

Electronic Supplementary Information

**Evidence of Structural Variability among Synthetic and Biogenic Vaterite**

*G. Falini, S. Fermani, M. Reggi, B. Njegić Džakula and D. Kralj*

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**Materials and Methods**

***Synthetic vaterite minerals preparation***

The chemicals used to prepare the reactant solutions, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> (all Merck), were analytically pure and the deionized water was of high quality (conductivity <0.055 μS cm<sup>-1</sup>). Sodium carbonate / bicarbonate solution was prepared by dissolving anhydrous Na<sub>2</sub>CO<sub>3</sub> and/or NaHCO<sub>3</sub> in water, while calcium chloride solution was made by diluting an appropriate amount of CaCl<sub>2</sub> stock solution.

The preparation of the respective vaterite seed was performed in a thermostated double walled glass vessel with a 400 cm<sup>3</sup> capacity. The vessel was tightly closed by a Teflon cover, thus minimizing the exchange of carbon dioxide between the air and the reaction system. Precipitation was always initiated by mixing the equal volumes (200 cm<sup>3</sup>) of CaCl<sub>2</sub> and freshly prepared Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solutions. The appropriate amount of pAsp additive was always added to the carbonate solution, to which CaCl<sub>2</sub> solution was then rapidly added. The initial concentrations of reactants, total calcium and total carbonate, were equimolar for the two systems,

vat1:  $c_i(\text{Ca}) = c_i(\text{CO}_3) = 1.0 \cdot 10^{-3} \text{ mol dm}^3$  (pH<sub>i</sub> = 10.37; S<sub>v</sub> = 3.71) and

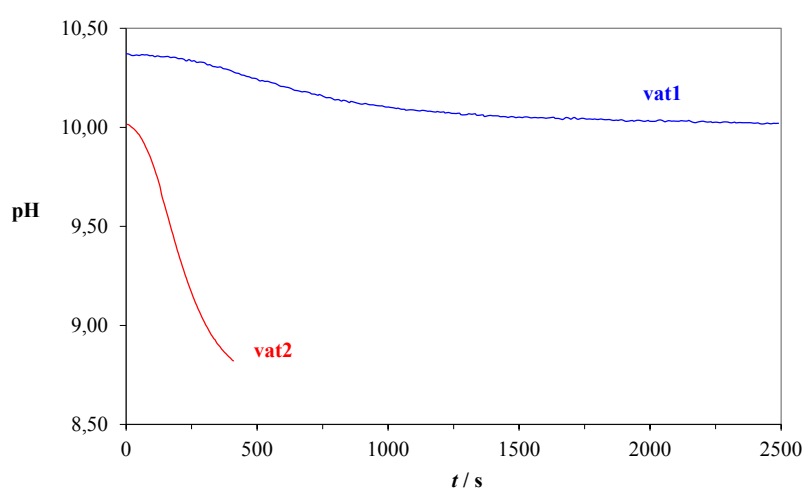
vat2:  $c_i(\text{Ca}) = c_i(\text{CO}_3) = 2.5 \cdot 10^{-3} \text{ mol dm}^3$  (pH<sub>i</sub> = 10.01; S<sub>v</sub> = 6.36).

During the experiments, the systems were continuously stirred at a constant rate by means of a Teflon-coated magnetic stirring bar and all experiments were carried out at 25 °C. The progress of the reaction was followed by measuring the pH of the solution using a combined glass-calomel electrode (GK2401C) connected to a digital pH meter (PHM 290, Radiometer). The respective progress curves, pH versus time and  $c(\text{Ca}_{\text{tot}})$  versus time are shown in Figures S-Aa and S-Ab, respectively. The inset in Fig S-Ab shows the respective desaturation curves, S<sub>vat</sub> versus time.

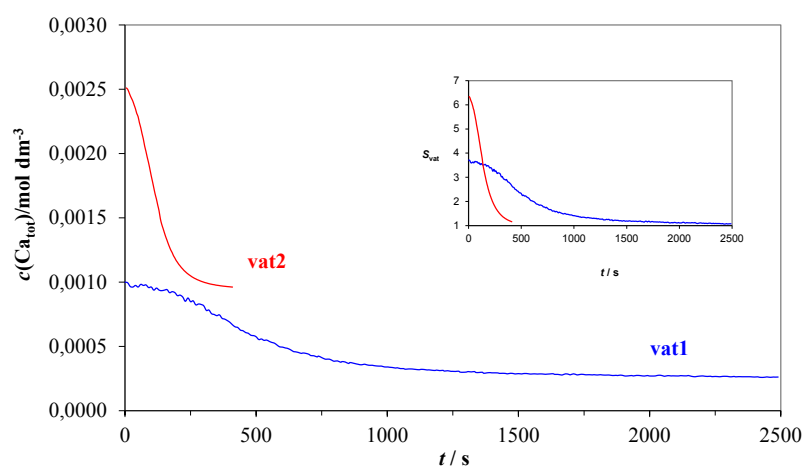
At a predetermined time (about 400 or 2500 sec), the total volume of the suspension was filtered through a 0.22 μm cellulose nitrate membrane filter (Millipore), washed with small portions of water, and dried at 105 °C.

Calculations of the initial solution composition, as well as of the composition at any time during the process, were based on pH measurements. The total calcium chloride and sodium carbonate / bicarbonate concentrations initially added to the system were used for calculating the molar concentrations and activities of the 11 ionic species assumed to be present in solution in significant amounts. The supersaturation was defined as,  $S_{\text{vat}} = (II/K_{\text{sp}}^0)^{1/2}$ , where  $II$  is the ion activity product,  $II = a(\text{Ca}^{2+}) \cdot a(\text{CO}_3^{2-})$ , and  $K_{\text{sp}}^0$  is the thermodynamic equilibrium constant of dissolution of vaterite at 25 °C: ( $K_{\text{sp}}^0 = 1.221 \cdot 10^{-8}$ ).

The detailed calculation procedure, which takes into account the respective protolytic equilibria and equilibrium constants, as well as the charge and mass balance equations, is given in previous papers (e.g. Njegić Džakula et al..<sup>20</sup>).



a



b

**Figure S-A.** Progress curves (a) pH versus time and (b)  $c(\text{Ca}_{\text{tot}})$  versus time of spontaneous precipitation of vaterite initiated at different initial reactant concentrations. Vat1:  $c_i(\text{Ca}) = c_i(\text{CO}_3) = 1.0 \cdot 10^{-3} \text{ mol dm}^3$  ( $\text{pH}_i = 10.37$ ;  $S_v = 3.71$ ) and vat2:  $c_i(\text{Ca}) = c_i(\text{CO}_3) = 2.5 \cdot 10^{-3} \text{ mol dm}^3$  ( $\text{pH}_i = 10.01$ ;  $S_v = 6.36$ ). The inset in (b) shows the respective desaturation curves,  $S_{\text{vat}}$  versus time.

### ***Biogenic vaterite samples preparation***

The asteriscus otoliths for this study were taken from the head of the fish *Chondrostoma nasus* collected from the Isonzo River (Italy). After dissecting them from the fish ears, they were washed with sodium hypochlorite (NaOCl) for 1 hr to remove any superficial contaminant organic tissue, then with Milli-Q water (resistivity 18.2 M $\Omega$  cm at 25 °C; filtered through a 0.22  $\mu$ m membrane), and finally air-dried. No distinction was made between sex and left or right ear otoliths.

*Herdmania momus* specimens for this study were collected by scuba diving from marine floats in Eilat at the northern tip of the Gulf of Aqaba (Red Sea), Israel. Specimens were cut into small tissue pieces, which were then treated with 7% NaClO to remove the organic tissues. NaOCl was replaced frequently and vials were shaken gently for 6 weeks until all organic tissues were removed. Spicules were filtered to remove debris and washed 3 times in 100% ethanol.

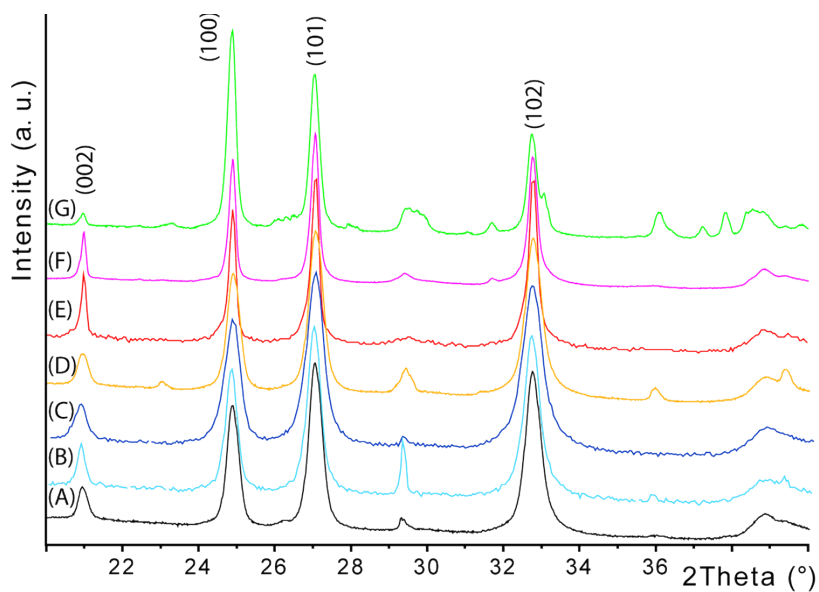
The treatment with the NaClO solution is supposed not to affect the content and structure of the intracrystalline organic matrix. Organic matrix is entrapped into the mineral phase, which is insoluble in the NaClO solution.

Pearls were kindly supplied by Prof. Feng (China). Unfortunately, the authors did not succeed in obtaining a geological vaterite sample to be used as a standard and compared with the biogenic ones.

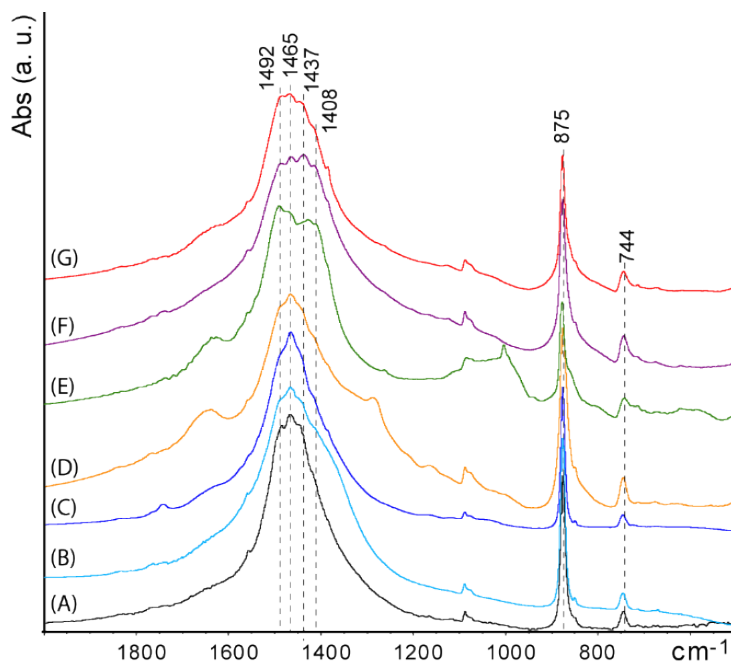
XRD profiles of each section were collected using an X-Celerator powder diffractometer (PANalytical), using Cu K- $\alpha$  radiation ( $\lambda = 1.540$  Å). For the sake of comparison, the XRD profile of aragonite powders was collected under the same conditions.

FTIR analyses were performed by using a FTIR Nicolet 380 (Thermo Electron Co). The measurements were performed in the wavelength range from 4000 to 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. Disks were made by mixing a small amount (< 1 mg) of sample with 100 mg of KBr and applying a pressure of 48.6 psi to the mixture using a hydraulic press.

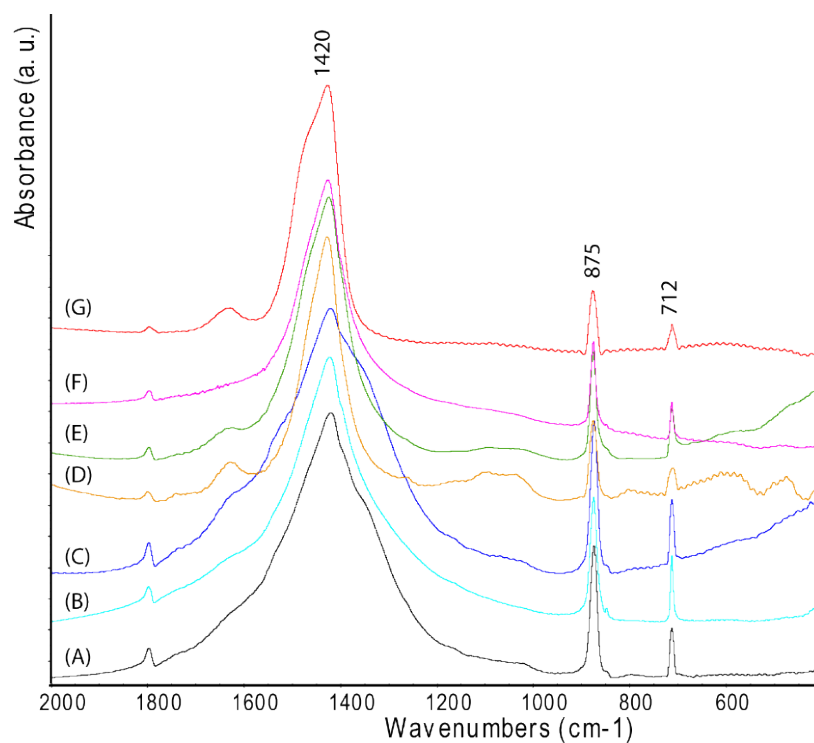
The SEM observations were conducted in a scanning electronic microscope using a Phenom<sup>TM</sup> microscope (5 kV, FEI) for uncoated samples and a Hitachi FEG 6400 microscope (20 kV) for samples coated with gold.



**Figure S1.** X-ray diffraction pattern of the vaterite samples: (A) vat1; (B) vat2; (C) vat1-pAsp; (D) vat2-pAsp; (E) *H. momus* spicule; (F) *C. nasus* asteriscus otolith; (G) lacklustre pearl. The Miller index are the main reflection are indicated in parenthesis.



**Fig. S2** FTIR spectrum of: (A) vat1; (B) vat2; (C) vat1-pAsp; (D) vat2-pAsp; (E) *H. momus* spicule; (F) *C. nasus* asteriscus; (G) lacklustre pearl.



**Figure S3.** FTIR spectra of the vaterite minerals after the thermal treatment: (A) vat1; (B) vat2; (C) vat1-pAsp; (D) vat2-pAsp; (E) *H. momus* spicule; (F) *C. nasus* asteriscus otolith; (G) lacklustre pearl.

**Table S1.** Transition temperatures and enthalpies of the thermal induced transition from vaterite minerals to calcite.

	$T_{tr}$ (°C)	$\Delta H$ (J/g)
vat1	477	26.8
vat2	395	27.4
vat1-pAsp	478	24.8
vat2-pAsp	431	25.4
otolith	420	31*
spicule	431	29*
pearl	533	-**

\* The endothermic band was very broad and did not allow an accurate measure of the transition enthalpy.

\*\* The enthalpy was not measurable due to instrumental limitation of the highest temperature.