Experimental report.

The aim of the study was to investigate the structure of short-range ordered aluminosilicates (imogolite and allophane) generally found in volcanic soils. Actually, we try to elucidate the role of natural nanoparticles on the mobility of heavy metals in these soils. Therefore, the structure of these nanoparticles needs to be precisely characterized.

The structure of imogolite ($Al_2SiO_7H_4$) is well known since 1972,[1] whereas the structure of allophane still needs to be clarified. Imogolite consists of a hollow nanotube with a diameter of about 2 nm and a few tens of nanometer length. On contrary allophanes are mostly described as nanospheres with diameter ranging from 3 to 5 nm and with an identical chemistry. However the spherical shape has only been shown by few TEM pictures and it is rather seen as a kind of amorphous phase than well defined spheres.

Extraction of pure aluminosilicates (allophane and imogolite) from soils is quite difficult so nanoparticles were synthesized and compared to natural ones. The samples were characterized at a local scale using NMR and XAS but a larger scale characterization was necessary to investigate the shape of nanoparticles. In this context, the use of the Pair Distribution Function analysis seems to be well suited.

Materials and methods

PDF data collections have been performed on beamline D2AM at an incident beam energy of 25 keV (λ = 0.499 Å) without analyzer and using capillaries as sample holders. The measurement time was quite long (about 12 hours) in order to reduce experimental noise, particularly at high Q values. PDF curves G(r) were computed using PDFgetX2 software[2] and experimental curves were fitted using pdfgui software.[3] Experimental curves of synthetic samples were fitted using a model of imogolite proposed by Cradwick et al. (1972)[1], whereas natural sample fitting was completed with a structural model of maghemite to take into account the presence of a minor iron oxide impurity.

Results.

Figure 1 exhibits the PDF curves G(r) of the synthesized imogolite and allophane and of the natural sample. First of all, high similarities are observed between the two synthetic samples curves, imogolite and allophane, until 10 Å. Moreover, the main peaks of synthetic sample curves could be noted on the natural one despite the presence of small amount of iron oxide.

Concerning the fitting results, the good correlation between the experimental curve of imogolite and the model until 15 Å confirms that the local structure of our synthetic sample consists of an imogolite-type structure as described by Cradwick.[1] This result is consistent with previous NMR experiments.
An unexpected result concerns the good fit of the allophane curves (natural and synthetic) by the same tubular model up to 10 Å. In the 10-15 Å range, allophane and imogolite seem to have the same local structure. However the poor quality of fit after 10 Å for allophane prevent us to conclude on its structure at a larger scale (short nanotube ? imogolite fragment ?...).

More data with better resolution and statistics are required to obtain a better description of the structure of these complex nanoparticles.

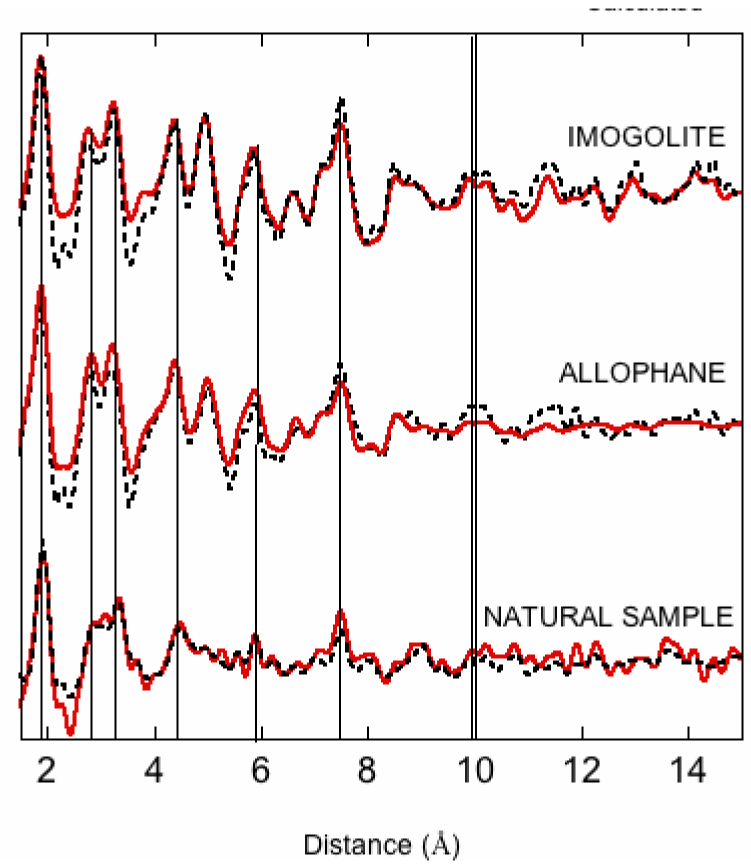

Figure 1. Pair Distribution Functions of synthetic and natural samples.

References

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