MS26-P05 Unraveling the structure of Vaterite using precession electron diffraction tomography

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Among the three crystallized anhydrous polymorphs of $CaCO_3$, vaterite is the least stable form under natural conditions and has been identified as a constituent of various biominerals such sea crustaceans, mollusk pearls, fish otoliths ascidians and even human organic tissues (heart valve) or plants. As a metastable phase, vaterite is involved in the first step of crystallization of the two stable calcite and aragonite polymorphs and in several carbonate-forming systems. Its complete structural determination would consequently shed important light to understand scaling formation and biomineralization processes. While vaterite hexagonal substructure ($a \approx 4.1$ Å and $c \approx 8.5$ Å) and the organization of the $(CO_3)^{2-}$ and Ca^{2+} within a single layer is known, conflicting interpretations regarding the stacking sequence remain and preclude the complete understanding of the structure. Indeed, earlier workers reported the presence of additional Bragg peaks and diffuse features in diffraction patterns of vaterite together with twinned domains, and the likely coexistence of several polymorphs [1-2].
In order to resolve the ambiguities in the structural description of vaterite, we performed precession assisted electron diffraction tomography (PEDT) to collect single crystal data on beam sensitive nanocrystalline vaterite. Several data sets were collected with low-dose technique at low-temperature with a nano-size beam and processed using programs PETS, Jana2006 and Dyngo [3]. Our results unambiguously demonstrate that vaterite grows up mostly as a coherent intergrowth of two ordered and twinned polymorphs having the same composition. Their structures were solved ab initio and described as commensurate modulated structures. The models were refined against electron diffraction data using the dynamical refinement procedure including both modulation and twins. Our results are also consistent with Rietveld refinement from x-ray powder data [3] at low and ambient temperature. This study brings a new perspective by giving a better understanding of the existing stacking sequences and the possible rotations of the $(CO_3)^{2-}$ groups in vaterite.

References:

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