\_1\_98RH is filled with water



677 molecules, which have a stabilizing influence on the interlayer, affecting the crystallinity of the  
 678 particle.<sup>121</sup> Although the structural distortion of our CSH\_1\_55RH model may reflect a limitation of the  
 679 force field used here, another potential explanation is the small size and isolated nature of our model  
 680 C-S-H nanoparticle. In real C-S-H samples, nanoparticles are agglomerated together within a larger  
 681 solid matrix, which may help mitigate the stresses associated with sample drying.



682

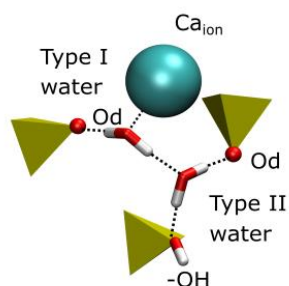
683 **Figure 8.** (top left) Cross-section of CSH\_1\_55RH after 5 ns. Type I and type II water oxygens (red and  
 684 grey dots, respectively) are shown as a cloud of coordinates sampled over a 5 ns trajectory. (bottom left)  
 685 Same as the previous panel for CSH\_1\_98RH\_monolayer sampled over 0.1 ns. Water forms thin films on  
 686 the external surfaces and in the interlayer nanopore. (top and bottom right) Distribution of water on the  
 687 upper external basal surface of the CSH\_1\_55RH and CSH\_1\_98RH nanoparticles. Water molecules  
 688 (transparent blue surfaces) surround  $\text{Ca}^{2+}$  ions (turquoise spheres), confirming that these cations  
 689 correspond to the most hydrophilic areas on the C-S-H surface.

690 Indeed, whereas the diffuse scattering is well represented (see Figure 5A) in the calculated diffraction  
 691 patterns for our C-S-H nanoparticle, these calculated patterns lack the Bragg peaks observed in the  
 692 experimental patterns. This implies that the nanoparticle is probably too small to possess a coherent  
 693 domain size able to reproduce the periodicity of the real sample. In small nanoparticles, the  
 694 comparatively high importance of surface energy (vs. bulk energy) can result in significant structural  
 695 relaxation,<sup>122</sup> as observed in our 55RH model. In this context, the greater distortion of the 55RH than

696 the 98RH model suggests more unfavorable interfacial energy at the lower hydration level, in  
697 agreement with almost twice lower coordination number of  $\text{Ca}^{2+}$  with water molecules,  $N_{\text{Ca-H}_2\text{O}}$ ,  
698 predicted for CSH\_1\_55RH than for CSH\_1\_98RH\_monolayer ( $\text{H}_2\text{O}$  per  $\text{Ca}^{2+}$  1.8 vs. 3.4, respectively).

699 Bearing in mind the above-mentioned differences in crystallinity between the two models, we now  
700 characterize the water distribution and H-bonding characteristics of interfacial and interlayer water.  
701 Due to the presence of highly negatively charged deprotonated surface oxygens (Od) and bridging  
702 edge oxygens (Obe), the surface of C-S-H is negatively charged. This controls the distribution of  $\text{Ca}^{2+}$   
703 ions on the surfaces and in the interstitial cavities created by defects. In turn, these adsorbed  $\text{Ca}^{2+}$  ions  
704 are strong centers of charge that generate hydrophilic centers at the surface.<sup>123–125</sup> According to our  
705 simulations, most calcium ions are bonded to the deprotonated oxygen atoms at the surface, forming  
706 inner-sphere complexes, and they complete their coordination shell using water molecules. Therefore,  
707 for both CSH\_1\_55RH and CSH\_1\_98RH\_monolayer, we discriminate between two types of water  
708 molecules on the C-S-H surface: (i) type I water molecules are those that coordinate surface Ca ions,  
709 while (ii) type II water includes all other interfacial/interlayer water molecules. Importantly, type I  
710 water molecules hardly accept any H-bonds, since the O atom of these molecules points towards the  
711  $\text{Ca}^{2+}$  ion as shown by the results of neutron diffraction<sup>126</sup> and molecular orbital calculations.<sup>123</sup>

712 According to our simulations, in CSH\_1\_55RH, type I water represents 61% of the water in the sample,  
713 which is roughly 1.8  $\text{H}_2\text{O}$  per Ca ion. The distribution of locations sampled by type I and type II water  
714 molecules during a 5 ns trajectory is highlighted in Figure 8 as red and grey dots, respectively. Both  
715 types of water predominantly form thin films on the basal and edge surfaces, representing 89% of the  
716 total water, with the remainder observed in the distorted interlayer. Type I water molecules donate  
717 the majority of H-bonds to deprotonated silanol oxygens (Od) and to water oxygens (Ow). The  
718 deprotonated oxygens receive about 0.5 H-bonds per Od with an average bond length ( $d$ ) of 1.73 Å,  
719 and water oxygens receive roughly 0.3 H-bonds per Ow with  $d = 1.99$  Å. Type II water molecules  
720 interact more strongly with deprotonated silanol oxygens (0.7 H-bonds accepted per Od with  $d = 1.66$   
721 Å) and less strongly with water oxygens (0.12 H-bonds received per Ow with  $d = 2.06$  Å). Both types of  
722 water donate fewer H-bonds to the hydroxyl groups of surface silanols (0.2 H-bonds in total per Oh  
723 with  $d = 1.97$  Å).



724

725 **Figure 9.** Examples of some of the typical connections formed at the surfaces of the C-S-H nanoparticle.  
 726 Ca ions (turquoise) coordinate type I water oxygens (red and white licorice), which donate H-bonds to  
 727 deprotonated oxygens (red sphere) of surface silanols (yellow polyhedra) and to type II water molecules.  
 728 The type II water molecules accept H-bonds from type I water molecules and donate H-bonds to  
 729 deprotonated oxygens (red sphere) of surface silanols (yellow polyhedra) and to the oxygen (red and  
 730 white licorice) of surface silanols (yellow polyhedra).

731 The cross-section of CSH\_1\_98RH\_monolayer reveals that the structure is much less distorted than  
 732 that of CSH\_1\_55RH (Figure 8). The relative abundance of water in CSH\_1\_98RH allows the interlayer  
 733 to be filled with water as seen by the interlayer spacing of about 13 Å (XRD value 13.1(2) Å for a fully  
 734 hydrated C-S-H, Supporting Information Figure S1C).

735 The water molecules coordinated around calcium ions in the interlayer prevent the C-S-H layers from  
 736 collapsing into each other (Figure 4). In this simulation, the amount of water present in the interlayer  
 737 is 26% of the total. Hence, the ratio of interlayer water to interfacial water is roughly 2.5 times that of  
 738 CSH\_1\_55RH. Not surprisingly, the larger share of the interlayer water affects the overall distribution  
 739 and H-bonding behavior of water molecules in CSH\_1\_98RH. More precisely, in our  
 740 CSH\_1\_98RH\_monolayer, type I water comprises 53% of the total (i.e., about 530 out of 1000 water  
 741 molecules found in the first monolayer from the C-S-H surface), so approximately 3.4 H<sub>2</sub>O per Ca<sup>2+</sup>.  
 742 (Figure 8). As in CSH\_1\_55RH, type I water donates the majority of H-bonds to the surface of C-S-H and  
 743 to other water molecules (Figure 9). However, it donates not only to Od (0.8 H-bonds received per Od  
 744 with  $d = 1.68$  Å), but also to the surface bridging oxygens Ob (0.2 H-bonds per Ob,  $d = 1.85$  Å), and  
 745 bridging edge oxygens Obe (0.2 H-bonds accepted per Obe,  $d = 1.91$  Å). Type II water molecules donate  
 746 a significant majority of H-bonds to the surface deprotonated oxygens Od, about 1.3 H-bonds per Od  
 747 with  $d = 1.66$  Å (Figure 9). The rest of H-bonds is shared between other water molecules (0.3 H-bonds  
 748 received per Ow,  $d = 1.96$  Å), and surface bridging oxygens (0.2 H-bonds per Ob,  $d = 1.86$  Å) and  
 749 hydroxyl oxygens (0.4 H-bonds per Oh atom,  $d = 1.95$  Å). The latter is contrary to CSH\_1\_55RH, where  
 750 silanol hydroxyl groups are quite hydrophobic. The reason is likely due to the abundance of water  
 751 molecules in CSH\_1\_98RH, which provides more H-bonding opportunities and the possibility of  
 752 creating an H-bonding network.

Overall, the interfacial water properties and structure are mostly similar in the partially hydrated system (CSH\_1\_55RH) and in the first monolayer of the fully hydrated system (CSH\_1\_98RH\_monolayer). Observed differences in interfacial water structure in the two systems are ascribed to the greater degree of Ca hydration, fully hydrated interlayer, and the presence of bulk water in the fully hydrated system.

#### 4 CONCLUSION

We have established an *in silico* nanoparticle model for C-S-H and validated it using experimental data. This combined approach enabled us to study the properties of the different types of water present in C-S-H conditioned at varying relative humidity values. We also compared our results to a low-CO<sub>2</sub> substitute for C-S-H, C-A-S-H. The results show consistent structural characteristics of water for the C-S-H samples with the two Ca/Si ratios studied (1 and 1.27) as well as for the C-A-S-H samples. The main mechanism for water adsorption is the coordination of water by hydrophilic Ca<sup>2+</sup> ions, which induces a strong H-bond network with other water molecules and with surface oxygen atoms. The silanol groups play a minor role in this wettability mechanism: the C-S-H surface is characterized by a combination of wet and dry regions, where wet areas are dominated by the presence of hydrophilic calcium ions with strong hydration shells (Figure 8), whereas dry areas expose only silica chains and silanol hydroxyls.

The results of the simulations show that the presence of water in C-S-H can have a strong influence on the atomistic-level integrity of the layered structure. As shown in Figures 3 and 8, the more hydrated structure shows a larger degree of mesoscale ordering, with a larger domain coherent size. This effect could be due to the fact that the modelled C-S-H nanoparticle contained only two silicate layers, such that the interactions of water molecules with the surface played a large role in the total intermolecular interactions within the whole system. Similar results, where the water molecules exert a strong influence on the bulk properties of inorganic nanoparticles, have been presented previously for other systems.<sup>127</sup>

The wettability mechanism depicted here is susceptible to change at higher Ca/Si ratios, with the formation of secondary portlandite. Whereas the exact location of the (nano)portlandite phase is still a matter of discussion,<sup>11</sup> its presence and different surface structure could modify the overall structural characteristics of the adsorbed water. Future experiments with samples containing higher Ca/Si ratios should be performed to verify this hypothesis.

## 783 SUPPORTING INFORMATION

784 Neutron diffraction with isotopic substitution method theory, XRD, TGA, ATR FT-IR, and WSI results,  
785 water stoichiometry, creating defects in C-S-H model, MD parameters of the CSH\_1\_55RH and  
786 CSH\_1\_98RH model systems, example of partial charges calculations, synthesis amounts, synthesis and  
787 conditioning protocol, radial distribution functions for water, the total H<sub>2</sub>O/Si vs Ca/Si.

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