Electron Diffraction Tomography (EDT) allows acquiring 3D single-crystal diffraction data from isolated crystallites of few tens of nanometers [1]. This is a crucial benefit when the phase of interest is available only as nanosized crystals, either isolated or as part of polyphasic or polytypic assemblages, and when its structure is characterized by large cell parameters or pseudo-symmetry. EDT method can be coupled with low-dose STEM-based and ultra-fast acquisition routines, making it possible to collect satisfactory datasets from very beam-sensitive samples, like organics or proteins [2]. Moreover, high-quality EDT data are also suitable for dynamical refinement algorithms [3].

The development of EDT method opens fascinating new perspectives for Mineralogy and Material Sciences, particularly concerning the characterization of poorly crystalline materials, like alteration crusts or metamict minerals [4], of nano-exsolution and precipitates in metallic alloys [5] and of isolated bio-minerals or bio-medical sensors sampled directly inside a biological environment [6]. Moreover, nano-crystalline phases often show unusual structural features that are stable only at the nanoscale, and may be of primary importance for understanding natural phenomena or tailoring synthetic routes and engineering applications.

Karibibite, Fe$_3$(AsO$_4$)$_4$(As$_2$O$_5$)(OH), was firstly recognized as an alteration product of löllingite in 1973 [7]. It normally occurs as yellow crusts and sub-micrometer thick fibers. Karibibite has been reported in several worldwide occurrences, but never in crystals suitable for X-ray single-crystal structural study. The orthorhombic symmetry and unit-cell parameters (a=7.3 Å, b=28.0 Å, c=6.5 Å) were obtained by combining powder X-ray and conventional electron diffraction.

Karibibite was recently investigated by EDT method. Data were collected from a single fiber about 150 nm large. The reconstructed 3D diffraction volume confirmed the cell parameters from literature and delivered extinction symbol Pn-a. On the basis of EDT intensities, two consistent ab-initio solutions were obtained in space group Pnma by SIR2014 [8] and δ-recycling [9]. The crystal structure of karibibite consists of bands of Fe$^{3+}$O$_6$ octahedra decorated with (As$_2$O$_5$) dimers and chains of (AsO$_5$) trigonal pyramids. This means that in karibibite As is unusually coordinated in two different arsenite groups, both with the same oxidation state (3+) [10]. The structure was finally confirmed by X-ray Rietveld refinement.