Unraveling the structure of vaterite using precession electron diffraction tomography

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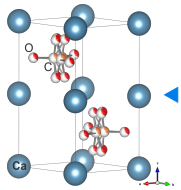
1. MOTIVATIONS

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 or plants. Vaterite is involved in the first step of crystallization of the two other polymorphs and in several carbonate-forming systems. While its structural determination appears important to understand scaling formation and biomineralization processes, this has not been fully successful.

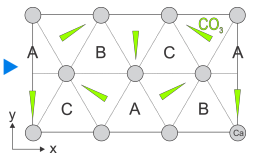
Problems arise from the nature of vaterite that forms nanocrystal not suitable for an x-ray single crystal experiment. Nowadays, the hexagonal substructure of vaterite (a ≈ 4.1 Å and c ≈ 8.5 Å) [1] and the organization of the $(CO3)^{2-}$ and Ca^{2+} within a single layer is known, but conflicting interpretations regarding the stacking sequence and the symmetry remain and preclude the complete understanding of the structure [2-3].

To tackle this issue, we used the transmission electron microscope as an electron diffractometer to collect single crystal data at nanoscale and solve the structure.



Vaterite basic hexagonal pseudocell after Kamhi (1963).
a_0=4.13Å, c_0=8.49Å
($P6_3/mmc$)
Disordered carbonate group (CO_3)[1]

$(CO_3)^{2-}$ organization within a single layer with the 3 types of empty Ca_6 trigonal prism A, B and C.

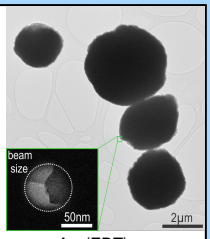


2. METHODOLOGY: 3D electron crystallography

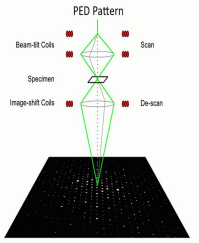
▶Acquisition of single crystal electron data on a synthetic vaterite sample using **Precession-assisted Electron Diffraction Tomography (PEDT)**.

▶Beam sensitive sample: **"low dose" conditions** at T=100K

▶Beam size ≈ 65-80 nm (nano diffraction)

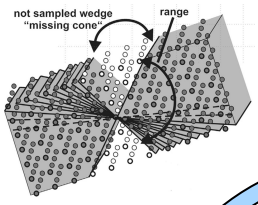


Precession Electron Diffraction **(PED)**



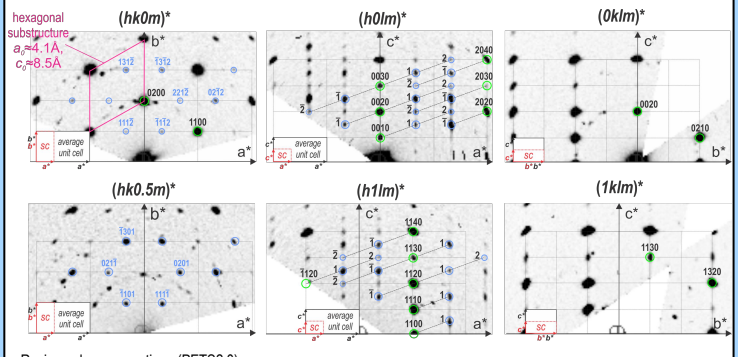
[7] Vincent, R. and Midgley, P.A. *Ultramicroscopy* 1994, 53, 271-282.

Electron Diffraction **Tomography** (EDT)
towards a "complete" dataset

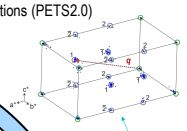


[8] Kolb, U. et al., *Ultramicroscopy* 2007,107, 507.2

3. INDEXATION AND SYMMETRY



Reciprocal space sections (PETS2.0)



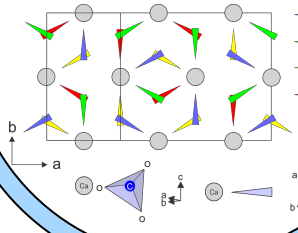
➔commensurate modulation

The periodicity along *c* shows unambiguously the presence of an ordered 4-layer polytype and thus excludes all 6-layer models.

➔ Carbonate stacking disorder along *c*

LONG STORY SHORT

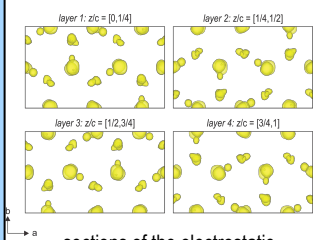
vaterite $CaCO_3$ = ordered 4-layer monoclinic polytype (4M), stacking -0+0 (*)



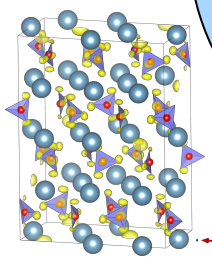
(3+1)D		3D
average modulated cell: $a=a_0≈4.1Å$, $b=b_0\sqrt{3}≈7.1Å$, $c=c_0≈8.5Å$, $α≈β≈γ≈90$, $\mathbf{q}=\frac{2}{3}\mathbf{a^*}+\frac{1}{2}\mathbf{c^*}$ (2 orders)	3a x b x 2c	supercell: $a_{sc}=3a_0≈12.3Å$, $b_{sc}=b_0\sqrt{3}≈7.1Å$, $c_{sc}=2c_0≈16.9Å$, $α≈β≈γ≈90$
$C2/m11(α0\frac{1}{2})s0$, $α=\frac{2}{3}$	symmetry	$C2/c11$ [4]

4. SUPERSPACE MODEL (SSM)

The structure was solved in the superspace using the charge flipping algorithm (superflip program) in JANA2006. The electrostatic potential map represented in the supercell gives a clear view of the carbonate orientation within the layers and their stacking.



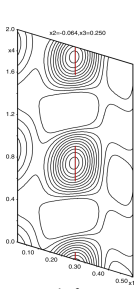
sections of the electrostatic potential map



◀ model represented in the supercell

(*)The stacking is expressed according to the carbonate rotation from one layer to the next one as "+" = 60° rotation clockwise, "-" = 60° anticlockwise and "0" =180° rotation.

▶ MODEL: 10 atomic positions using crenel functions for C and O to account for the 3 possible carbonate orientations in the Ca_6 trigonal prisms.



example for one oxygen site

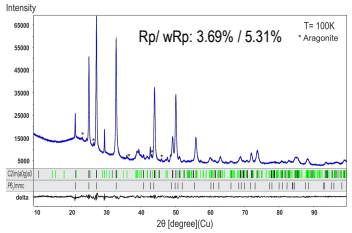
5. SUPERSPACE MODEL (SSM) REFINEMENT

▶kinematical refinement (twin)

Robs / wRobs for 365/413 main refl.: 21.84% / 26.15%
Robs / wRobs for 629/815 satellite1 refl.: 27.06% / 28.41%
Robs / wRobs for 406/823 satellite2 refl.: 31.67% / 35.04%
Nparam=34.

▶x-ray powder Rietveld refinement

Robs / wRobs for 146/147 main refl.: 6.06% / 9.17%
Robs / wRobs for 261 /261 satellite1 refl.: 6.05% / 9.173%
Robs / wRobs for 254 /255 satellite2 refl.: 5.46% / 6.36%
a, b, c: 4.1251(8) Å, 7.1105(3) Å, 8.4589(3) Å
Nparam=29.
density= 2.6794(1)g.cm^{-3}



▶dynamical refinement [5-6] : in progress (modulation + twin). Problem: disordered crystals

▶Are there any other polytypes ?

As far, our results show no proof of the existence of another polytype as it was suggested in the literature [3]. A second polytype compatible with the data would crystallize as a coherent intergrowth in one of the "maximum degree of order" (MDO) 2-layer polytypes (*Cmcm* or *C12/c1*) whose reflections would be superimposed on the 4M polytype ones.

REFERENCES

[1] Kamhi, S.R. *Acta Cryst. A* 1963, 16 (8), 770.
[2] Christy, A.G. *Cryst. Growth Des.* 2017, 17, 3567-3578.
[3] Kabalah-Amitai, L et al., *Science* 2013, 340, 454-456.
[4] Demichelis R.; Raiteri, P.; Gale, J. D.; Dovesi, R. *Cryst. Eng. Comm.* 2012, 14, 4447.
[5] Palatinus, L.; Petricek, V.; Correa, C.A. *Acta Cryst.* A 2015, 71, 235.
[6] Palatinus, L.; Correa, C.A.; Steciuk, et al., *Acta Cryst.* B 2015, 71, 740-751.
[7] Vincent, R. and Midgley, P.A. *Ultramicroscopy* 1994, 53, 271-282.
[8] Kolb, U. et al., *Ultramicroscopy* 2007,107, 507.2

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