Structure characterization of bio-mineralogical materials by automated electron diffraction tomography: vaterite and hydroxyapatite

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In many geological environments an important fraction of rocks consists of nanocrystalline minerals. While some phases form nanocrystals only in special conditions connected with fast cooling or shock events, others are always confined to the nanosize due to kinetic reasons or because related with weathering and mineralization processes. Similarly, novel synthetic advanced materials and polluting agents in industrial wastes and atmospheric particulate often appear only in form of nanocrystals. Physical and chemical properties of such phases are strictly related with their crystal structure, which is then fundamental for understanding their potential use and toxicity. Electron diffraction is able to pick-up information from single nanoscopic grains, allowing the investigation of minority phases in polyphasic samples and of extremely limited amounts of material. In the last years automated diffraction tomography (ADT)\textsuperscript{[1-3]} emerged as an efficient method for routine ab-initio structure determination of nanocrystalline phases.\textsuperscript{[4-5]} ADT characteristics make it particularly suitable for the investigation of biominerals, normally available only in the form of nanoscopic grains. Biominerals can be directly studied inside biological tissues, and their crystal structure and orientation connected with the contiguous organic environment.\textsuperscript{[6]} In this contribution we will show two case studies where ADT was used for the structure characterization of bio-mineralogical materials: vaterite and hydroxyapatite.

Vaterite, one of the common natural CaCO\textsubscript{3} polymorphs, plays a pivotal role in weathering and biomineralization processes. Vaterite is a kinetically favored polymorph that often precipitates before calcite and aragonite. The knowledge of its structure is key information for understanding nucleation processes that involve CaCO\textsubscript{3} and can facilitate the synthesis of bio-mimetic nanomaterials and the prevention from carbonate scales in industrial processes. ADT allowed for the first time to acquire three-dimensional diffraction data from a single vaterite nanocrystal.\textsuperscript{[7]} The vaterite structure was recognized as monoclinic with parameters geometrically related to previously proposed hexagonal and orthorombic models. It is characterized by an arrangement of alternating Ca\textsuperscript{2+} and (CO\textsubscript{3})\textsuperscript{2-} layers. Moreover, vaterite crystals are always characterized by stacking disorder and local modulation that can be approximated by a 6-layer superstructure. The so-determined structure model is the only one to be consistent with the Raman spectra and a number of independent physical properties reported by previous authors.

Hydroxyapatite nanocrystals compose all human calcified tissues: tooth enamel, dentine and bone. On the basis of XRPD diffraction, two structural models have been proposed for hydroxyapatite in centrosymmetric space groups $P6_3/m$ and $P2_1/b$. These models differ for the position of the (OH)-groups along the direction c. ADT allowed the study of single acicular hydroxyapatite crystals from human tooth enamel and dentine and to solve its structures independently from nine single crystals. Unexpectedly the best solution was always achieved in space group $P6_3$. This implies the presence of an electrostatic potential along the direction c, which corresponds to the main elongation of the acicular crystals. Evidences of piezo- and pyro-electricity in hydroxyapatite
were early reported in literature,[8-9] as well as observations about the significance of electric fields during apatite formation under in vivo or biomimetic conditions.[10] The fact that at the nanoscale hydroxyapatite crystallizes in a non-centrosymmetric spacegroup has important impact for medical and bio-mimetic applications.


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