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RECENT PROGRESS IN THE SYNTHESIS OF IMOGOLITE AND IMOGOLITE-LIKE CLAY MINERALS. A FOCUS ON THE SPHERE/TUBE TRANSITION.

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Imogolite has been discovered more than 50 years ago in the weathering products of volcanic soils in Japan [1]. It has been quickly realized that imogolite is a ubiquitous clay mineral which can be readily synthesized in the laboratory using rather simple co-precipitation receipts [2].
From this initial discovery researchers have started to explore the possible modifications of the imogolite nanotubes. Many successful examples are now available [3,4]. Some of these chemical modifications were shown to be coupled with important structural modifications. The discovery of double walled germanium based imogolite] or the larger hybrid imogolite with a hydrophobic internal surface are good examples [5,6]. This growing number of new materials derived from imogolite and sharing the same imogolite local structure (ILS) is now making a new whole family of nanoclays.
The study of the synthesis of these new ILS materials has triggered much progress in the understanding of their formation mechanism. In this presentation, we will go through the recent discoveries about the formation mechanism of imogolite-like nanoclay. We will focus on recent investigations of the early constitution stage of imogolite. We will show that from the same starting conditions, it is possible to produce imogolite, allophane or mixture of both shapes.
Theses results demonstrate that imogolite and at least some allophanes can be considered as polymorphs of the ILS material. The control of the spherical or tubular shapes has barely been investigated. Bac et al. showed that in the case of germanium based imogolite, it is possible to go from mainly spherical to mainly tubular shape by changing the pH and salinity [7]. Abidin et al. using DFT simulations proposed that it is due to local properties of the Si-OH internal groups [8]. As sphere/tube transitions are also observed for hybrid ILS with the internal surface covered by Si-CH_3 groups an extension of this work as to be considered.
We propose a new hypothesis related to the mechanical properties of proto-imogolite. Using a simplified model accounting for border stress on small proto-imogolite, we show that it exits a size threshold for the sphere/tube transition. We suppose that this transition can at least in part explain the control in shape between ILS tube (imogolite) and sphere (proto-imogolite/allophane). We believe this mechanism to be very general and may be of interest for other clay minerals for which a spontaneous curvature exists and a coexistence of spherical and tubular shapes has been described (for example halloysite).

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