

# WHAT IS STACKING IN OUR PIPES : THE STRUCTURE OF VATERITE

Vaterite is metastable phase of calcium carbonate at ambient conditions at the surface of the earth & is responsible for stacking problems in the pipes

Vaterite, one of the common natural CaCO<sub>3</sub> polymorphs, plays a pivotal role in weathering and biomineralization processes. Vaterite is important for the problems of scales in pipes, biomineralization of mollusks and pearls. Differently from calcite and aragonite (CaCO<sub>3</sub> polymorphs), vaterite can be found only in the form of nanosized crystals, not suitable for structure determination by X-Ray diffraction. The structure of vaterite is still an unsolved dilemma (has eluded

**The challenge:** Vaterite consists of single crystal aggregates with size of 50 nm or less

**Solution:** Automated 3D Diffraction Tomography with precession diffraction

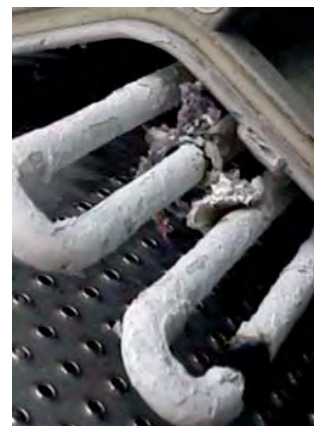
structure determination for almost 100 years!) despite its common occurrence, its relevance in biomineralization processes and the impressive number of published studies around the subject .

All previous structural models for vaterite derived from X-Ray diffraction show geometrically related cells that are difficult to distinguish on the basis of the low-quality data available for nanocrystalline vaterite. Here we report for the first time ab initio determination of vaterite structure from precession electron diffraction data collected via the 3D diffraction tomography approach. Completed 3D diffraction data were available from a single vaterite nanocrystal (50 nm or less). The structure of vaterite was determined in monoclinic space group C2/c and is characterized by a layer arrangement of Ca<sup>2+</sup> ions alternated by {CO<sub>3</sub>}<sup>2-</sup> groups. This structure is consistent with the Raman spectra and a number of experimental findings reported by previous authors.

All analysed vaterite nanocrystals showed stacking disorder and local modulation. The modulation was described by a 6-layer superstructure triclinic cell, resulting in a more satisfactory fit to synchrotron powder diffraction data. The structure was solved ab-



scales in pipes



initio by direct methods in the triclinic space group C-1. The structure is similar to the two-layer monoclinic model with the same basic motif of Ca<sup>2+</sup> layers connected to orthogonal {CO<sub>3</sub>}<sup>2-</sup> groups.

Local atomic coordination is preserved. Electron diffraction tomography showed its great potential for studying the structure of nanomaterials that elude

conventional methods because of small crystal size, low purity, structural complexity or low availability.

Crystal Structure	
Ca <sub>1.5</sub> C <sub>1.5</sub> O <sub>4.5</sub> (2-layer model)	Ca <sub>9</sub> C <sub>9</sub> O <sub>27</sub> (6-layer model)
<b>Monoclinic C2/c</b>	<b>Triclinic C-1</b>
a = 12.17 Å	a = 12.17 Å
b = 7.12 Å	b = 7.12 Å
c = 9.47 Å	c = 25.32 Å
β = 118.94°	α = 90°
	β = 99.12°
	γ = 90°

Experimental data
tilt range: ±60° step: 1°
No ind. reflections: 416
No ind. atoms: 45
R = 34%

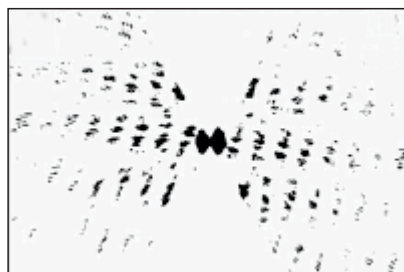
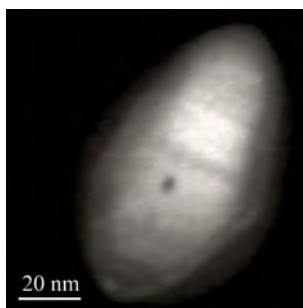
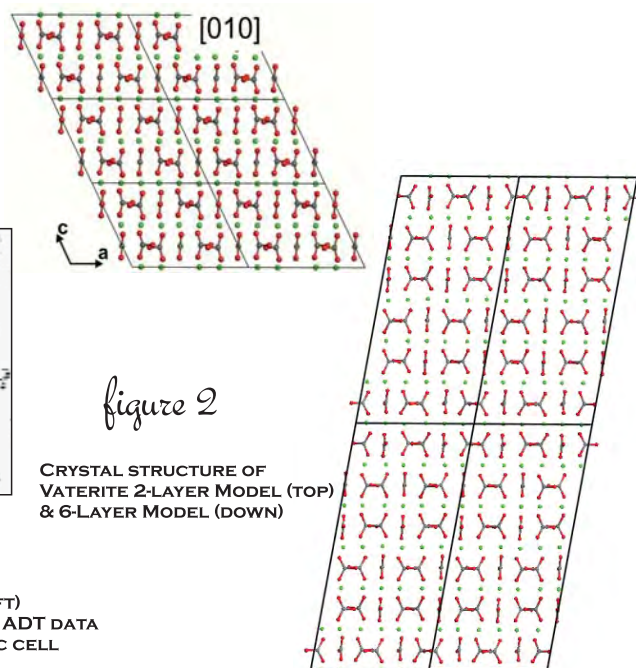
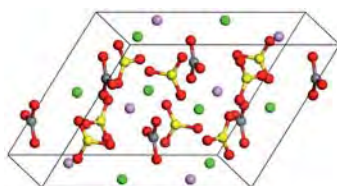


figure 1



STEM IMAGE OF VATERITE NANOPARTICLE (LEFT)  
3D RECIPROCAL SPACE RECONSTRUCTED FROM ADT DATA  
VIEW DOWN THE TILT AXIS (DOWN) MONOCLINIC CELL