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## The atomic structure of imogolite nanotubes: A 50 years old issue reinvestigated by X-ray scattering experiments and molecular dynamics simulations

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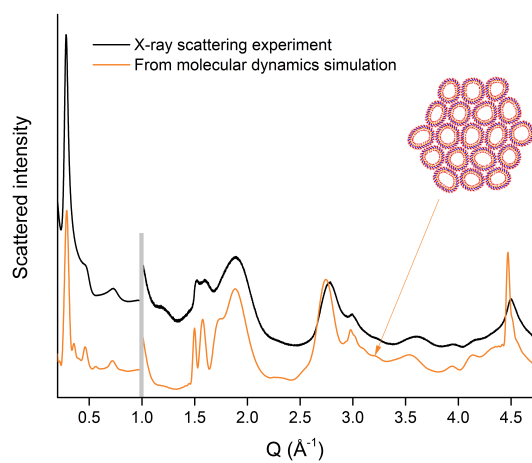
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## Graphical Abstract

**The atomic structure of imogolite nanotubes: a 50 years old issue reinvestigated by X-ray scattering experiments and Molecular Dynamics simulations**

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## Highlights

**The atomic structure of imogolite nanotubes: a 50 years old issue reinvestigated by X-ray scattering experiments and Molecular Dynamics simulations**

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- The atomic structure of synthetic imogolite nanotubes is revisited.
- X-ray scattering experiments are coupled to molecular dynamic simulations.
- Nanotubes with  $N = 13$  or  $14$ ,  $N$  being the number of  $\text{SiO}_4$  units along a circumference, are identified.
- Deformations of tubes in bundles must be taken into account in the analysis of the X-ray scattering diagrams.

# The atomic structure of imogolite nanotubes: a 50 years old issue reinvestigated by X-ray scattering experiments and Molecular Dynamics simulations

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## Abstract

Imogolites are clay nanotubes consisting of a curved di-octahedral gibbsite-like layer  $[(OH)_3AlO_3]$  and of isolated  $(OH)SiO_3$  tetrahedra connected by three mutual oxygen atoms to the octahedra, with  $N$  silicon tetrahedra along a circumference. There is a consensus that synthetic imogolites have a larger  $N$  value than natural ones, which may depend on the method of synthesis. However,  $N$  values reported in the literature over the last fifty years are given as uncertain or are not consistent. In this work, we reinvestigate the structure of synthetic imogolite nanotubes for which a value of  $N = 12$  was reported. We perform X-ray scattering experiments on nanotubes in suspension and on the same sample as a dry powder after removing water. The analysis of diffractograms is based on Molecular Dynamics simulations allowing us to

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obtain imogolite nanotubes with different  $N$  values. We find that the sample is made of a mixture of nanotubes with  $N = 13$  and  $N = 14$ . Our study points towards strong deformation of the nanotubes, assembled in bundles, in their dry state, which has to be taken into account in the analysis of measured diffractograms.

*Keywords:* imogolite, nanotube, structure, X-ray scattering, Molecular Dynamics simulations

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## 1. Introduction

Fine fibrous aluminosilicate clay particles, named imogolite, were first reported in 1962 in Japan (Yoshinaga and Aomine, 1962). Since then, they have been found worldwide as a recurrent component in soils developed from volcanic ash or in weathered pyroclastic deposits. Despite many studies, their structure remained a mystery during the ten years following their discovery. The first structural models involved paracrystalline order and various chains of  $AlO_6$  octahedra linked sideways by  $SiO_4$  tetrahedra (Wada, 1967; Wada and Yoshinaga, 1969; Russel et al., 1969). An important milestone was the determination of the morphology of an imogolite fiber by high resolution electron microscopy in 1970 (Wada et al., 1970). The fibre unit observed in micrographs corresponds to a hollow tube with an inner diameter of 0.7–1 nm and an outer diameter of 1.7 – 2.1 nm (Wada et al., 1970). Two years later, Cradwick et al. (1972) proposed a structural model accounting for this tubular shape in an article which is still a must-read. The nominal composition of imogolite nanotubes (INT) is established to be  $Al_2SiO_7H_4$ . An imogolite nanotube consists of a curved di-octahedral gibbsite-like layer

18 [AlO<sub>6</sub>] and of isolated SiO<sub>4</sub> tetrahedra connected by three mutual oxygen  
 19 atoms to the octahedra (Fig. 1(a)), with the apex of the tetrahedra pointing  
 20 inside the nanotube (Fig. 1(b)). H atoms are bounded to O atoms on outer  
 21 and inner surfaces. The nanotube's point group is C<sub>2N<sub>h</sub></sub> and it is periodic  
 22 along its long axis with a period  $T \approx 8.4 \text{ \AA}$  (Fig. 1(c)). Equivalently with  
 23 the formalism used to describe carbon nanotubes, INTs can be characterized  
 24 by a chiral vector  $(N, 0)$ <sup>1</sup> (Guimarães et al., 2007; Monet et al., 2018).  $N$  is  
 25 the number of SiO<sub>4</sub> tetrahedra on a circumference, as shown in Fig. 1(b).

26 A drawback of natural imogolites is that they do not form large deposits  
 27 compared to other clay minerals, implying their separation from parent ma-  
 28 terials. By working on the formation conditions of INTs in the environment,  
 29 Farmer et al. (1977) were the first to propose a synthesis protocol for imogo-  
 30 lite. Their approach consisted in hydrolyzing a dilute solution of aluminum  
 31 chloride and monomeric orthosilic acid in presence of sodium hydroxide, fol-  
 32 lowed by an acidification step to adjust the pH below 5. This suspension  
 33 was heated during almost five days. Modulations of the synthesis conditions  
 34 were further reported by the same group two years later (Farmer and Fraser,  
 35 1979). They varied the precursors ratios, changed the anion species of the  
 36 Al inorganic salt (ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>, used salt-free solutions of organic  
 37 precursors (ASB: aluminum-tri-*sec*-butoxide and TEOS: tetraethoxysilane).

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<sup>1</sup>Each atomic corona is achiral, i.e. it is superimposable on itself after a mirror op-  
 eration, the mirror plane containing the axis of the tube, as it is the case for  $(N, 0)$   
 single-walled carbon nanotubes. But atomic corona cannot be in phase one with the other  
 because of their different radii. One cannot superimpose their individual mirror planes  
 and, interestingly, the whole nanotube structure is chiral.

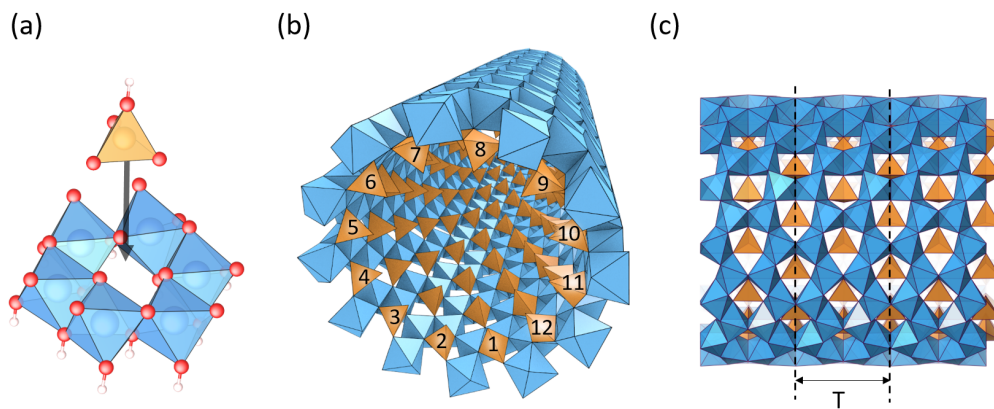


Figure 1: (a) Local view of the di-octahedral gibbsite-like layer and of the location of an  $SiO_4$  tetrahedron, being the  $AlO_6$  octahedra being in blue and the  $SiO_4$  tetrahedron in orange; oxygen atoms are in red and hydrogen ones are white; (b) three-dimensional representation of a  $N = 12$  nanotube; (c) side-view of the nanotube, evidencing its period  $T$ .

38 The optimum temperature of synthesis was found around  $100^\circ\text{C}$ . Since then,  
 39 most of the studies were generally based on one or the other of these proto-  
 40 cols (inorganic or organic route) with marginal changes. However, we should  
 41 not overlook the remarkable study conducted by Shin-ichiro Wada, who in-  
 42 vestigated over a period of seven years the synthesis of imogolite at room  
 43 temperature in conditions similar to their formation in natural environment  
 44 (Wada, 1987).

45 Both natural and synthetic imogolite nanotubes are found to be rather  
 46 monodisperse in diameter. The outer diameter of INTs is classically deduced  
 47 from observations by transmission electron microscopy (TEM) (Wada et al.,  
 48 1970, 1972, 1979; Wada, 1987; Koenderink et al., 1999; Bursill et al., 2000;  
 49 Mukherjee et al., 2005) or from the intertube distance determined by electron

50 diffraction or X-ray scattering (XRS) (Cradwick et al., 1972; Barrett et al.,  
51 1991; Yang and Su, 2007; Bonelli et al., 2009; Kang et al., 2010; Thill et al.,  
52 2012; Hongo et al., 2013; Lee et al., 2014; Amara et al., 2015; Du et al., 2017;  
53 Liao et al., 2018). We shall discuss later the drawbacks of determining the  
54 intertube distance from the position of the first diffraction peak. A review of  
55 the literature over the past 50 years shows an overall increase in outer diam-  
56 eter and in intertube distance for synthetic INTs compared to natural ones,  
57 except for the ones synthesized at room temperature (Table S1). The nature  
58 of the anions seems to allow a modification of the diameter (Yucelen et al.,  
59 2012). The diameter values obtained from different references appear coher-  
60 ent for natural INTs and for INTs synthesized with  $\text{Si(OH)}_4/\text{AlCl}_3/\text{NaOH}$   
61 precursors. Some discrepancies on the reported diameters are evidenced for  
62 nanotubes synthesized using  $\text{TEOS}/\text{AlCl}_3/\text{NaOH}$  and  $\text{TEOS}/\text{ASB}/\text{HClO}_4$   
63 precursors, which are most likely related to the limit of the experimental  
64 measurements or to biases in some analyses.

65 The diameter values are directly related to the number  $N$  of silicon atoms  
66 along a circumference (Fig. 1(b)). Numerical simulations calculate a well-  
67 defined minimum of energy as a function of the number  $N$  of silicon atoms  
68 along the nanotube circumference. However, these simulations cannot be  
69 used to predict the value(s) of  $N$  since they are performed in vacuum and do  
70 not take into account the interactions between the nanotube and its synthesis  
71 environment. Very few articles dealt with the determination of  $N$ , i.e. the  
72 determination of the atomic structure of the nanotube, either for natural  
73 and synthetic INTs. Their conclusions are reported in Table 1. It will be  
74 discussed in more details in section 3.5. However, both uncertainty in  $N$



75 values for a given type of nanotube and discrepancies between  $N$  values for  
 76 the same type of nanotube are already evident in Table 1.

Table 1: Value of the integer  $N$  defining the number of silicon atoms along a circumference for natural and synthetic nanotubes, as deduced from the analysis of electron diffraction (in blue) or X-ray scattering (in black) experiments. TEOS: Tetraethoxysilane; ASB: Aluminum-tri-*sec*-butoxide.

Type	Synthetic precursors	N value	Ref.
Natural	-	10 or 11 or 12	Cradwick et al. (1972)
	-	10 or 11	Alvarez-Ramírez (2007)
Synthetic	TEOS/AlCl <sub>3</sub> /NaOH	12	Alvarez-Ramírez (2007)
	TEOS/ASB/HClO <sub>4</sub>	12 or 14	Kang et al. (2010)
	Na <sub>4</sub> SiO <sub>4</sub> /AlCl <sub>3</sub> /NaOH	13	Alvarez-Ramírez (2007)
		10 or 12	Guimarães et al. (2007)

77 After this review of the structural studies of imogolite nanotubes over  
 78 the last fifty years, it appears that little progress has been made since the  
 79 seminal article of Cradwick et al. (1972). Natural and synthetic INTs have  
 80 the same point group  $C_{2Nh}$  and nominal composition ( $Al_2SiO_7H_4$ ), but the  
 81 values of the integer  $N$ , which defines their structures, have not been unam-  
 82 biguously determined. In this framework, we re-investigate the structure of  
 83 synthetic INTs (TEOS/AlCl<sub>3</sub>/NaOH), for which external diameters ranging  
 84 from 2.2 to 3.2 nm were reported, together with a value of  $N$  equal to 12  
 85 (see Tables 1 and S1). We propose a complete X-ray scattering (XRS) study,  
 86 combining laboratory and synchrotron radiation experiments on nanotubes  
 87 either in suspension or in dry powder. The analysis of XRS diagrams is  
 88 based on Molecular Dynamics (MD) simulations performed to obtain ther-

malized INTs with different values of  $N$ . The calculated XRS diagrams are compared to the experimental ones. We find that the sample is made of a mixture of nanotubes with  $N = 13$  and  $N = 14$ . Our analysis points towards strong deformation of the nanotubes in their dry state, which makes the analysis of XRS diagrams tricky. Finally, previous XRS investigations from the literature are discussed in the perspective of our results.

## 2. Material and methods

### 2.1. Sample preparation and characterization

Imogolite nanotubes were synthesized from a solution of TEOS with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and NaOH as detailed in Belorizky et al. (2010). After hydrothermal synthesis, the suspension was purified by diafiltration with ultra-pure water and concentrated by ultrafiltration. A part of the original purified suspension was kept for determining the morphology of the nanotubes by transmission electron microscopy (TEM). A highly dilute dispersion of imogolite nanotubes was prepared at  $1 \text{ mg}\cdot\text{mL}^{-1}$  in ethanol and then a drop was laid on a carbon-coated copper grid. TEM observations were made using a JEOL1400 microscope from Imagerie-Gif core facility, operated at 120 kV. The length and diameter distributions were determined using the Fiji software (Schindelin et al. (2012)). The rest of the suspension was dried in an oven at  $60^\circ\text{C}$ . The resulting thin film was crushed and sieved ( $100 \mu\text{m}$  mesh size) in order to obtain a fine powder. Based on thermogravimetric analysis (TGA) - see S.I. and figure S1, the dried powder used for XRS measurements was heated at  $200^\circ\text{C}$  for 2 hours.

112 *2.2. X-ray scattering experiments*

113 Measurement on the liquid suspension was carried out on an X-ray source  
114 produced by a Cu rotating anode (MORPHEUS platform, Laboratoire de  
115 Physique des Solides). The beam was collimated and monochromatized by  
116 parabolic confocal W/Si multilayers mirrors (Osmic), providing a  $0.6 \text{ mm}^2$   
117 beam at a wavelength of  $\lambda = 1.5418 \text{ \AA}$ . The INT suspension was held in  
118 a borosilicate glass capillary of 1 mm diameter (WJM-Glas, Müller GmbH,  
119 Germany). A two-dimensional diffraction pattern was acquired on a MAR  
120 detector with  $150 \mu\text{m}$  pixel size, the sample to detector distance being fixed  
121 to 300 mm. The scattered intensity as a function of the wavevector  $Q$  was  
122 obtained by angular integration of the two-dimensional pattern. Geomet-  
123 ric and polarization corrections together with correction for air adsorption  
124 between the sample and the detector were applied to the data.

125 Dehydrated imogolite nanotubes were obtained by heating at  $200^\circ\text{C}$  dur-  
126 ing 2h a powder held in a borosilicate glass capillary (diameter 0.7 mm).  
127 The capillary was flame-sealed immediately after hot removal from the oven  
128 to avoid any water adsorption from atmospheric air. X-ray scattering data  
129 were collected at the SOLEIL synchrotron, on the CRISTAL beamline us-  
130 ing the 2-circle powder diffractometer equipped with 9 silicon-strip detectors  
131 (Mythen2 , Dectris Ltd). The monochromatic X-ray beam with a wavelength  
132 of  $\lambda = 0.7287 \text{ \AA}$  was extracted from the U20 undulator beam by means of  
133 a Si (111) double monochromator. Synchrotron radiation is linearly polar-  
134 ized in the plane of the storage ring, so no polarization correction is required  
135 for measurements carried out in the vertical plane as it is the case with the  
136 2-circle goniometer on CRISTAL beamline.

137 *2.3. Molecular dynamics simulations*

138 The first simulated system consists of isolated nanotubes, having  $N = 13$   
139 or 14 Si atoms along their circumference and composed of eleven unit cells  
140 along the nanotube axis  $z$ , with periodic boundary conditions applied along  
141 all dimensions of the simulation box. The period  $T$  along the long axis  
142  $z$  is fixed to 8.45 Å, to account for the experimental XRS data. Molec-  
143 ular dynamics (MD) simulations were performed with the LAMMPS code  
144 (Plimpton (1995)), using a version of the CLAYFF force field (Cygan et al.  
145 (2004)) integrating the recent improvements proposed for imogolite nan-  
146 otubes (Scalfi et al. (2018)), further refereed to as the *extended CLAYFF*  
147 force field (eCLAYFF). Coulomb interactions were handled with a solver  
148 that performs Ewald summation in k-space, the accuracy being equal to  
149  $10^{-5}$ ; the cut-off distance of the Lennard-Jones potential was chosen equal to  
150 8.5Å in order to avoid an atom to be in interaction with itself. The CLAYFF  
151 forcefield is widely used in the literature when one is concerned with clay-  
152 like materials. In a recent article, Cygan et al. (2021) reviewed its success  
153 in predicting properties of bulk nanoporous materials and their interfaces ;  
154 an entire paragraph is devoted to nanoporous materials with channels-like  
155 geometries and in particular to imogolite. The minimum energy state of our  
156 models was found by first performing an energy minimization at  $T = 0$  K, us-  
157 ing the Polak-Ribiere version of the conjugate gradient (CG) algorithm (until  
158 the net forces in the model is lower than  $10^{-7}$  kcal/(mol.Å)). Minimization  
159 was followed by a 10 ps long NVT simulation at 300 K, using a Nosé-Hoover  
160 thermostat, with timestep 0.5 fs.

161 In a second step, in order to study the bundling of tubes, three different

162 bundles made of 19 tubes were built by MD: two with INTs having  $N = 13$   
163 or  $N = 14$  and one with a mix of 10 tubes having  $N = 14$  and 9 tubes having  
164  $N = 13$ . The bundle with  $N = 14$  INTs was obtained by packing the nan-  
165 otubes organized on a two-dimensional (2D) hexagonal lattice with a lattice  
166 parameter  $d = 27 \text{ \AA}$  ( $26.5 \text{ \AA}$  for  $N = 13$ ) and re-minimizing the energy of the  
167 entire bundle, considering only one unit cell along the  $z$  axis to minimize cal-  
168 culation time. The mixed bundle was obtained by positioning, at the lattice  
169 sites (lattice parameter  $d = 27 \text{ \AA}$ ), tubes having either  $N = 13$  or  $N = 14$   
170 depending on the extraction of a random number. The three bundles were  
171 first minimized at 0 K. The resulting models contain bundles of parallel tubes  
172 having a compact arrangement and an almost perfect circular cross section.  
173 With a view to studying the influence of the deviation of the tubes' cross  
174 section from this perfect circular case on the diffraction diagram, we intro-  
175 duced an anisotropic distribution of deformations around the tubes' surface  
176 inside the bundles. This was done by adding a layer of water – 4 to 5 wt%  
177 in mass – at different positions around the bundle and further by raising the  
178 temperature to 500 K for 10 ps, so that (i) shape deformation modes can  
179 be thermally activated and (ii) the water molecules can exert random and  
180 inhomogeneous forces on the tubes. In a final step, all the water molecules  
181 were removed from the models and the bundle was further equilibrated at  
182 300 K for 10 ps (we have checked that the equilibrium is reached at 10 ps:  
183 the temperature of the system is found to be between 290 and 310 K after  
184 1 ps). This operation worked perfectly: the bundles obtained this way are  
185 formed by a set of tubes with significant -but realistic and energy viable-  
186 radial deformations. The calculation of the XRS diagrams from the results

187 of the MD simulations is detailed in Appendix section. LAMMPS files with  
188 atomic positions of undeformed nanotubes ( $N = 13$  and  $14$ ) and with atomic  
189 positions for bundles of deformed nanotubes (19  $N = 13$  tubes, 19  $N = 14$   
190 tubes, 9  $N = 13$  tubes and 10  $N = 14$  tubes) can be uploaded from the  
191 github repository <https://github.com/rolsstef/StructureLammpsFiles>.

### 192 **3. Results and discussion**

#### 193 *3.1. Length and diameter distributions*

194 The morphology of individual nanotubes is determined from transmission  
195 electron microscopy images. (Fig. 2(a)). The corresponding length distribu-  
196 tion is presented in Fig.2(b). It displays a log-normal shape with a mean value  
197 around 290 nm, such a shape having already been reported in the literature  
198 (Yang et al., 2008; Yucelen et al., 2013). We also attempted to determine  
199 the nanotube diameter from TEM observations. The resulting distribution is  
200 reported in Fig. 2(c). The measured INT diameters are mostly in the 2.4-2.8  
201 nm range. The error bar on diameter determination is at least  $\pm 0.1$  nm. It  
202 can thus be inferred that INTs diameters are in between 2.5 and 2.7 nm.

#### 203 *3.2. Comparison between X-ray scattering diagrams of an INTs suspension 204 and of a dry powder*

205 The XRS diagrams of synthetic imogolite nanotubes in suspension and of  
206 the resulting dry powder for wave-vectors  $Q$  smaller than  $1 \text{ \AA}^{-1}$  are reported  
207 in Fig.3(a). The diagram of the suspension presents broad modulations due  
208 to the nanometric lateral extent of the nanotubes. This scattering diagram  
209 is, in first approximation, proportional to the square of the modulus of the

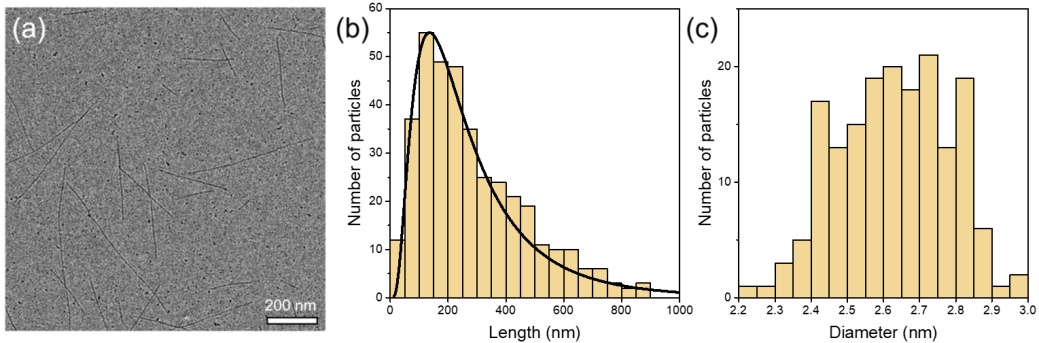


Figure 2: (a) Representative TEM image of Si-INTs and corresponding histograms of the nanotubes (b) length distribution (curve: log-normal fitting) and (c) diameter distribution.

210 form factor of a single tube (see Section S3 in Supplementary data). In  
 211 the dry state, narrower peaks are observed in Fig.3(a) due to the assembly  
 212 of INTs into bundles (Fig. S3). In the hypothesis that nanotubes hold the  
 213 same shape after drying, the powder scattering diagram is the product of the  
 214 squared form factor and of a structure factor for wave-vectors smaller than  
 215  $1 \text{ \AA}^{-1}$  (see section S4 in Supplementary data). The zeros of the form factor  
 216 should thus give minima in the powder scattering diagram. However, this is  
 217 not the case for the minimum at  $Q = 0.514 \text{ \AA}^{-1}$  (Fig. 3(a)). This feature  
 218 suggests that imogolite nanotubes undergo radial deformations when they  
 219 self-assemble into bundles.

### 220 3.3. Wide-angle X-ray scattering: nanotube period and coherence length

221 Fig. 3(b) presents the powder wide-angle X-ray scattering (WAXS) dia-  
 222 gram, for  $Q$  greater than  $1 \text{ \AA}^{-1}$ . As discussed in the Appendix, the tubes are  
 223 not coherent in  $z$ -position within a bundle, so that at large wave-vectors, the  
 224 intensity is proportional to the angular average of the square of the modulus

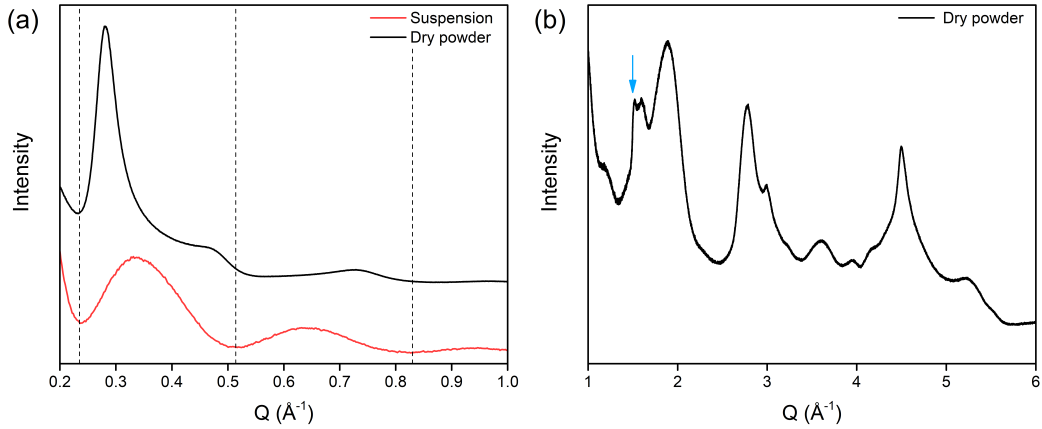


Figure 3: XRS diagrams of an INTs suspension (red) and of a powder (black) for wavevectors  $Q$  (a) smaller than  $1 \text{ \AA}^{-1}$  and (b) above  $1 \text{ \AA}^{-1}$ . Vertical lines in (a) locate the minima of the suspension XRS diagram. Curves are translated for the sake of clarity. The blue arrow in (b) points to  $Q = 4\pi/T$  where  $T$  is the period of the nanotubes along their long axis.

225 of the form factor of a single nanotube. The asymmetric peak highlighted  
 226 by the blue arrow in Fig. 3(b) can be used to determine the period of the  
 227 INTs along their long axis (see Monet et al. (2018) and references therein).  
 228 In brief, diffraction by any nanotube with a period  $T$  along its long axis  $z$   
 229 gives diffuse scattering intensity located in planes at  $Q_z = l\frac{2\pi}{T}$ , with  $l$  integer.  
 230 When the scattered intensity is non-zero at the wave-vector  $\vec{Q} = (0, 0, l\frac{2\pi}{T})$ ,  
 231 angular powder average gives abrupt sawtooth peaks at  $Q_z = l\frac{2\pi}{T}$  (Warren,  
 232 1941). For nanotubes of finite coherence length, these peaks are smoothed  
 233 and the period value can be derived by determining the position of the in-  
 234 flexion point of its rising edge (Fig.S4). In our case, the rising edge observed  
 235 in Fig. 3(b) corresponds to the 002 peak with a period  $T$  equal to  $8.4 \text{ \AA}$ .

236 The 002 peak can also be used to determine the coherence length along



237 the nanotube axis (Monet et al., 2018). Comparison with calculated XRS  
238 diagrams for a powder of tubes ( $N = 14$ ) obtained by MD simulations shows  
239 that the coherence length along the nanotube axis is of about 200 Å (see  
240 Section S5 and Fig. S4). This value is 15 times shorter than the aver-  
241 age tube length determined from TEM observations. This small coherence  
242 length should be attributed to the occurrence of defects. Yucelen et al. (2012)  
243 evidenced different types of defects at the atomic scale in INTs, most of them  
244 involving Al vacancies. The skeleton of the nanotube being its  $AlO_6$  diocta-  
245 hedral layer, which is the locus of instabilities and constraints, the coherence  
246 length can be strongly reduced with respect to the nanotube length. The  
247 growth of INTs is based on several ingredients, with the formation of amor-  
248 phous precursors and/or of curved proto-imogolite tiles, the incorporation of  
249 precursors or of proto-imogolites at the growing ends and the self-assembly  
250 of already formed nanotubes by an oriented attachment process (Yang et al.,  
251 2008; Yucelen et al., 2013; Du et al., 2017). Interestingly, Yucelen et al. (2013)  
252 evidenced that the minimum nanotube length that can form is around 20 nm,  
253 a value close to the measured coherence length. It is therefore tempting to  
254 hypothesize that the reduced coherence length along nanotubes axes could  
255 be attributed to the process of oriented attachment between a growing nan-  
256 otube and a short one, with the appearance of defects within the attachment  
257 section. To confirm this conclusion, it would be interesting to compare the  
258 true length and the coherence length of natural nanotubes, which form over  
259 a much longer time frame.

260 *3.4. Analysis of XRS diagrams from MD simulations*

261 *3.4.1. Determination of the values of  $N$*

262 We first compare the experimental diffractogram of the suspension with  
263 the XRS diagram of powder of single nanotubes obtained for  $N = 13$  and  
264  $N = 14$  INTs (Fig. 4(a)). The minima of the  $N = 14$  diagram are located  
265 at slightly larger wave-vectors than those deduced from the experimental  
266 diagram while those of the  $N = 13$  INTs diagram are found at slightly smaller  
267 wave-vectors. Linear combinations between the two calculated curves give  
268 the experimental minima positions for a mixture of 50%  $N = 13$  and 50%  
269  $N = 14$  INTs. Characteristic radii of the tubes are given in Table S2. The  
270 mean diameters associated to the outer oxygen atoms of the tubes are 23.4  
271 and 25 Å for INTs with  $N = 13$  and  $N = 14$ , respectively. This is in  
272 agreement with our TEM results (Fig. 2), especially considering that INTs  
273 can deform and flatten when deposited on the carbon coating surface for  
274 TEM observations. The mean diameters are in the average of those reported  
275 in the literature for INTs synthesized with the same precursors (see Table S1  
276 in Supplementary data).

277 *3.4.2. Radial deformation of nanotubes in bundles*

278 Having determined the  $N$  values of the nanotubes in suspension, we can  
279 now analyze the diffractogram obtained for dry samples in Fig. 4(b). Imogo-  
280 lite nanotubes organize in bundles, on a two-dimensional (2D) hexagonal  
281 lattice, during the drying stage. The first diffraction peak around  $0.28 \text{ \AA}^{-1}$   
282 corresponds to the 10 peak of this 2D lattice. Its width is inversely propor-  
283 tional to the number of tubes per bundle (Paineau et al. (2017)). Considering  
284 bundles formed of  $n = 19$  tubes in our calculations allows to correctly ac-

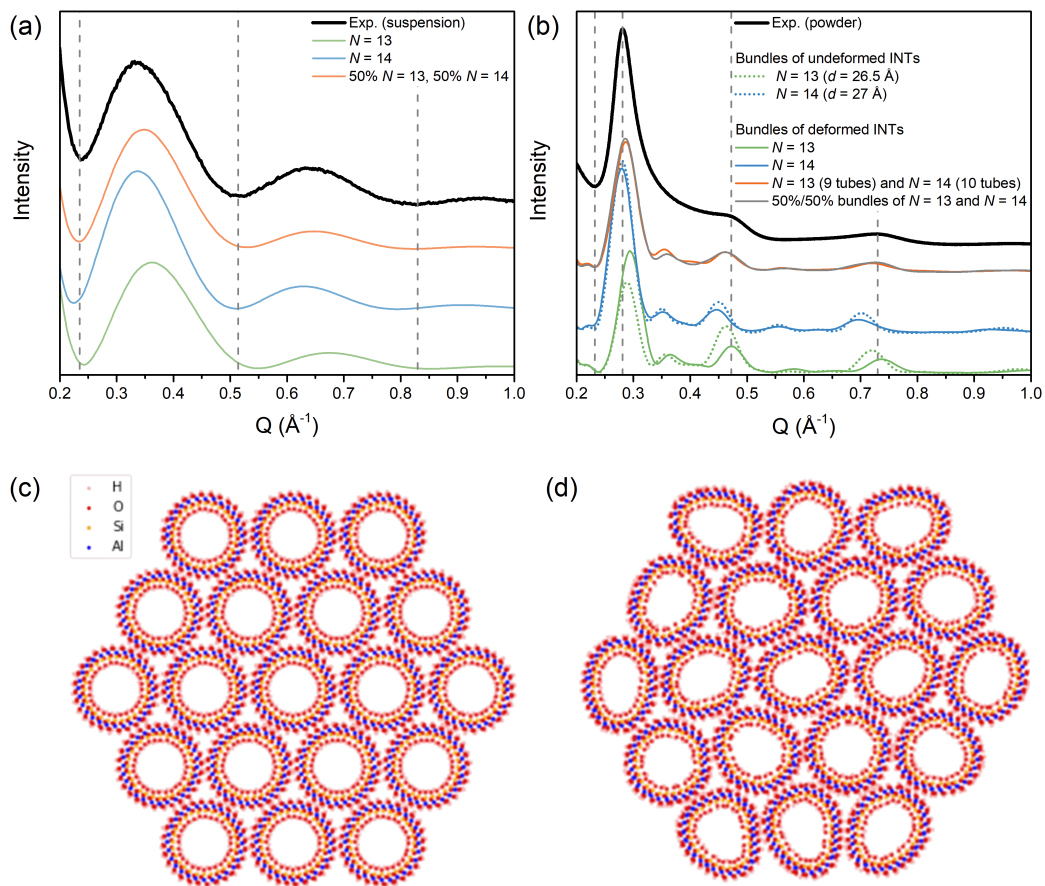


Figure 4: Comparison between calculated XRS diagrams and experimental ones obtained for (a) an INTs suspension and (b) a dry powder. Calculations are made with (1) a powder of isolated  $N = 13$  INTs,  $N = 14$  INTs and a mixture of 50%–50%  $N = 13$  and  $N = 14$  tubes; (2) powders of bundles with (i) 19 undeformed  $N = 13$  tubes and of 19 undeformed  $N = 14$  tubes (dotted green and blue curves, respectively); (ii) bundles of deformed tubes with 19  $N = 13$  tubes, 19  $N = 14$  tubes, a mixture of 10  $N = 14$  and 9  $N = 13$  tubes and 50%-50% bundles with 19 deformed  $N = 13$  and  $N = 14$  tubes (green, blue, orange and grey curves). Vertical lines locate minima and maxima of the experimental diagrams. Curves are translated for the sake of clarity. Top view of a bundle with (c) 19  $N = 14$  undeformed INTs or (d) 19  $N = 14$  deformed INTs.

285 count for this width. One may however note that considering exactly  $n = 19$   
286 tubes per bundle is an approximation. The aggregation of the tubes during  
287 drying leads *a priori* to bundles of different sizes.

288 The undeformed tubes from MD simulations are bundled together in order  
289 to reproduce as well as possible the experimental powder diffraction pattern  
290 as illustrated in Fig. 4(c). Inter-tube distances are chosen equal to  $d =$   
291  $26.5 \text{ \AA}$  and  $27 \text{ \AA}$  for  $N = 13$  and  $N = 14$  INTs, respectively. Calculated  
292 diagrams are shown in Fig. 4(b) as green and blue dotted curves, respectively.  
293 The calculated diagrams display similarities with the experimental one, in  
294 particular for the position of the first maximum. However, the maxima  
295 around  $0.47 \text{ \AA}^{-1}$  and  $0.73 \text{ \AA}^{-1}$  are too intense for  $N = 13$  tubes and they are  
296 positioned at too small wave-vector values for the two calculated diagrams.

297 Comparison between the XRS diagrams of the suspension and of the dry  
298 powder in subsection 3.2 indicates that the nanotubes could be deformed  
299 radially when bundled. Based on MD simulations with three tubes, Tamura  
300 and Kawamura (2002) found that the central imogolite nanotube was strongly  
301 deformed. We have thus simulated bundles composed of deformed tubes,  
302 with the procedure detailed in subsection 2.3, with 19  $N = 13$  tubes, 19  
303  $N = 14$  tubes (as shown in Fig. 4(d)) and 10  $N = 14$ , 9  $N = 13$  tubes.  
304 This mixed bundle is considered because starting from a suspension with  
305 50%  $N = 13$  and 50%  $N = 14$  INTs, one can expect that neighbouring  
306 tubes are combined together into bundles during the drying process whatever  
307 their  $N$  value, so that mixed bundles are formed.<sup>2</sup> Histograms of the lattice

---

<sup>2</sup>If one assumes that the pairing of  $N = 13$  and  $N = 14$  tubes is random, the probability to have a bundle with  $n$  tubes  $N = 14$  and  $(19-n)$  tubes  $N = 13$  is  $\frac{C_{19}^n}{2^{19}}$ .

308 parameter  $d$ ,  $d$  being the distance between 2 nearest neighbors, and of the  
 309 acute angle  $\gamma$  between three nearest neighbors are presented in Fig. S5. We  
 310 find that  $\langle\gamma\rangle = 60^\circ$  for all bundles, so that an average hexagonal arrangement  
 311 is preserved. The mean lattice parameter  $\langle d \rangle$  is equal to 25.8 Å, 27.1 Å and  
 312 26.4 Å for  $N = 13$ ,  $N = 14$  and mixed bundles, respectively. The difference  
 313  $\delta_d$  between the mean inter-tube distance and the mean values of the outer  
 314 nanotube diameter, determined from the positions of outer hydrogens, is the  
 315 same for the minimized  $N = 13$  and  $N = 14$  bundles ( $\delta_d=1.1$  Å).

316 Fig. 4(b) presents the XRS diagrams (continuous lines) calculated from  
 317 simulated bundles of deformed INTs. The comparison between the dotted  
 318 and the continuous lines shows that the deformation smooths the peaks above  
 319  $0.4 \text{ \AA}^{-1}$ , in better agreement with the experiment. For comparison, we also  
 320 report in Fig. 4b the XRS diagram for a powder of mixed bundles (9 tubes  
 321  $N = 13$  and 10 tubes  $N = 14$ ) as well as the one for a powder where half of the  
 322 bundles are made with 19 deformed  $N = 13$  tubes and half of them with 19  
 323 deformed  $N = 14$  tubes. To quantify the deviation between the experimental  
 324 and simulated curves, one minimum  $Q_{mes,min}$  and three maxima  $Q_{mes,max}(i)$   
 325 ( $i = 1 - 3$ ) positions are selected (evidenced in Fig. 4(b) by vertical lines).  
 326 The deviation of the simulated positions from the experimental ones are  
 327 evaluated through the parameter  $\Delta$  defined as

$$\Delta = \sqrt{\frac{(Q_{mes,min} - Q_{sim,min})^2}{Q_{mes,min}^2} + \sum_{i=1}^3 \frac{(Q_{mes,max}(i) - Q_{sim,max}(i))^2}{Q_{mes,max}(i)^2}} \quad (1)$$

328 The obtained  $\Delta$  values for bundles of deformed INTs are 0.054, 0.074,  
 329 0.034 and 0.030 for  $N = 13$ ,  $N = 14$ , the mixed bundle (9+10 tubes) and  
 330 the combination of bundles with deformed  $N = 13$  and  $N = 14$  tubes,

331 respectively. The best agreements are thus obtained for the mixed bundle  
332 and for 50%-50% bundles of deformed  $N = 13$  and  $N = 14$  tubes.

333 These findings are corroborated by comparing the experimental WAXS  
334 diagram with calculated ones (Fig. 5). As stated in the Appendix, diagrams  
335 have to be calculated from the angular average of the squared form factor of  
336 individual nanotubes. Average is also taken over the nanotubes in the bundle  
337 when it is made of deformed nanotubes. Comparison between calculated  
338 diagrams for  $N = 13$  (or  $N = 14$ ) undeformed and deformed INTs shows  
339 that the radial nanotube deformation induces a smoothing of the oscillations,  
340 in better agreement with the experiment. More importantly, the WAXS  
341 diagram for mixed bundles of deformed tubes reproduce well the experimental  
342 diagram of the dry powder.

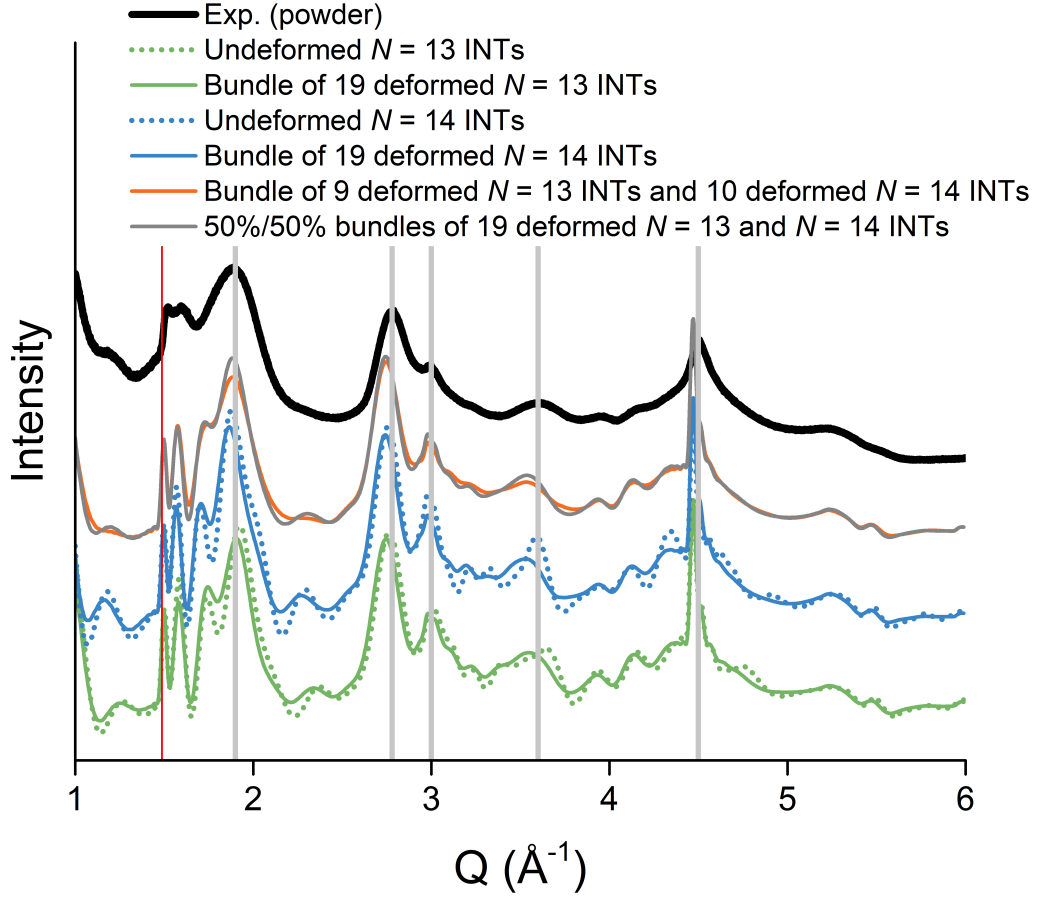


Figure 5: (a) Measured XRS diagram of an INT powder for wavevectors  $Q$  greater than  $1 \text{ \AA}^{-1}$  and calculated ones for the  $N = 13$  (dotted green curve) and  $N = 14$  (dotted blue curve) undeformed INTs, by averaging the angularly averaged squared form factors of the nanotubes in the bundles with 19 deformed  $N = 13$  INTs (continuous green curve), 19 deformed  $N = 14$  INTs (continuous blue curve), 10  $N = 14$ , 9  $N = 13$  deformed INTS ( continuous orange curve) and by taking the average of the green and blue curves (grey curve). Vertical lines are guide for the eye. The red one gives the position of the 002 peak.

343 *3.4.3. Robustness of the determination of  $N = 13$  and  $N = 14$  values*

344 It is worth mentioning here the methodology which has been recently  
345 developed by Monet et al. (2018) to determine the structure of nanotubes  
346 of complex stoichiometry from their powder XRS diagram, by considering  
347 helicoidal symmetry and minimizing the nanotube energy using a simple  
348 semi-empirical harmonic model. This method allowed one to determine the  
349 structure of INT analogs, namely  $Al_2GeO_7H_4$  nanotubes and  $Al_2SiO_6CH_6$   
350 and  $Al_2GeO_6CH_6$  nanotubes (Monet et al., 2018, 2020). The determination  
351 of the structure of the  $Al_2SiO_7H_4$  nanotubes studied in this article using this  
352 method is presented in section S8 in SI. The sample is found to be formed of  
353 both  $N = 13$  and  $N = 14$  nanotubes. The same conclusions are drawn from  
354 (i) the analysis of the suspension XRS diagram based on MD simulations  
355 with the elaborated extended CLAYFF model (Scalfi et al., 2018) and (ii)  
356 from the analysis of the powder XRS diagram with the method of Monet  
357 et al. (2018) and a simplified energetic model. The determined  $N$  values  
358 can thus be regarded with confidence. Finally, note that the limit of the  
359 simple methodology of Monet and co-workers is that it does not allow one  
360 to investigate radial deformations, which have been found to be important,  
361 because it is based on the use of the symmetry of the nanotube.

362 *3.5. Discussion of the literature findings and analyses*

363 We have shown that the interpretation of the powder XRS diagram of  
364 INTs is not a simple task, but that when coupled to simulations, it can  
365 bring a wealth of information. Previous analyses of electron diffraction im-  
366 ages or powder diffraction diagrams attempting to determine the  $N$  value of  
367  $Al_2SiO_7H_4$  nanotubes are reported in Table 1. In-depth analysis of electron



368 diffraction data on natural INTs allowed Cradwick et al. (1972) to propose  
369 three values of  $N = 10, 11$  or  $12$ , but they could not obtain a complete in-  
370 terpretation of their experimental data with any  $N$  value. All other articles  
371 in Table 1 compare experimental XRS diagrams to calculated ones to ob-  
372 tain the  $N$  values of the studied INTs. Alvarez-Ramírez (2007) estimated  
373 the  $N$  values of three types of INTs, namely natural INTs and INTs syn-  
374 thesized from different precursors, the structure of the INTs being obtained  
375 by Density Functional Theory (DFT) geometry minimization. In particular,  
376 for INTs synthesized with TEOS/ $\text{AlCl}_3$ / $\text{NaOH}$  precursors as the one studied  
377 here, Alvarez-Ramírez (2007) concluded that the number of silicon tetrahe-  
378 dra around the circumference is  $N = 12$ . However, the agreement between  
379 calculated and experimental XRS diagrams is not as good as what we report  
380 in Fig. 4(b) thus refuting the finding that the tubes have  $N = 12$  silicon tetra-  
381 hedra along their circumference. Contradictory results are also obtained for  
382 INT synthesized from  $\text{Na}_4\text{SiO}_4/\text{AlCl}_3/\text{NaOH}$  precursors. Alvarez-Ramírez  
383 (2007) finds that  $N = 13$ , while, with optimized Density Functional Tight  
384 Binding nanotubes geometries, Guimarães et al. (2007) concluded to the pres-  
385 ence of  $N = 12$  nanotubes but they could not exclude  $N = 10$  nanotubes.  
386 Finally, with atomic structures obtained using the CLAYFF potential, Kang  
387 et al. (2010) found  $N = 12$  and/or  $N = 14$  for INTs obtained with organic  
388 Si and Al precursors. Quite surprisingly, neither Guimarães et al. (2007)  
389 nor Kang et al. (2010) did consider odd values for  $N$  between the even ones  
390 they found, which would have also lead to good agreement between experi-  
391 ment and calculation. There is no energetic argument to avoid considering  
392 odd values. Indeed, the calculated energies per atom of an INT reported in

393 the literature are found to vary continuously with  $N$  (Tamura and Kawa-  
394 mura, 2002; Konduri et al., 2006; Guimarães et al., 2007; Zhao et al., 2009;  
395 Demichelis et al., 2010; Lee et al., 2011; González et al., 2014; Lourenco et al.,  
396 2014; Arancibia-Miranda et al., 2017; Elliott et al., 2017).

397 By reviewing the literature, we could see that the diameters of synthetic  
398 nanotubes are globally larger than their natural counterparts. Nevertheless,  
399 the reported values vary greatly from one study to another (Table S1), sug-  
400 gesting some possible experimental limitations (e.g. spatial resolution for  
401 TEM measurements) or approximations in the interpretation of the data.  
402 The purpose of this article is not to list the pros and cons between TEM,  
403 electron diffraction or X-ray scattering. However, as far as X-ray scattering  
404 is concerned, a brief historical overview of the interpretation of XRS data on  
405 INTs is instructive. By studying the growth mechanism of INTs, Mukher-  
406 jee et al. (2005) revisited the indexation of the solid state packing of INTs,  
407 which was later adopted by several other authors (Lee et al., 2014; Zanzottera  
408 et al., 2012; Hongo et al., 2013). The XRS diagram analyzed in ref. Mukher-  
409 jee et al. (2005) covers the  $Q$  range between 0.25 and  $1.2 \text{ \AA}^{-1}$  as reproduced  
410 in Fig.S7. From the fit of the four maxima positions, indexed as 100, 110,  
411 001 and 211, the authors deduced the following parameters for bundled alu-  
412 minosilicate nanotubes:  $a = b = 21.05 \text{ \AA}$ ,  $c = 8.51 \text{ \AA}$  and  $\gamma = 78^\circ$ . Based on  
413 these considerations, several puzzling points need to be underlined. First, in  
414 this non-hexagonal 2D lattice, intertube distances (the distance between the  
415 center of the neighboring tubes in the plane perpendicular to their long axis  
416  $z$ ) take two values:  $21.05 \text{ \AA}$  and  $26.5 \text{ \AA}$ . This monoclinic arrangement should  
417 therefore imply a strong deformation of the nanotubes. In addition, the point

418 group of the nanotubes,  $C_{2N}$ , is such that the period projected along the tube  
 419 axis is  $c/2$  and not  $c$  (see Fig. 1(c)). It follows that  $00l$  reflections are ex-  
 420 tincted for odd values of  $l$ , in contradiction with the 001 indexation of the  
 421 third maximum of the XRS diagram. Finally, the  $hkl$  notation assumes that  
 422 the tubes are organized in a coherent way in the  $z$  direction. The whole set of  
 423 Bragg peak positions calculated with the 3D unit cell reported by Mukherjee  
 424 et al. (2005) is shown in Fig.S8. Curiously, they have not been considered  
 425 in the indexation of the four maxima but we can hardly see how they could  
 426 be extincted in the experimental XRS diagram. Previous electron diffraction  
 427 studies of (Farmer and Fraser, 1979; Farmer et al., 1983) showed that syn-  
 428 thetic INTs did not form 3D crystals. This is also confirmed by the good  
 429 agreement between calculations and experiments found at large  $Q$  values in  
 430 this work and previous reports (Guimarães et al., 2007; Monet et al., 2018,  
 431 2020), assuming no correlations between nanotubes along  $z$ . Therefore, the  
 432 indexation at small wave vectors of imogolite XRS diagrams requires only  
 433 two integers  $hk$ .

434 This last remark allows us to discuss the crucial role of the form factor  
 435 when analyzing the small wave-vector part of XRS diagrams of INT powders  
 436 ( $Q$  smaller than  $1 \text{ \AA}^{-1}$ ). Let us consider the simple case of the undeformed  
 437 tubes within hexagonal bundles with unit cell parameters  $a = b = d$ ,  $d$  being  
 438 the inter-tube distance, and  $\gamma = 60^\circ$ . The scattered intensity is the product  
 439 of the squared form factor modulus  $|F_{INT}(Q)|^2$  and of a structure factor (see  
 440 section S4 in Supplementary data). For bundles of finite size,  $hk$  Bragg peaks  
 441 are enlarged while the position of their maxima is shifted with respect to the  
 442 equivalent position for bundles of infinite size (Thess et al., 1996; Rols et al.,

443 1999; Paineau et al., 2017), as illustrated in Fig. 6(a). The position of the  
 444 maxima are shifted to larger (smaller)  $Q$  values if their true position is on a  
 445 rising (decreasing) edge of  $\langle F^2 \rangle (Q)$  and they can be splitted into two peaks  
 446 if they are located at a minimum of  $\langle F^2 \rangle (Q)$ . As an example, the position  
 447 of the 10 peak as a function of the number of tubes in a bundle is reported  
 448 in Fig. 6, together with the value of the erroneous lattice parameter which is  
 449 derived from this position assuming that it is not displaced:

$$d = \frac{4\pi}{\sqrt{3}Q_{10}} \quad (2)$$

450 In practice, the X-ray scattering diagrams reported in the literature show  
 451 broad peaks due to finite-size bundles. For 7 INTs bundles, the  $d$  position is  
 452 underestimated by 2 Å. Moreover, no systematic study of the impact of de-  
 453 formation of tubes in bundles as a function of the number of tubes per bundle  
 454 exists. In any case, it is now evident that the intertube distances reported  
 455 in Table S1 should be considered with great caution as they were obtained  
 456 from the position of the maximum of the first peak and from equation (2).<sup>3</sup>

#### 457 4. Conclusions

458 Fifty years after the seminal article of Cradwick et al. (1972) describ-  
 459 ing the structure of imogolite nanotubes, a review of the literature reveals  
 460 that the number  $N$  of silicon tetrahedra around their circumference has not  
 461 been accurately determined, neither for natural nor for synthetic INTs. In

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<sup>3</sup>In table S1, note also that Lee et al. (2014) did not use Eq. 2 and that they calculated  $d$  as equal to  $\frac{2\pi}{Q_{10}}$ .

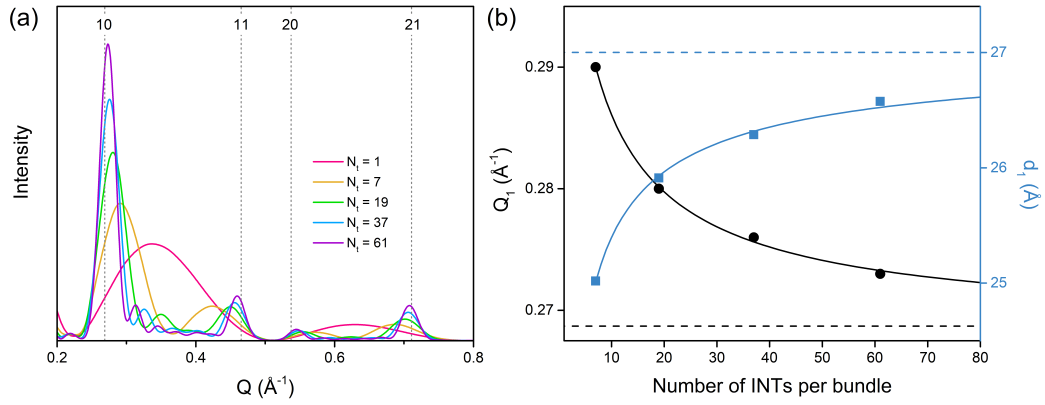


Figure 6: (a) Calculated XRS diagrams for a powder of undeformed  $N=14$  INTs in bundles,  $N_t$  being the number of tubes per bundle. The bundle parameters are  $d = 27 \text{ \AA}$  and  $\gamma = 60^\circ$ . Calculated curves are renormalized by  $N_t$ . Vertical lines give Bragg peak positions for bundles of infinite size,  $hk$  indices are noted above. (b) Position  $Q_1$  of the first maximum of the XRS diagram (black circles) and corresponding value of the "lattice parameter"  $d_1 = \frac{2\pi}{Q_1 \sin(\gamma)}$  (blue squares) as a function of the number of tubes per bundle. Dashed black and blue lines give respectively the position of the 10 peak for an infinite bundle and the true lattice parameter  $d$ . Solid black and blue lines are guides to the eye.

462 this article, we revisited this crystallographic issue. We focused on synthetic  
463 nanotubes obtained from TEOS and  $\text{AlCl}_3 \cdot \text{H}_2\text{O}$  precursors hydrolyzed with  
464 NaOH, for which it was stated that  $N$  equals 12 (Alvarez-Ramírez (2007)).  
465 The analysis of both suspension and powder XRS diagrams up to large wave-  
466 vectors was carried out thanks to MD simulations based on the extended  
467 CLAYFF model. Our results show unambiguously that synthetic INTs sam-  
468 ples are formed from both  $N = 13$  and  $N = 14$  nanotubes. Moreover, we  
469 highlight that the analysis of scattering diagrams is rather subtle as defor-  
470 mations of dry tubes assembled in bundles have to be taken into account,  
471 which had never been done before this work. It is hoped that this article can  
472 serve as a basis for re-investigating the structure of natural clay nanotubes  
473 and of synthetic analogues depending on the precursors used. Finally, the  
474 value of the coherence length along the tube axis could support a model of  
475 nanotube growth by oriented attachment.

## 476 **5. CrediT authorship contribution statement**

477 A. D'Angelo, S. Rouzière, E. Paineau, E. Elkaim, P. Launois and C.  
478 Goldmann carried out the experiments. A. D'Angelo, S. Rols and P. Launois  
479 performed XRS analysis and MD simulations. D. Toquer carried out the lit-  
480 erature review on nanotube diameters. P. Launois, E. Paineau, A. D'Angelo  
481 and S. Rols wrote the article which was reviewed by all authors.

## 482 **6. Declaration of competing interest**

483 The authors declare that they have no known competing financial inter-  
484 ests or personal relationships that could have appeared to influence the work

485 reported in this paper.

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496 TGA measurement and L. Bove for interesting discussions. Figure 1 was  
497 made from pictures created by G. Monet, whom we also thank here.

## 498 **8. Appendix Section: X-ray scattering calculations**

499 Each diffractogram is calculated from the atomic positions in the last  
500 frame of a molecular dynamics trajectory. The correlation length along the  
501 tube axis  $z$  is  $\sim 200 \text{ \AA}$  (see section 3.3), i.e. about  $22T$  where  $T$  is the  
502 period along the nanotube axis. Calculations of XRS diagrams are to be  
503 made for tubes with the same length. The size of the MD simulation box  
504 along the tubes axis is equal to  $11T$  for isolated nanotubes and to  $T$  for  
505 bundles. Nanotubes of correct length for XRS calculations are constructed  
506 by periodization over the box length, so that two boxes are considered for  
507 isolated INTs (translation of the first box by  $11T$ ) and 22 boxes with  $nT$

508 translations ( $n = 1 - 21$ ) are taken for bundles of INTs. We then use the  
 509 Debye formula, which allows to calculate the intensity scattered by a powder  
 510 in terms of the interatomic distances:

$$I(Q) \propto \sum_{j,k} f_j(Q) f_k(Q) \frac{\sin(Qd_{jk})}{Qd_{jk}} \quad (3)$$

511 where  $f_{j(k)}(Q)$  is the atomic form factor of atom  $j$  ( $k$ ) and  $d_{jk}$  is the distance  
 512 between atoms  $j$  and  $k$ . Intensity calculations have been speed up using  
 513 highly parallel calculation on GPUs Neverov (2017). Convolution of the  
 514 calculated diagrams to the experimental resolution is useless (see section  
 515 S10).

516 The powder constituent can be a nanotube or a bundle of nanotubes. For  
 517 tubes organized in bundles, two parameters have to be considered: their rel-  
 518 ative orientations and their phasing along the  $z$  axis of the bundle. At small  
 519 wave-vectors  $Q$ , when the homogeneous approximation applies, the relative  
 520 orientations or translations along  $z$  of the tubes inside bundles should have  
 521 no impact on the XRS diagram. We have verified this by performing calcula-  
 522 tions with tubes all having the same orientation and phasing along  $z$  and with  
 523 nanotubes of random orientations and/or relative positions in  $z$ . At large  $Q$ ,  
 524 the orientational coherence and  $z$ -phasing between the tubes will modify the  
 525 XRS diagram. In particular, without  $z$ -phasing, the intensity can be calcu-  
 526 lated by simply considering a powder of isolated tubes, i.e., by taking the  
 527 coordinates of the atoms of a single tube in Eq. (3). If tubes are correlated  
 528 for their  $z$  positions, their Wide Angle XRS (WAXS) diagram will present  
 529 narrower modulations than for uncorrelated tubes. From this view point,  
 530 the WAXS diagram of aluminosilicate nanotubes in Fig. 3(b) presents strong



531 similitudes with those of methylated aluminosilicate and aluminogermanate  
532 nanotubes (Monet et al., 2018) and with the one of hydroxylated aluminoger-  
533 manate nanotubes (Monet et al., 2020), for which reasonable agreement be-  
534 tween experimental and calculated diagrams was found considering isolated  
535 nanotubes. Most interestingly, Farmer and co-workers (Farmer and Fraser,  
536 1979; Farmer et al., 1983) compared electron diffraction diagrams of natural  
537 and synthetic nanotubes. The 002 layer line presents discrete reflections for  
538 natural aluminosilicate nanotubes while it consists in a continuous streak for  
539 synthetic ones, as clearly shown in Fig.2 of ref. (Farmer et al., 1983). Natural  
540 INTs thus form three-dimensional small crystals while synthetic ones are not  
541 coherent in  $z$ -position within a bundle. This is probably due to the fact that  
542 bundles, in the case of synthetic nanotubes, are formed during the drying of  
543 their suspension, without the tubes having the option to reorganise further  
544 to minimise bundle energy.

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