1 **<u>Revision 1</u>**

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4 **Dissolution-reprecipitation and self-assembly of serpentine nanoparticles**

5 **preceding chrysotile formation: Insights into the structure of proto-**

6 **serpentine**

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ABSTRACT

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20   Any poorly crystalline serpentine-type mineral with a lack of recognizable textural or

21   diffraction features for typical serpentine varieties (i.e. chryotile, lizardite, antigorite) is

22   usually referred to as proto-serpentine. The formation of the so-called proto-serpentine seems

23   ubiquitous in serpentinization reactions. It is related to dissolution-precipitation of strongly

24   reactive particles prior to true serpentine formation (e.g. in veins where both chrysotile and

25   proto-serpentine are described). However, the structural characteristics of proto-serpentine

26   and its relation with serpentine crystalline varieties remain unclear. In this study a model

27   describing the transformation from proto-serpentine to chrysotile is presented based on

28   experimental chrysotile synthesis using thermogravimetric analyses, transmission electron

29   microscopy and high-energy X-ray diffraction with pair distribution function analyses. The

30   combination of the high resolution TEM and high-energy X-ray diffraction enables to resolve

31   the local order of neo-formed particles and their structuration processes occurring during pure

32   chrysotile formation (i.e. during the first three hours of reaction). The formation of individual

33   nanotubes is preceded by the formation of small nanocrystals that already show a chrysotile

34   short-range order, forming porous anastomosing features of hydrophilic crystallites mixed

35   with brucite. This is followed by a hierarchical aggregation of particles into a fiber-like

36   structure. These flake-like particles subsequently stack forming concentric layers with the

37   chrysotile structure. Finally, the individualization of chrysotile nanotubes with a

38   homogeneous distribution of diameter and lengths (several hundreds of nanometer in length)

39   is observed. The competitive precipitation of brucite and transient serpentine during incipient

40   serpentinization reaction indicates that both dissolution-precipitation and serpentine-particle

41   aggregation processes operate to form individual chrysotile. This study sheds light into

42   mineralization processes and sets a first milestone towards the identification of the factors

43   controlling polymorph selection mechanisms in this fascinating system.

INTRODUCTION

Serpentine is a common mineral containing structural water with an ideal chemical formula $Mg_3Si_2O_5(OH)_4$. The serpentine group of minerals contains different varieties, among which the most commons forms are antigorite, consisting of periodic modulated layers, (Kunze, 1956), lizardite, consisting of flat periodic layers, (Wicks and O'Hanley, 1988), and chrysotile and polygonal serpentine, consisting in fibers, (Yada, 1967; Middleton and Whittaker, 1976). Serpentines are mainly found in altered Earth oceanic lithosphere. Lizardite and chrysotile are both involved it hydrothermal systems and are found in the same stability domains (moderate temperature, bellow 400°C), whereas antigorite is the high-pressure/high temperature serpentine variety (Evans et al., 1976; Evans, 2004; Wunder and Schreyer, 1997). Chrysotile is one of the most common and studied cylindrical fibrous serpentine and consists in the succession of tetrahedral sheets inserted between brucite-type magnesian octahedral layers. The structural misfit between tetrahedral and octahedral sheets induces a concentric or spiral curvature around the x or y axis (Whittaker, 1956b; Whittaker, 1956c; Whittaker, 1956a; Middleton and Whittaker, 1976) with a fivefold symmetry (Cressey and Whittaker, 1993; Cressey et al., 2010) and with the tetrahedral sheet inside (Pauling, 1930). Chrysotile is considered as a thermodynamically metastable serpentine variety having a strong chemical reactivity toward the formation of lizardite, even in the pure Mg system (Grauby et al., 1998; Evans, 2004). The relationships between layered and tubular serpentine minerals, the overlap between individual polymorphs and the frequent occurrence of turbostratism in serpentine minerals (Trittschack et al., 2012) are of great interest in natural settings where both lizardite and chrysotile coexist. Moreover, an advanced understanding of the atomic scale mineral transformation mechanisms in the serpentine system remains necessary to understand mobile elements or trace-metals cycle during oceanic lithosphere alteration.

70   While the structure of well-crystallized serpentine varieties has been determined from

71   X-ray and electron diffraction and transmission electron microscopy (TEM), proto-serpentine

72   is increasingly described as poorly crystalline serpentine precursor of undetermined fibrous

73   serpentines in experimental (Dufaud et al., 2009; Bloise et al., 2012; Godard et al., 2013;

74   Lafay et al., 2013) and natural (Andreani et al., 2008; Andreani et al., 2004; Plümper et al.,

75   2012) systems, especially in association with chrysotile. Chrysotile is generally present in

76   supersaturated systems and veins. In this context, the alteration of mantle-silicate minerals by

77   hydrothermal fluids is usually characterized by the development of cracks filled with

78   serpentine or by pseudomorphic polycrystalline serpentine features originated from

79   dissolution/precipitation processes (Wicks and Whittaker, 1977; Putnis, 2002). The

80   dissolution of mantle silicate (pyroxene and olivine) appears largely controlled by its

81   crystallographic orientation and fluid composition (Velbel, 1993; Velbel, 2009; Daval et al.,

82   2010; Daval et al., 2013) but, to our knowledge, the direct relation between dissolution

83   properties (e.g. rate, mechanisms) and secondary phase precipitation has never been explored.

84   However, the formation of serpentine mineral precursors to chrysotile, which subsequently

85   recrystallize into lizardite, is probably taking place in reaction rims at fluid-mineral interfaces

86   and is surely linked to surface reactivity.

87   During the last decades various experimental studies have attempted to reproduce

88   natural serpentinization features and to ascertain the main parameters controlling

89   serpentinization processes (Seyfried Jr and Dibble Jr, 1980; Macleod et al., 1994; James et al.,

90   2003; Seyfried Jr. et al., 2007; McCollom and Bach, 2009; Hövelmann et al., 2011). In this

91   way, serpentine phase's stability domains are continuously refined. Moreover, serpentine

92   synthesis methods, especially for chrysotile, have been developed since the mid of the last

93   century (Noll, 1950; Yada and Iishi, 1974; Yada and Iishi, 1977). Recent research has

94   attempted to develop more efficient synthesis protocols and to characterize the effect of

95 foreign elements on the mineral growth processes (Bloise et al., 2009; Korytkova and

96 Pivovarova, 2010; Korytkova et al., 2011; Lafay, Montes-Hernandez, et al., 2014). Some of

97 these studies have also aimed to get a better understanding of structural factors governing

98 natural chrysotile health hazards (Falini et al., 2006; Foresti et al., 2009; Turci et al., 2011).

99 The transformation from precursor phases (aqueous, colloidal or solid) to mineral

100 structures and the relation between mineral polymorphs is currently a very active research

101 area in the (bio)geosciences (De Yoreo et al., 2015). However, until now very few studies

102 have been devoted to the identification of the first steps of serpentine nucleation and growth at

103 laboratory scale, and many questions still remain unanswered concerning the transition from

104 the so-called proto-serpentine to crystalline serpentine. In a previous contribution we

105 highlighted that chrysotile synthesis at 300°C was characterized by the initial formation of a

106 poorly crystallized serpentine associated with brucite. Here we show that the competitive

107 precipitation of brucite and serpentine, progressively consumed via dissolution precipitation

108 processes, preceded the individualization and growth of single chrysotile nanotubes via a

109 progressive Ostwald ripening process (Lafay et al., 2013). The dissolution-precipitation

110 process was effective during the first 20 hours of reaction. The broad X-ray diffraction peaks

111 in the diffraction pattern of the serpentine precursor crystallites (first 2 hours of reaction) is

112 surely due to small coherent domain sizes, and also probably to turbostratic disorder along the

113 stacking direction, and to an amorphous component difficult to be interpreted from laboratory

114 X-ray data. In summary, dissolution re-precipitation processes could be systematically

115 involved in the transformation from proto-serpentine to the final crystalline varieties (Jancar

116 and Suvorov, 2006; Lafay et al., 2013).

117 In this study we expand on the efforts to decipher the nature of the amorphous and

118 nanocrystalline phases precursors that can be formed during the early steps of chrysotile

119 formation. For that purpose, this experimental study was based on an accurate sampling

period (half an hour) during the first steps of chrysotile synthesis (i.e. the first three hours). A

combination of thermogravimetric, TEM and high energy X-ray diffraction data, including

pair distribution function analyses, were performed in order to obtain new insights into the

structural characteristics of the serpentine precursor. Hereafter, an accurate model for

chrysotile structuration is proposed.

MATERIALS AND METHODS

Experimental synthesis

Semi-continuous chrysotile syntheses were conducted at 300°C and saturated pressure

($\approx$ 79 bar) respecting serpentine stoichiometry (Mg/Si = 1.33); starting with 300 ml of 1M

NaOH solution, 1.302 g of silica gel (H_2SiO_3) and 5.082 g of magnesium chloride

hexahydrate ($MgCl_2.6H_2O$). The reactants were placed in a hastelloy C22 reactor (autoclave

with an internal volume of 0.6 L). The suspension was immediately stirred and heated using

constant mechanical agitation (300 rpm) and a heating jacket adapted to the reactor as early

described in Lafay et al. (2013). Six samples were collected from 10 ml dispersions sampled

approximately every half hour, between 40 minutes and three hours of reaction. After

centrifugation and fluid removal, the solid product was dried at 90 °C during 48 hours and

recovered for further thermogravimetric analyses (TGA), TEM and High-energy X-ray

diffraction measurements.

A synthetic brucite was produced by reacting 0.25 mol of chloride hexahydrate in 250

ml of 1M NaOH solution. Minerals consists in pure $Mg(OH)_2$ hexagonal flakes with a size

ranging from few dozens of nanometers to few hundreds of nanometers and a width of about

20 nm.

Solid product characterization

Solid products were characterized by differential thermal analysis (DTA) and TGA

with a TGA/SDTA 851e Mettler Toledo instrument using about 10 mg of powder placed in a

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146   platinum crucible of 150 µl with a pinhole. Analyses were performed using a heating rate of

147   10 °C min^{-1}, and inert N$_2$ atmosphere of 50 ml min^{-1}. Sample mass loss and associated thermal

148   effects were obtained by TGA/DTA in a temperature range from 30 °C to 1200 °C. The

149   instrumental theoretical T precision is ±0.5 °C and the weight sensitivity down to 0.1 µg.

150   TGA apparatus was calibrated in terms of mass and temperature. Calcium oxalate was used

151   for the sample mass calibration. The melting points of three compounds (indium, aluminum

152   and copper) obtained from the DTA signals were used for the sample temperature calibration.

153   The TGA first derivative (so called differential thermogravimetry DTG) was used to better

154   identify mass loss steps and to determine the loss of mass associated with brucite and

155   serpentine phases (Viti, 2010; Lafay et al., 2013; Bloise et al., 2015).

156   Additionally, samples were loaded into kapton capillaries for high-energy synchrotron

157   X-ray diffraction measurements (HEXD). HEXD experiments allow recording a long

158   momentum transfer (Q) diffraction pattern, including good statistics for the diffuse scattering.

159   These patterns are usually called 'total scattering patterns'. Total scattering experiments are

160   usually performed to study the local order of amorphous or poorly crystalline materials, where

161   the diffuse scattering accounts for a high proportion of the total X-ray scattering. HEXD

162   patterns of amorphous or disordered materials are usually analysed using the Pair Distribution

163   Function (PDF or g(r)) approach. In short, the PDF is the Fourier transform of the reduced

164   structure factor, F(Q):

165        $$F(Q) = Q[S(Q) - 1] \qquad\qquad\qquad \text{(eq. 1)}$$

166        $$g(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_0^\infty Q[S(Q) - 1]\, sin(Qr)\, dr \qquad\qquad \text{(eq. 2)}$$

167   where r is the interatomic distance, ρ is the number density and $S(Q)$ is the structure factor.

168   The resulting PDF is a map of the interatomic distances in the sample. The PDF method

169   provides a different way to analyse short-range order, using a real space representation of the

170   scattering data. The PDF method has been use to describe the first stages of formation

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171 inorganic materials and the structure of poorly crystalline minerals (Becker *et al.*, 2010;

172 Caraballo *et al.*, 2015; Fernandez-Martinez *et al.*, 2010; Gilbert *et al.*, 2004; Michel *et al.*,

173 2007). Given the high amount of diffuse scattering present in the diffraction pattern of

174 disordered minerals and of mineral precursors, the PDF provides a useful way to describe the

175 structural characteristics of these phases.

176 Total scattering patterns were acquired at beamline ID15B of the European

177 Synchrotron Radiation Facility (ESRF), Grenoble, France. Scattering data were collected with

178 a Perkin-Elmer flat-panel detector using the rapid-acquisition pair distribution function (PDF)

179 technique (Chupas et al., 2003). Measurements of the samples and empty capillary were made

180 at ambient temperature in a range of Q from 0–25 Å^{-1}. The X-ray wavelength ($\lambda = 0.14252$ Å)

181 was refined using a NIST certified CeO_2 standard. Total scattering structure functions and

182 pair distribution functions were obtained using the PDFGetX3 software.

183 TEM was used to determine the shape and sizes of chrysotile nanotubes and of their

184 precursors. For that purpose, powders of samples were dispersed in ethanol and one drop of

185 the sample suspension was deposited on a holey carbon foil placed on conventional copper

186 micro-grids. TEM experiments were performed at the Institut de Minéralogie et de Physique

187 des Milieux et Cosmochimie (Paris, France) using a JEOL 2100F microscope operating at 200

188 kV, equipped with a field emission gun and a high-resolution pole piece achieving a point-to-

189 point resolution of 1.8 Å, and at Cinam (Marseille, France) using a JEOL 3100 microscope

190 operating at 300 kV equipped with a LaB6 filament achieving a point-to-point resolution of

191 1.6 Å.

192 Structural models for simulations

193 Models of minerals structures were used to simulate PDFs and interpret experimental

194 observations. For that purpose we created atomistic models of chrysotile nanotubes by rolling

195 lizardite layers along the [010] direction, and using average diameter dimensions obtained

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196 from TEM images, of 7 and 14 nm for the radii of the inner and outer layers, respectively. The

197 curvature of the layers induces slight shortening and lengthening of Si-O and Mg-O inter-

198 atomic distances. However, maximum values of these distortions remain physically plausible

199 (see Electronic Annex). PDFs and diffraction patterns from these models were calculated

200 using routines from the Diffpy-CMI library (Juhás et al., 2015). Diffraction patterns were

201 calculated using the Debye equation formalism from non-periodic models of the structures

202 (Warren, 1969). Isotropic thermal displacement parameters for all atoms were set to $8 \cdot 10^{-3}$ Å^2.

203 VESTA (Momma and Izumi, 2011) was used to represent the mineral structures used in this

204 study.

205
206 <div align="center">**EXPERIMENTAL RESULTS**</div>
207
208 <u>TGA, DTG, and DTA</u>

209 TGA and DTG/DTA result are summarized in Figure 1, Tables 1 and 2. All TGA

210 curves are characterized by a continuous weight loss divided in different dehydroxylation

211 steps that show some variations from 1 to 3 hours of reaction. The total weight losses at 800

212 °C for all samples is about 29 % for the two first samples and 22-27 % for the four last

213 samples (Table 1). The weight loss below 200°C is attributed to release of molecular water;

214 this value remains higher than ~9 % (usually lower than 5 % for pure synthetic and natural

215 chrysotile (Falini et al., 2004; Viti, 2010; Lafay, Montes-Hernandez, et al., 2014)) suggesting

216 a high water retention by a porous material. The main weight loss occurs in the 200-800 °C

217 range showing a single or double stage, i.e., two distinct DTG maxima, (Table 2) that can be

218 linked to brucite and serpentine dehydroxylation. Before 1h30 min of reaction, DTG curves

219 are characterized by a peak at a temperature comprised between 250 and 400 °C related to the

220 decomposition of brucite particles (Blaauw et al., 1979; Wang et al., 1998). Dehydroxylation

221 peak for brucite completely disappears after 2 hours of reaction. Note that in previous

222 experiments brucite was clearly observed up to 4 hours of reaction (Lafay et al., 2013).

<div align="center">10</div>

223   However we found relicts of brucite after 3 hours of reaction (see TEM measurements

224   section). The time-discrepancy for brucite disappearance could be due to the use of different

225   reactors, implying different vessel material and different volume. After 1h30 min a clear

226   dehydroxylation event appears at 537 °C (Fig. 1c) linked to a weak endothermic peak at 541

227   °C (Table 1). The development of a strong endothermic peak between 2 hours and 2h50 min

228   of reaction corresponds to the decomposition of particles from the serpentine group (Cattaneo

229   et al., 2003). Here, the weight loss relative to serpentine destabilization (400-700 °C) for the

230   two lasts samples remain in the 11.5-14 % range and is consistent with theoretical water

231   content for serpentine minerals. The DTG peak splits after 2h25 of reaction (one component

232   centred at 535°C and one at 460 °C, Table 2, Fig. 1e) underlying the presence of two kinds of

233   particles or representing the breakdown stage of distinct inner and outer OH groups (Franco et

234   al., 2006). Additionally, the endothermic DTA peak shifts to higher temperature (553°C, Fig.

235   1d). After 2h50 min of reaction the DTG doublet remains present and linked to DTA

236   endothermic doublet. However the main weight loss component centred at ca. 554°C (Fig. 1f)

237   supports the presence of a dominant serpentine component.

238   Since the beginning of the reaction (i.e. after only 40 minutes of reaction) an

239   exothermic peak is observed in the DTA curves in the 670-715°C range with an onset

240   oscillating between 640°C and 660°C (except after 1 hour, peak at 634 °C). The peak position

241   does not match with the typical temperature of ca. 820 °C sharp exothermic peak related to

242   the crystallization of the remaining amorphous anhydrous meta-chrysotile ($Mg_3Si_2O_7$) into

243   forsterite (Mg_2SiO_4) (Viti, 2010). However, we relate this peak to the process of end of

244   dehydration and massive crystallization of forsterite and enstatite. The shift of exothermic

245   DTA peak toward lower temperature referring to pure serpentine in longer experiments (Table

246   1) might be due to a combination of the difference in shape, size and density of particles

247   obtained during the first steps of the chrysotile synthesis (Chatzistavrou et al., 2006;

248   Trittschack et al., 2013).

249   In addition to the reaction pathway described in (Lafay et al., 2013), a more detailed

250   description of the fluctuation observed in the DTA and TGA/DTG curves is given here for the

251   early stages of chrysotile synthesis. We confirmed the presence of brucite in the early stage of

252   the reaction. The oscillating DTG/DTA signal ranging from 200 °C to 800 °C is linked to a

253   continuous evolution of the abundance, and physical properties of brucite and serpentine-type

254   particles attesting for a non-apparent-equilibrium of the system until three hours of reaction.

255   TEM

256   TEM investigations reveals major changes of particles sizes and morphologies during

257   the first stages of serpentine synthesis until the formation of chrysotile with a typical average

258   width ranging between 16 and 20 nm and a variable length from 100 nm to 800 nm. The

259   tunnel width remains extremely monodisperse after 3 hours of reaction and is about 7.5-8 nm.

260   During the first hour of reaction we note the presence of brucite associated with a

261   matrix of flake-like particles constituting an anastomosing network (Fig. 2a and b). The

262   presence of brucite in the early steps of the synthesis is consistent with TGA/DTG

263   measurements and previous work (Lafay et al., 2013). The sensitivity of this medium to

264   electron beam made it difficult to perform TEM characterization with high magnification.

265   After 40 minutes, the medium is already pre-structured, as shown by the dense regions and the

266   diffraction pattern in Figure 2a which is characterized by few diffraction bands rather than a

267   diffuse illumination signal. However no sharp diffraction spots specific for a satisfying crystal

268   structure were observed. A few tubular fibers (or conical) can be observed, yet their

269   occurrence remains rare. In addition, between 40 minutes (corresponding to the end of the

270   heating) and 1 hour of reaction, the anastomosed features are replaced by a porous medium

271   with large fiber-like morphologies as a result of particle aggregation (see Figure 2b). These

272   fiber-like aggregates display wide (up to 100 nm) and variable diameters and are poorly

273   structured with respect to typical synthetic chrysotile (maximum ~20 nm diameter). In this

274   highly energetic system, heterogeneous particles probably tend to reach a greater structuration

275   and homogenization to lower the misfit energy. The number of manifested individual tubes

276   increase with respect to experiment after 40 minutes.

277   After 1h30 of reaction the presence of individual particles is clearly visible and two

278   kinds of crystallites can be distinguished; small flakes co-existing with individual nanotubes,

279   characterized by various sizes and morphology (Fig. 2c). Only few tubes have the typical

280   width and length of the chrysotile reference (which is taken at the end of the reaction). Most

281   of them are smaller than 100 nm in length and they exhibit beveled edges and ovoid shapes

282   like nanorods.

283   Between 2 hours and 2h25 min of reaction individual chrysotile with characteristic

284   widths lower than 20 nm are observed (Fig. 3a). The apparent different width of nanotubes

285   walls might correspond to a difference in phyllosilicate sheets layers and/or atomic density.

286   After 2h50 min of reaction well crystalized individual nanotubes with thin walls become the

287   dominant species (Fig. 3b). This chrysotile type corresponds to the typical end-member

288   minerals observed after long synthesis experiments (Lafay et al., 2013). As mentioned before,

289   the apparent absence of brucite regarding the TGA signal is due to the presence of only rare

290   relicts of brucite (Fig. 3b). At this point, the chrysotile morphology can be considered as an

291   equilibrium morphology that lowers the energy due to the mismatch between octahedral and

292   tetrahedral sheets of serpentine in the MgO-SiO_2-H2O system (pure Mg system). The

293   occurrence of a double DTG/DTA signal after 2h25 min of reaction is consistent with TEM

294   observations underlying the presence of two kinds of chrysotile particles around 2h of

295   reaction.

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297   <u>High energy X-ray diffraction and Pair Distribution Function analysis</u>

298   Structure factors, S(Q), obtained from high-energy X-ray diffraction experiments and

299   the corresponding PDFs of the synthetic samples and synthetic brucite are presented in Figure

300   4. The most striking characteristic is the fact that, from the beginning of the experiment, all

301   the S(Q) and PDFs show similar features. As expected from TGA and TEM characterization,

302   brucite is present in the samples taken before 1h30 min, and its diffraction peaks can be

303   distinguished in the form of a shoulder in the diffraction peak at ~2.45 Å^{-1}. After 1h30 min of

304   reaction all the S(Q) and PDFs reveal features common to that of the chrysotile end-member.

305   An interesting evolution of the low Q peaks is observed (see Figure 4b). The (004)

306   diffraction peak, at 1.7 Å^{-1}, is only observed after 1h30 min. Note that this notation

307   corresponds to the lizardite planar structure (Mellini, 1982; Auzende et al., 2006), which has

308   been used to create chrysotile atomistic models; the *c* axis corresponds to the stacking along

309   the radial direction of the nanotubes. Analysis of the PDFs (Fig. 4c) gives information about

310   the evolution of the coherent domain size, and, again, about the presence of brucite. The

311   decaying intensity of the inter-atomic correlations at long distances is due to a coherent

312   domain size effect, which changes slightly from ~27 Å at 40 min up to 32 Å for the chrysotile

313   obtained after 2h50 min. The relatively small increase in the coherent domain size for

314   experimental product is probably due to the existence of defects formed during minerals

315   structuration.

316   The structuration of chrysotile particles is accompanied by an increase of the Si-O and

317   Si-Si bond intensity in the PDFs (Fig. 4d). We used synthetic brucite and synthetic chryotile

318   obtained after 3 hours of reaction as endmembers to fit all the intermediate PDFs. Note here

319   that the PDFs for chrysotile after 2h50 min and 30h of reactions (Lafay et al., 2013) are

320   identical. All patterns can be fitted using a linear combination between this two end members

321   (see Fig. 5). Here the brucite component is not significant and is no longer required after 1 h

322   30 min of reaction. This result indicates that the chrysotile local order is already present in the

323   samples at early stages of crystallization and that, after 1h30 min of reaction, the chrysotile

324   end-member PDF is enough to fit experimental PDFs results.

325   Additionally, simulations of the evolution of the low-Q part of experimental S(Q)

326   curves (Fig. 4a and b) have been performed by creating chrysotile nanotube structures formed

327   by one, two or four concentric walls (Fig. 6). The simulations reveal that the peak at ~1.7 Å$^{-1,}$

328   corresponding to the (004) reflection in lizardite, increases proportionally to the number of

329   concentric stacked layers. The structure factor of experimental products after 40 minutes of

330   reaction display no features characteristic for multi-wall nanotubes. After 1h and 1h30

331   minutes the experimental S(Q) match with a model of two concentric wall layers. Between

332   1h30 min and 2h of reaction the serpentine products acquire the characteristic features for a

333   coherent concentric stacking of at least four serpentine-sheets. The structure factor does not

334   change anymore after 2h of reaction. Note that the only way to reproduce the peak intensity is

335   the stacking of concentrical curved lizardite sheets. Tests using physical mixing of single-

336   walled particles with different diameters never reproduced the low Q level of intensity

337   observed for well crystallized chrysotile.

338   **DISCUSSION AND IMPLICATIONS**

339   Serpentinitization of ultramafic rocks is a widespread hydration reaction that take

340   place from subsurface lithospheric environment to deep subduction zones and considerably

341   affects rheological and chemical properties of peridotite rocks. It is know that fluid circulation

342   in natural environments contributes to large scale mass transfer and Mg/Si ratio changes

343   during serpentinitization (Niu, 2004; Boschi et al., 2006). Pristine mineral alteration involves

344   a dramatic decrease of rock density and rock strength (Escartin et al., 2001). Moreover, rock

345   hydration processes induce small-scale chemical redistributions and important element

346   entrapment (e.g. B, Li, Cl, As, Sb) likely to be released or exchanged during serpentine phase

347 transformation-recrystallization (Vils et al., 2011) and serpentine dehydration in convergent

348 zones (Deschamps et al., 2013). Some aqueous species greatly increase serpentinization rate

349 in hydrothermal systems and various physichochemical parameters may affect serpentine

350 mineralogical properties (Korytkova et al., 2011; Andreani et al., 2013; Lafay, Janots, et al.,

351 2014). Prior to serpentine formation, proto-serpentine has already been described as an

352 amorphous material or 'matrix' in natural samples (Plümper et al., 2014). In most studies,

353 proto-serpentine is designated as a poorly crystallized and poorly organized serpentine

354 aggregate from which other serpentine varieties start to growth (Andreani et al., 2008), with a

355 fibrous microstructure (Dufaud et al., 2009; Ryu et al., 2011).

356   The structural transformation at atomic scale, from serpentine precursor to serpentine

357 endmembers, in the MgO-SiO_2-H_2O system account for small scale mass transfer at mineral

358 scale during olivine and pyroxene alteration. The study of chrysotile structuration from free-

359 fluid in experimental system - which can been linked to serpentine veins in natural systems

360 (Andreani et al., 2004) - enables the exploration of the progressive serpentine physical

361 properties changes and might account for small scale chemistry changes and mobile element

362 migration in serpentine veins (Benton et al., 2004).

363   <u>Structuration model from serpentine precursor to chrysotile formation</u>

364   The results from these analyses dismiss the hypothesis of a totally amorphous

365 material. In many studies, chrysotile is considered as a metastable varieties characterizing the

366 first steps of serpentine crystallization, and later re-crystallizing into polygonal serpentine and

367 lizardite (Grauby et al., 1998). In this study, we have focused only on the first part of this

368 process, with chrysotile being the final end-member of the reaction, considered as a reference.

369   As already shown in Lafay et al., (2013), we confirmed that the formation of

370 homogeneous chrysotile is preceded by a stage where transitory phases are rapidly consumed

371 and transformed at least partly by dissolution-precipitation processes to supply chrysotile

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372   growth. Such assumption is supported by (1) the precipitation of transient brucite and

373   serpentine that remains distinguishable by TGA and TEM analyses up to 2 hours of reaction,

374   (2) a progressive evolution of mineral phase properties and proportion accompanied by a loss

375   of total water visible by DTG/DTA pattern in the brucite-serpentine dehydroxylation range

376   from 40 minutes to 2 h of reaction, (3) the change in particle size from wide to thin fiber-like

377   particles.

378   An interesting feature from the DTG/DTA data is the important loss of mass related to

379   serpentine minerals before 1 hour of reaction, this despite the absence of the typical

380   dehydroxilation peak. This confirm the presence of small heterogeneous flack-type particles

381   not distinguishable by conventional X-ray powder diffraction analyses. However, the short-

382   range structure of chrysotile is already recognizable by PDF analyses after a short reaction

383   time (Figs 4 and 5). We reinforce the idea that TGA features are extremely sensitive to the

384   presence of dissolution-precipitation processes and the ensuing changes occurring in the

385   intermediate stage of reaction with the formation of transitory phases. The intensity of the

386   dehydroxylation peak appears to be dependent of the stacking properties and the formation of

387   long-range order in the chrysotile precursors. This could translate into a distribution of

388   dehydroxilation temperatures leading to the formation of several peaks (Fig. 1e) instead of the

389   single peak generally observed for crystalline chrysotile (Viti, 2010; Lafay et al., 2013; Bloise

390   et al., 2015)

391   High-energy X-ray diffraction measurements (including PDF analyses) coupled with

392   XRD modelling and TEM characterization enables to depict the specific case of chrysotile

393   formation. The different experimental observations converge towards a picture where

394   particles exhibiting chrysotile short-range order are already formed during the first stages of

395   reaction and co-exist with brucite (Figs. 2, 4 and 5) and probably other serpentine-type

396   particles (few tiny nanotubes are already present during the incipient reaction). TEM

397   observations after 1 hour of reaction show how these particles aggregate forming elongated

398   wide fiber-like shapes. Interestingly, the size of these aggregates is larger than the typical

399   diameters of the final chrysotile tubes (see Figure 2b). This could be an indicator for the

400   formation of an intermediate meso-structure that is later affected by dissolution-

401   (re)precipitation and structuration processes. The nanoscopic character of these nano-

402   crystalline flake-like particles suggests that they contain a large proportion of edge sites, with

403   -OH groups of variable reactivity.

404   For a reaction times greater than 1h30 min, an increase of the intensity of the

405   diffraction peak along the stacking direction is observed, which can be explained by an

406   increase in stacking of serpentine sheets and the structuration of chrysotile with a multi-wall

407   structure (Fig. 6). This coincides with the observation of individual nanorods and the first

408   visible structured nanotubes. We estimate that before 1h of reaction, the possible existence of

409   structured nanotubes (*i.e.*, coherent concentric serpentine sheets) remains too small to be

410   distinguishable by high-energy X-ray diffraction measurements. Obviously, after 1h30 min

411   the system remains heterogeneous, but previously observed poorly structured nano-fibers tend

412   to be replaced by short nanotubes (nanorods) and individual nanotubes (Fig. 2c). This

413   observation is consistent with the appearance of the typical serpentine dehydroxylation peak

414   in the DTG/DTA pattern. In the final stage, a continuous structuration through stacking of

415   coherent serpentine-sheets (Fig. 5) and the formation of longer tubes (Figure 3) is observed

416   with only minor changes in the diffraction patterns.

417   In addition to the dissolution-precipitation processes previously discussed, we

418   postulate that the kinetic sequence goes from a disordered pre-structured gel phase with

419   numerous nucleation centers (Fig. 1a) that evolves through time, to a high energy fiber-like

420   morphologies with various diameters and forms (tubular, flakes-like and conical). We propose

421   that the tubular geometry observed with monodisperse diameter can be considered as the

422 equilibrium morphology for the present conditions and chemical system. Several clues

423 suggest that transformation observed here are in adequation with later chrysotile to lizardite

424 transition proposed from previous experimental studies (Grauby et al., 1998) and

425 mineralization occurring in natural systems.

426   Our identification of pre-formed short-range ordered particles also support a

427 mechanism of self-assembly or aggregation-based growth (Fig. 7) to minimize energy. This

428 mechanism of particle-attachment has now been identified in various synthetic, biogenic, and

429 geologic environments (De Yoreo et al., 2015). Aggregation and oriented attachment of pre-

430 formed nanoparticles have been reported to be active mechanisms of other common mineral

431 formation such like goethite (Banfield et al., 2000; Guyodo et al., 2003), ferrihydrite (Li et

432 al., 2012) magnetite (Baumgartner et al., 2013) or gypsum (Stawski et al., 2016; Van

433 Driessche et al., 2012), to name the most representative ones. This mechanism is comparable

434 to the one proposed for the structuration of imogolite (Levard et al., 2010), another tubular

435 mineral variety. However, while geological contexts are varied, few studies have addressed

436 hydrothermal conditions due to the difficulty associated with their study. Here, we show an

437 ex-situ study of hydrothermal growth of serpentine from a proto-serpentine precursor.

438   At an advanced stage of crystallization, after brucite consumption, the presence of

439 Ostwald ripening processes cannot be neglected. The present results provide a way to address

440 the role of this aggregation process in the incipient formation of serpentine in natural systems.

441 The differentiation towards other serpentine varieties remains to be explored. For that

442 purpose, further investigations under different physicochemical parameters (e.g. temperature,

443 pressure, impurities, CO_2/H_2O activity) are on-going to ascertain the mechanisms of

444 formation of other serpentine varieties such as lizardite and antigorite. It should be noted that

445 the proficiency to understand the structuration mechanism of nanomaterials remains of great

446   interest for example in applied physics for single- or multi-wall carbon nanotube synthesis

447   (Martel et al., 1998).

448   **Acknowledgments**

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656

657

658   **Table 1:** Summary of TGA weight loss data for samples series. Temperature ranges were

659   divided on the base of approximated TGA loss for molecular water ($^{\alpha}$) brucite mineral ($^{\gamma}$) and

660   serpentine group minerals ($^{\beta}$).

661

662   **Table 2:** Summary of DTG and DTA peak temperatures for samples series corresponding to

663   curves on Fig. 2.

664

665   **Figure 1**. Thermal analyses of the sample series performed in N_2 atmosphere. 10 °C/min

666   heating rate and 0–800 °C temperature range. Thermogravimetric losses (TGA) are in wt%

667   and temperature deflection (DTA) are in °C. DTG has no unit. Typical dehydroxylation range

668   for brucite and serpentine dehydroxylation are also reported as well as typical serpentine

669   appearance (thick red arrow).

670

671   **Figure 2.** Representative samples powder TEM images for several reaction advancements. a)

672   flake-likes particles (left and middle) and porous anastomosed medium with rare thick

673   individual tubular or conical fibers after 40 minutes, the Selected area (electron) diffraction is

674   around b) fibers likes serpentine particles self-assembly (left and right) with individual brucite

675   (indicated by the white arrows) and aggregate (center) with few individual nanotubes after 1

676   hour, c) disoriented serpentine nanorods and individual poorly crystallized nanotubes after 1

677   hour and half (black arrows pin-pointed the beveled (conical) termination of serpentine

678   particles. The scale bar corresponds to 100 nm.

679

680   **Figure 3**. Representative samples powder TEM images of individual nanotubes after 2 hours

681   (a) and 2 hours 50 minutes (b) of reaction, typical width of chrysotile tunnel (8nm) and wall

682   (6 nm) is indicated in right-corner enlarged view, relicts of brucite is pin-pointed by the

683   arrow.

684

685   **Figure 4.** (a)Experimental structure factor patterns for different reaction advancements. Low

686   q region is enlarged in (b) (1.2-2 Å^{-1} range), with the (004) diffraction peak indicated by the

687   white arrow. Brucite and the chrysotile end-member (3h of reaction) are reported as

688   references. (c) Pair Distribution Functions (PDFs) of experimental products at different

689   reaction times. The first 10 Å are enlarged in (d).

690

691 **Figure 5.** Experimental PDF patterns for different reaction advancement from Fig. 4c (solid

692 lines) and best fits from the linear combination (dotted lines) using brucite and chrysotile

693 (reference after 2h50 min of reaction) as the two mineral endmembers. The proportion of the

694 brucite component used for the simulations is also reported, for more detail refer to the text.

695

696 **Figure 6.** (a) Experimental structure pattern from Fig. 4b and (b) examples of modeled

697 structure factor patterns with the corresponding modelled structures (including one single

698 lizardite layers and multiple layers tubes) starting with a lizardite structure (inset).

699

700 **Figure 7**. Proposed conceptual model for chrysotile nucleation and growth mechanisms. From

701 left to right, structure evolution starts from single nano-sheets of serpentine, initial

702 dissolution-reprecipitation is accompanied by aggregation and stacking along c axis and size

703 homogeneization to form nanorods then monodisperse nanotubes assemblage.

704

705

	reaction time (min) this study						reaction time (min) Lafay et al., (2013)		
	40	**60**	**90**	**120**	**145**	**170**	**360**	**720**	**1800**
T range (°C)	TGA loss (%)						TGA loss (%)		
30-200 [α]	10.8	12.8	9.7	8.8	10.5	10.5	4.5	5.9	4
200-400[γ]	10.3	9.7	7.6	3.4	2.6	2.2	2.7	1.8	1.1
400-800 [β]	8.5	6.9	8.2	10.5	13.6	11.5	12	11.1	12
sum at 800	29.6	29.4	25.5	22.7	26.7	24.2	19.2	18.8	17.1

Table1

Table 2

	reaction time (min) this study						Reaction time (min) Lafay et al., (2013)		
	40	**60**	**90**	**120**	**145**	**170**	**360**	**720**	**1800**
for DTG	277 w	344 ss	338 ss						
peak T°C	363 ss	391 sh	386 sh		460 ss	457 s	366 w		
	391 sh	625 w	537 s	553 ss	535 ss	554 ss	593 ss	600 ss	600 ss
	584 w								
	675 w								
for DTA peak T°C	687 exo s	335 endo w	341 endo w	555 endo ss	457 endo s	552 endo s	599 endo w	590 endo w	594 endo w
		634 exo s	541 endo w		536 endo s				
			687 exo ss	715 exo ss	670 exo ss	708 exo ss	775 exo ss	814 exo ss	827 exo ss

Note: w = weak, s= strong, ss= very strong (main peak), sh = shoulder, endo = endothermic, exo = exothermic
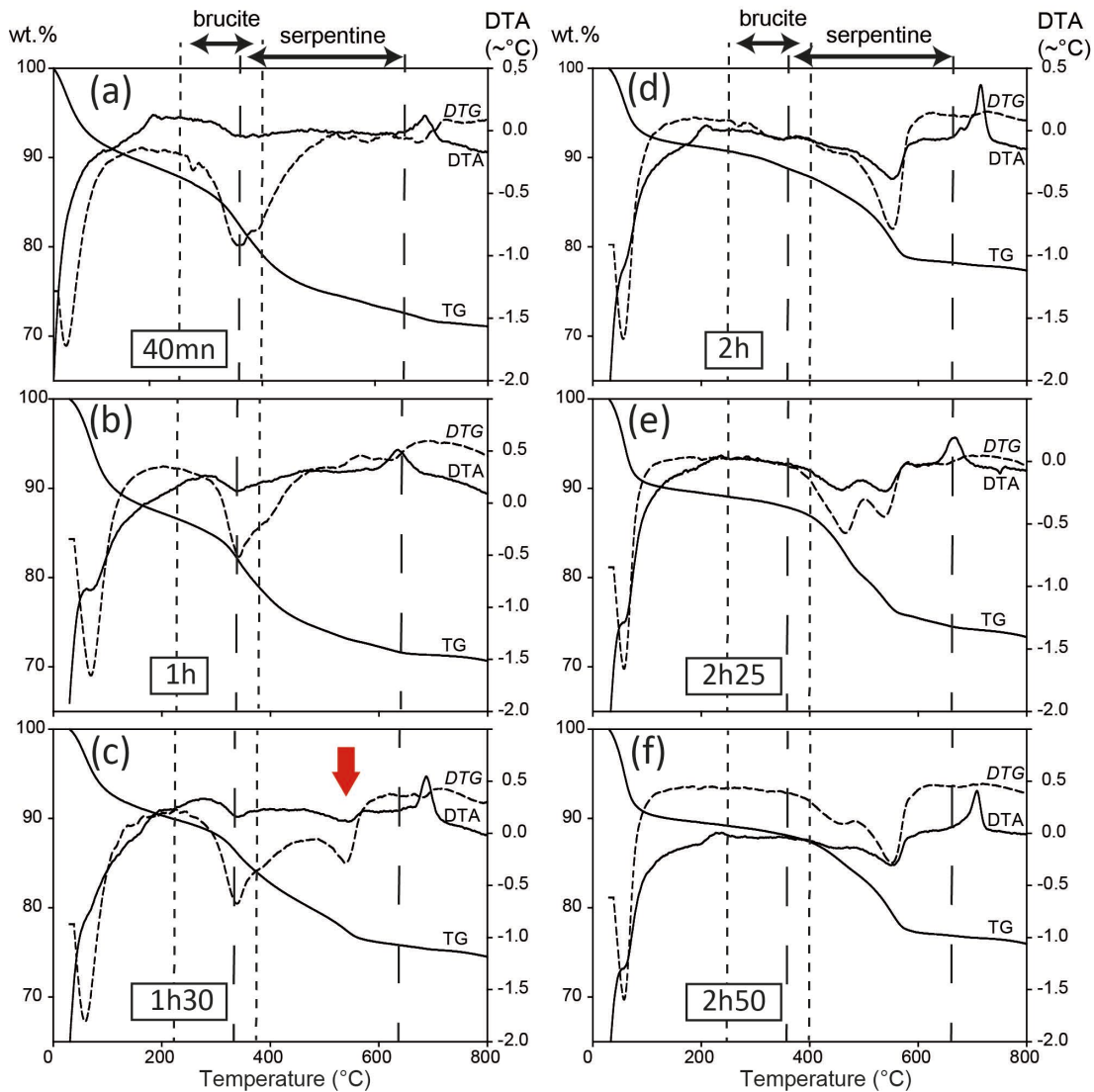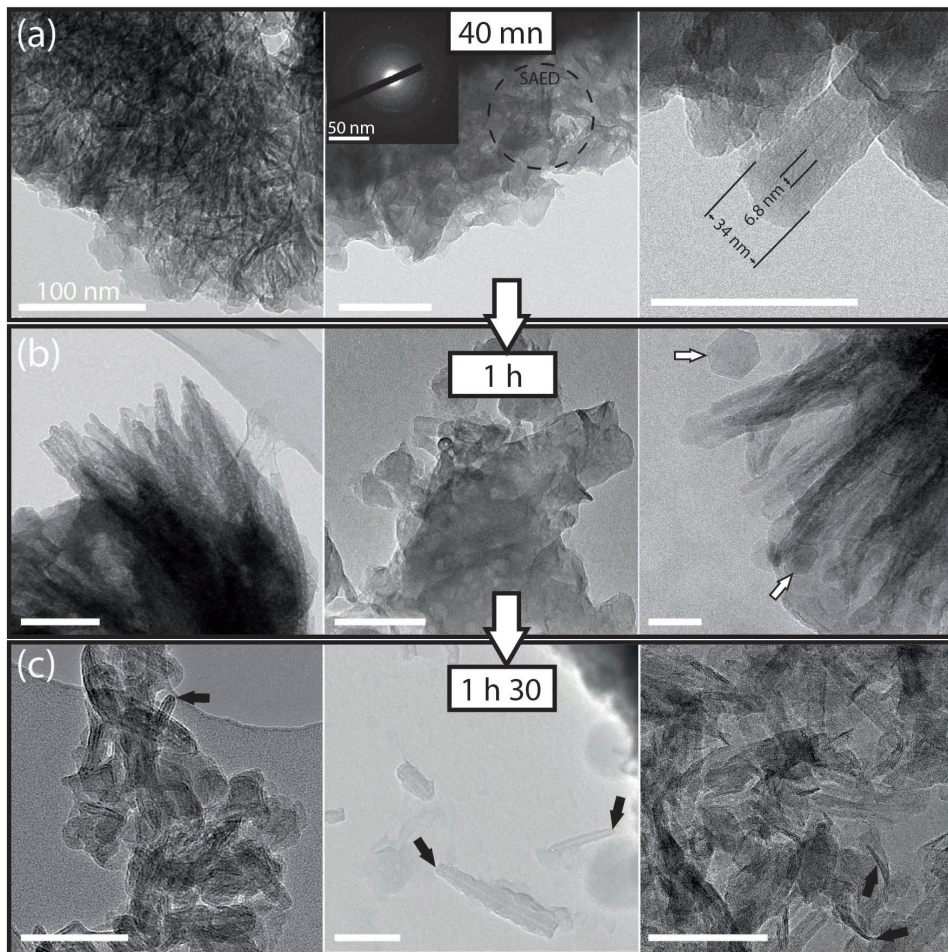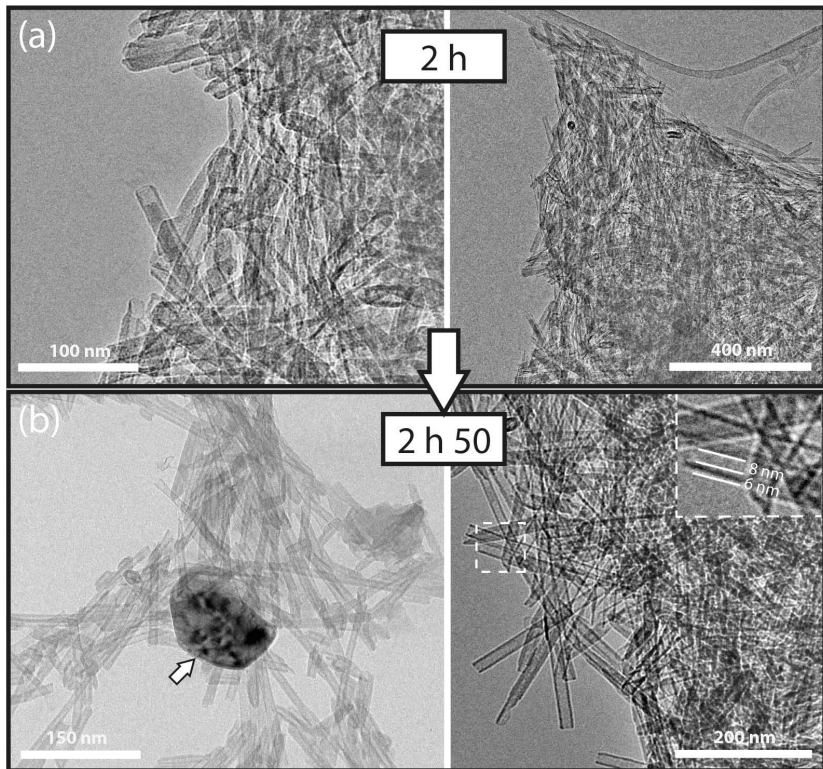
Figure 1

Figure 2

(a) 40 mn
SAED
50 nm
100 nm
6.8 nm
34 nm

(b) 1 h

(c) 1 h 30

Figure 3

(a) 2 h
100 nm
400 nm

(b) 2 h 50
150 nm
8 nm
6 nm
200 nm

Figure 4

Figure 5

(a) Experimental (b) Simulated
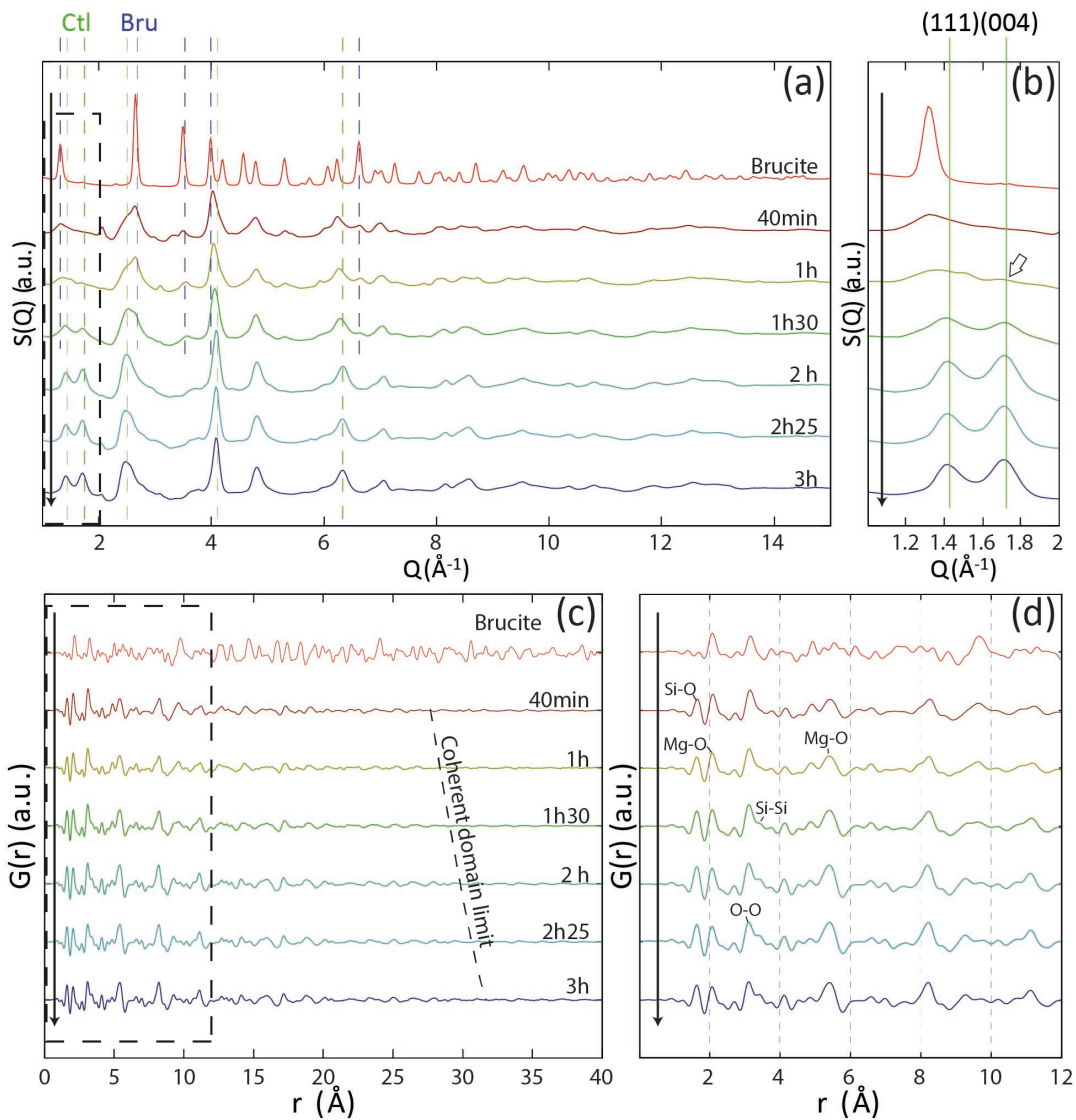
(111) (004)

Single wall

Double wall

70° rotated along b axis

Quadruple wall

Reaction progress
Layers stacking

Figure 6

Figure 7

~100 nm

Presence of Brucite

0 Reaction progress (hours) 1 2

Dissolution precipitation

Single flakes
crystalilte precursors

c

aggregation to form highly
hydrated single layer chrysotile

Dehydration and
layer stacking along
c axis

Dissolution/precipitation
Size homogeneization

Nanorods

Growth in length

Nanotubes