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Research paper

A mechanism for the sphere/tube shape transition of nanoparticles with an imogolite local structure (imogolite and allophane)

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ABSTRACT

Imogolite and allophane are two strongly curved nanominerals. Indeed, imogolite has a tubular shape with a diameter of only 2.5 nm. Allophane is often presented as a spherical nanostructure with a diameter of about 5 nm. The mechanism explaining the strong curvature of these two nanominerals has been extensively discussed. However, whether or not these two nanomaterials are related to each other is not clear and the mechanism responsible for the selection between the two different shapes is not well established. In this article, we propose that imogolite and allophane are nanopolymorphs of the imogolite local structure and that the transition from spherical to tubular shape occurs at an early stage of the precipitation because of edge stress in proto-imogolite. This hypothesis for the shape selection is supported by the use of a nanomechanical model tuned to mimic the main characteristics of imogolite-like nanomaterials.

1. Introduction

It is commonly observed that a material can adopt a variety of structures. For simple elements, this is the notion of allotropy. For minerals, this is the notion of polymorphism. Carbon is an emblematic example for allotropy as it can form both diamond and graphene. At the nanoscale, carbon atoms with a sp2 hybridization can arrange in the form of nanospheres (fullerene), nanotubes of various chirality and wall number, sheets and other exotic shapes recently called nanoallotropes (Georgakilas et al., 2015). The perfect control of the different shapes is however difficult for carbon nanoallotropes. The same phenomena is observed for aluminosilicates presenting an imogolite-like local structure (ILS) with composition $Al_2SiO_3(OH)_4$. In this case, it is possible to talk about nanopolymorphs as imogolite and allophane can enter the category of nanocrystals. Allophane having an ILS are described as 4–5 nm spheres (Henmi and Wada, 1976) while imogolites are very long nanotubes with a monodisperse diameter between 2 and 2.8 nm depending on the formation conditions. Imogolite are believed to be obtained from proto-imogolites, which are described as curved pieces of ILS with an average edge size of 5 nm (Levard et al., 2010). Unlike carbon, very efficient control over the different shapes is possible through adapted synthesis.

The ILS is a very original structure for clay minerals. Generally, the silicon atoms form a polymerized tetrahedral sheet in which each Si atom is linked to a dioctahedral (e.g. Kaolinite or Halloysite) or trioctahedral (e.g. Chrysotile) sheet by a single Si—O—Al or Si—O—Mg bond. This is not the case in the ILS where Si atoms are isolated and form three bonds within the lacuna of the dioctahedral aluminum sheet (Cradwick et al., 1972). The ILS is characterized by a strong curvature. Imogolite has a well-defined radius going from 2 nm for natural imogolite to 2.8 nm for synthetic nanotubes. It is possible to vary the size of imogolite by changing the temperature (Wada, 1987), the type of chemical precursors (Yucelen et al., 2012) or by replacing Si atoms by Ge atoms (Wada and Wada, 1982). However, the nanotubes formed in the same conditions have all the same diameter. The reasons explaining this well-defined curvature have been discussed soon after the imogolite discovery (Farmer et al., 1977). The early explanation was that the tetrahedric Si site has to create bonds in the lacuna of the dioctahedral sheet which is larger than its relaxed size. Indeed, if one consider gibbsite as a reference structure for uncurved 2D dioctahedral Al sheet, the O—O distance (~edge length of the Al octahedron) is 2.9 Å whereas the O—O edge distance in the relaxed Si tetrahedron is ~2.6 Å. This size mismatch is the most obvious reason for the spontaneous curvature associated with the ILS. However, the size mismatch between the relaxed Si tetrahedron and the O—O distance of the dioctahedral Al sheet is not sufficient to explain the very strong spontaneous curvature of imogolite. It is also important to consider the role of the electrostatic charges and hydrogen bonds (H Bond). The role of the internal Si—OH groups in the stability of imogolite nanotubes has been explored by density functional theory (DFT) (Lee et al., 2011). It is demonstrated that the H bond network inside the nanotubes contribute to the stability in size and to the selection of a preferential Zig-Zag organization (Demichelis et al., 2010; Lee et al., 2011).

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An indirect experimental confirmation of the role of an internal H bond network has been obtained by Bottero et al. (2011). Indeed, they obtained a synthetic nanomineral having an ILS by using triethoxymethylsilane as a silicon source in the co-precipitation step. The obtained nanoparticles are still curved; the concave part being covered by Si—CH_3 groups instead of Si—OH making strongly hydrophobic nanoconfined cavities. This chemical modification prevents the formation of an internal network of H bond. It is observed that these nanotubes are significantly larger than their natural Si—OH analogue (Amara et al., 2015) confirming indirectly the important role of H bond for the determination of their spontaneous curvature.

The spontaneous curvature of imogolite has been studied by many different types of molecular dynamic (MD) and DFT techniques. It is always concluded that it exists a spontaneous curvature of minimum energy (Tamura and Kawamura, 2002; Alvarez-Ramirez, 2007; Li et al., 2008; Demichelis et al., 2010) even if the model may predict different values. An elegant analytical expression has been proposed considering a dissymmetric surface tension on a flexible thin material (Guimarães et al., 2007). This expression seems to capture the essential physics behind the curvature of ILS and nicely describes the shape of the energy minimum obtained by different simulations. Based on such simplified analytical expressions, it is possible to successfully explain the single to double wall transition in germanium based imogolite (Thill et al., 2012). A generalized version has been used to describe the structure and thermodynamic of curved clay minerals (Belloni and Thill, 2016). While this phenomenological model enables to nicely relate the spontaneous curvature to the mechanical properties of ILS, it does not allow to predict the sphere/tube transition essentially because it neglects border effects.

DFT simulations have been coupled to experiments to propose a mechanism for the selection of the two types of curvature (spherical and tubular). It is concluded that the ions and pH seems to play an important role (Abidin et al., 2007; Bac et al., 2009). The use of Si—CH_3 groups for the internal surface of the ILS nanominerals maintains a spontaneous curvature without the formation of H bond network and electrostatic interactions. Modifications of the synthesis proposed by Bottero et al. (2011) allow to obtain both shapes with hybrid Si—CH_3 ILS. Obviously, in this case, the transition from spherical to tubular morphology cannot be linked to the deprotonation of Si—OH groups or the formation of internal H bond network and this result calls for an alternative explanation.

In this work, we propose a hypothesis for the shape transition saying that it is linked to a competition between surface and border tensions in proto-imogolite. To test this hypothesis, we use a simplified computer model to explore the curvature of proto-imogolites of various sizes. We used a hybrid model which is close to the atomistic description of the ILS and thus allows us to account for border effects. We will not try to perform a realistic mechanical description of imogolite or allophane as in MD or DFT models. We rather explore a general problem using a simplified mechanical system. The questions of interest are: i) Is it possible to correctly mimic the mechanical behavior of imogolite with such a simplified description? ii) Is it possible to observe a transition from a spherical to a tubular shape without interaction with the solvent? We will then discuss the implications of this simplified curvature mechanism on the formation mechanism of the different ILS nanominerals.

2. Methods

2.1. Numerical model of the hybrid ILS

In the Guimarães et al. (2007) model, a plastic 2D thin material is subjected to different surface tensions on its two sides. In this case, the mechanical energy per unit surface as a function of the radius of curvature R of the 2D material reads

$$E = \frac{Yh^3}{3R^2} - \frac{\sigma h}{R} + \sum \quad (1)$$

where Y is the Young modulus of a 2D slab of thickness 2 h, σ is the difference in surface tension between the two surfaces and Σ is a constant. This equation can be identified with a quadratic expression of the form

$$E = E_0 + \frac{K_c}{2}\left(\frac{1}{R} - \frac{1}{R_0}\right)^2 \quad (2)$$

with $K_c = 2Yh^3/3$ and $R_0 = 2Yh^2/3\sigma$. Considering the estimation of the Young modulus of the ILS which is predicted to be of the order of 300 GPa and considering the thickness of the dioctahedral sheet to be 2 h = 2.9 Å, K_c is about 150 kT. This simple expression enables to reproduce the shape of the curve E = f(R) obtained by advanced DFT simulations. For example, the results of Guimarães et al. (2007) for the energy of imogolite of various radius can be fitted with Eq. 2 using $K_c = 156$ kT and $R_0 = 9.2$ Å.

Here, a simplified description of the ILS is used consisting in an assembly of flexible octahedra and tetrahedra (Fig. 1). Harmonic bond and angle potentials are used to tune the shape and flexibility of the structure (Konduri et al., 2006). The assembly of flexible octahedra will play the role of the flexible 2D material and the difference in surface tension will be induced by the bonding on only one side of flexible tetrahedra. The amplitude of the surface tension difference is controlled by the size and rigidity of the tetrahedra.

The octahedra are sharing edge links as in a gibbsite-like structure. In the lacuna of the 2D gibbsite-like structure the tetrahedra share three common vertices with the octahedra. The centers of the octahedra and tetrahedra mimic the Al and Si atoms in the ILS, respectively. The vertices of octahedra and tetrahedra correspond to the positions of O atoms in the ILS. The interactions in the structure are computed using exclusively harmonic potentials for the stretching and bending of the center-vertices bonds and angles, respectively. The energy for the stretching term is given by $E_s \sim ½\, K_s(x - x_0)^2$ where K_s is the stretching rigidity of the bond and x_0 its equilibrium distance. For the bending energy $E_b \sim ½\, K_b(\theta - \theta_0)^2$ where K_b is the bending rigidity and θ_0 the equilibrium angle. We have considered a single object of a given size without periodic boundary conditions. Indeed, usual simulations with periodic boundary conditions impose a tubular shape. The structure is composed only of octahedra and tetrahedra and only tetrahedra bonded to three octahedra are considered. To prevent interpenetration of distant polyhedra upon curvature of very large structures, non-bond interactions are computed using Lennard-Jones potentials for points separated by at least three bonds. The Lennard Jones parameters are taken from the CLAYFF force field (Cygan et al., 2004) considering the vertices as O atoms and the centers of tetrahedral and octahedra as Si and Al atoms, respectively.

Konduri et al. (2006) have studied the curvature of Al/Si and Al/Ge imogolite using such simplified description with harmonic potentials. They show that this type of model can mimic the shape of the strain energy as a function of the radius of imogolite. From the comparison with MD simulations, they proposed values for the stretching rigidity and bond equilibrium distance of $K_s = 6.06$ eV Å^{-2} and $x_0 = 1.59$ Å for Si—O, $K_s = 2.52$ eV Å^{-2} and $x_0 = 1.97$ Å for Al—O. In their analysis, the bending angles of O—Si—O and O—Al—O were considered fixed at respectively 109.5° and 90°. These approximations certainly induce an underestimation of the stretching rigidities. For example, the harmonic approximation of the CLAFF potential around the energy minimum gives a stretching rigidity of $K_s = 40.5$ eV Å^{-2} and a distance at minimum energy of 1.43 Å. Such rigidity is in better agreement with the IR wavenumber around 1000 cm^{-1} for the absorbance attributed to the stretching of the Si—O bond. In the CLAYFF, the bending rigidity of the O—Si—O and O—Al—O angles is 1.302 eV rad^{-2}. Thus, compared