Oriented polycrystal samples of nacre-like aragonite: biomimetic and biomedical applications

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Map

- Aims of this study
- $CaCO_3$: why aragonite ?
- Techniques
- Results
- Outlooks

Aims of study

- synthetic nacre for osteopathy
  - natural nacre is highly osteoinductive
  - prostheses mainly in titanium
  - medical european law: forbids animal proteins in human body
- Electrodeposition of $CaCO_3$ in aragonitic form on titanium
- Caracterization of obtained microstructures and textures :
  - SEM backscattering
  - X-Ray diffraction

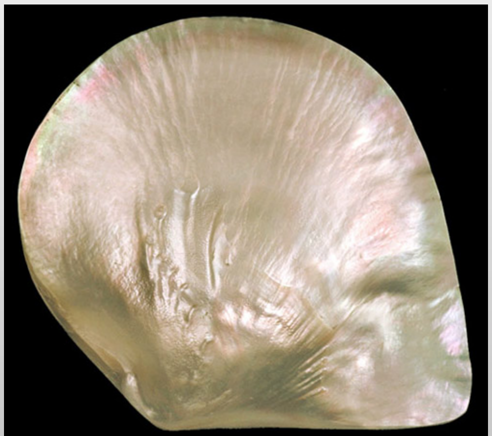
$CaCO_3$: 3 allotropic forms

- Calcite (R3c - trigonal) :
  too much stable form ➡ non-osteoinductive

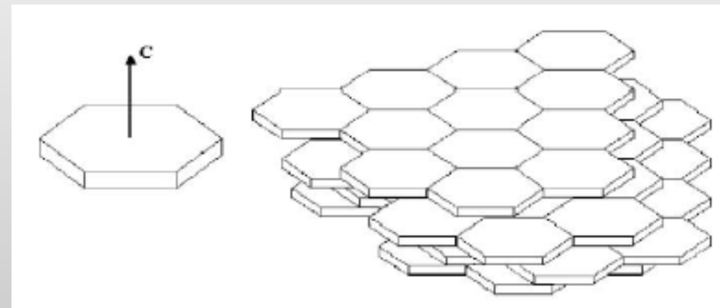
- Vaterite ($P6_3$/mmc - hexagonal) :
  non-stable form ➡ too much for applications

- Aragonite (Pmcn - orthorhombic) :
  metastable form ➡ ΔG^0(C->A) = -1kJ/mol

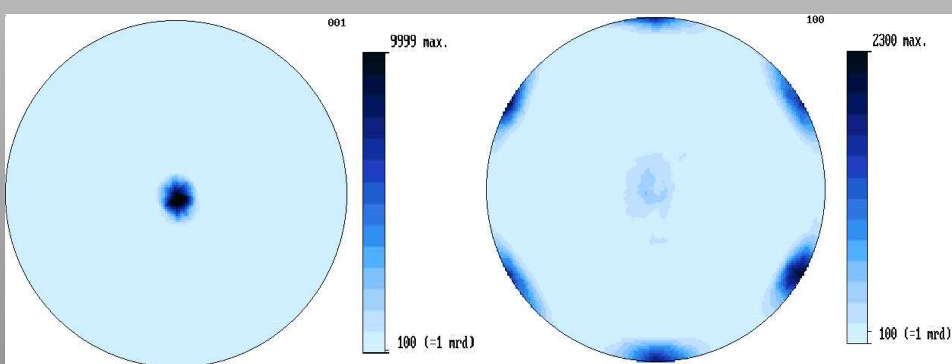
Nacre: natural Aragonite microstructure

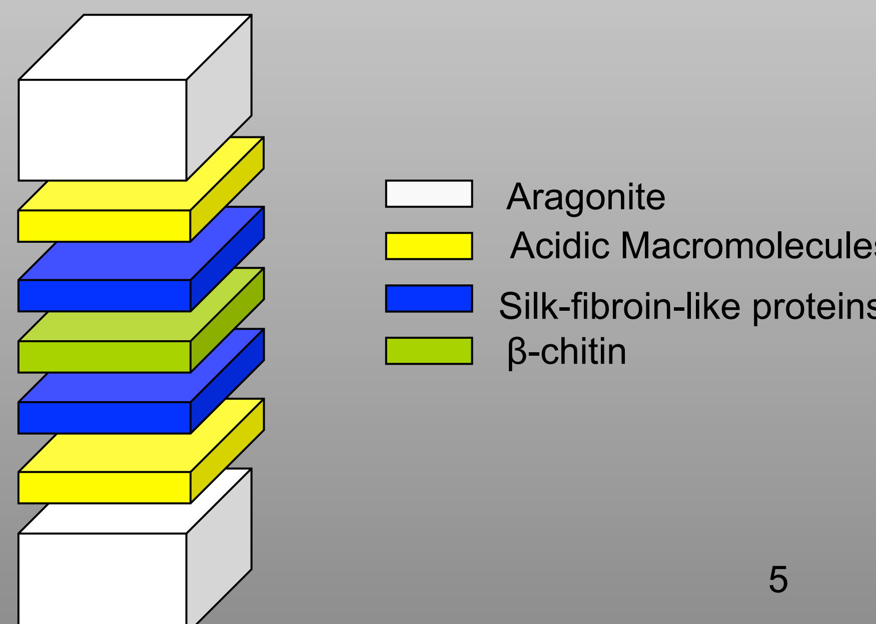


Pinctada maxima

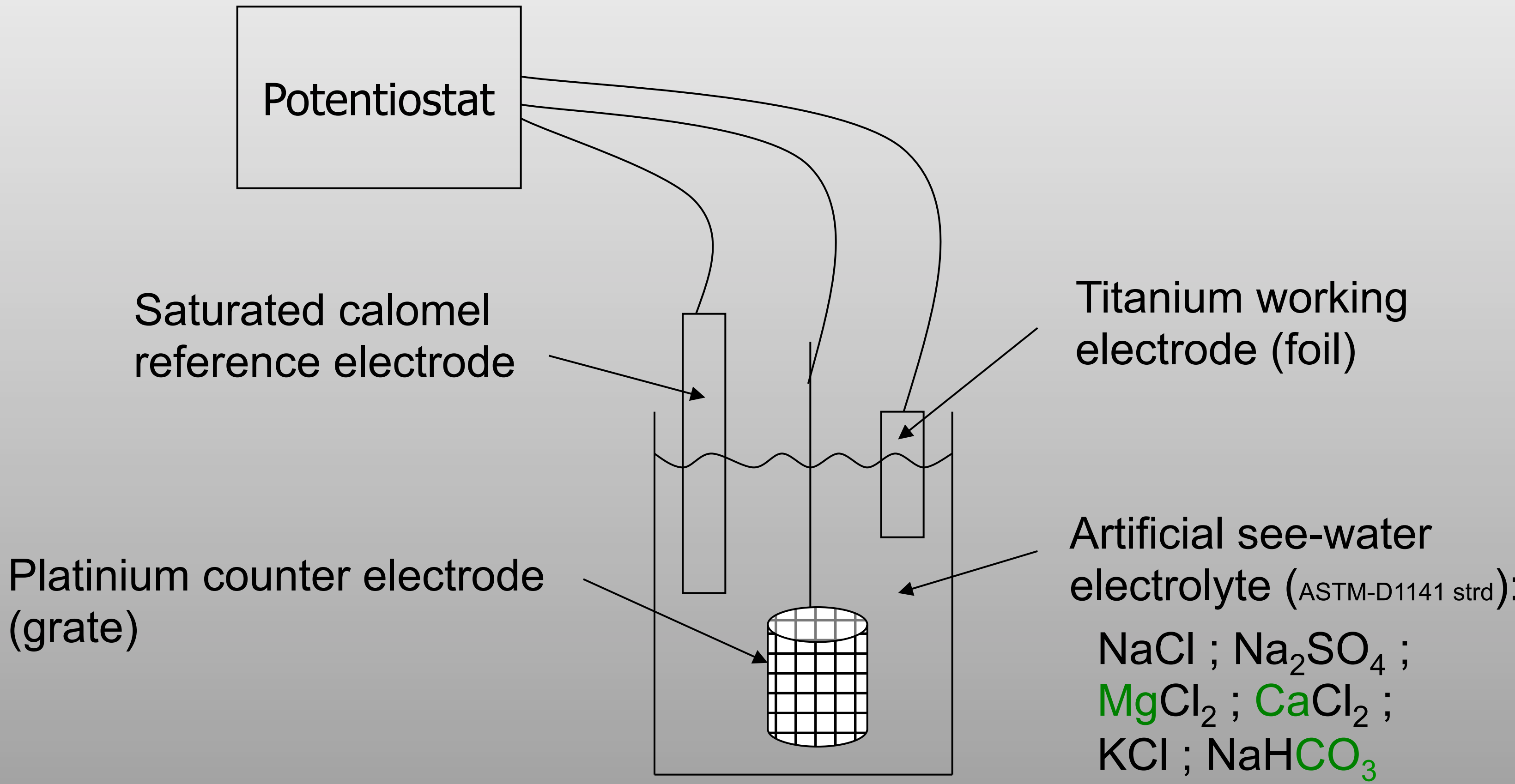


Nacre composition: aragonite and organic phases (2% – 5%)





Techniques: Electrochemical deposition



Electrochemical deposition

Chemical reaction:

- $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Highly negatif potentials $\rightarrow$ water reduction:

- $2H_2O + 2e^- \rightarrow 4OH^- + H_2$

- $NaHCO_3 \rightarrow Na^+ + HCO_3^-$
- $CaCl_2 \rightarrow Ca^{2+} + 2Cl$
- $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
- $Ca^{2+} + CO_3^{2-} \rightarrow \underline{CaCO_3} \searrow$

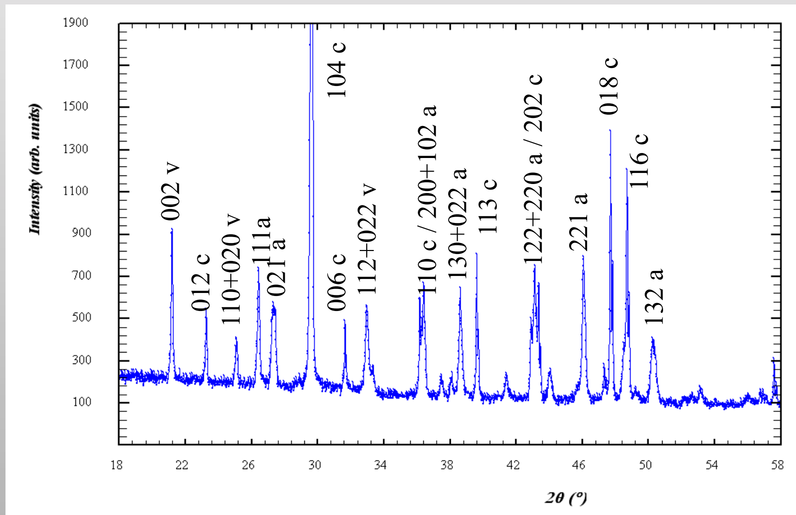
Employed techniques: # Texture analysis

- 4-Circles diffractometer for combined analysis
- Texture program : MAUD
    - Rietveld refinement: Texture index F^2, film thickness…

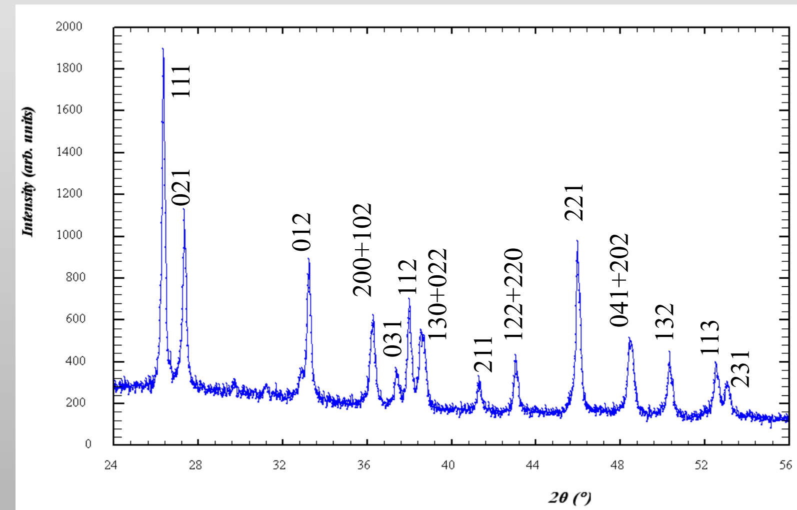
$\mathbf{y}_i^{calc} = \mathbf{y}_i^{background} + \sum S_\varphi \sum j_{\varphi\mathbf{h}}\, Lp_{\mathbf{h}}\, P_{\varphi\mathbf{h}}(\mathbf{y})\, [F_{\varphi\mathbf{h}}]^2\, \Omega_{\varphi\mathbf{h}}$ with $\mathbf{h}=[hkl]^*$

$P_{\varphi\mathbf{h}}(\mathbf{y})$ = preferred orientation correction factor

Results: Magnesium induction



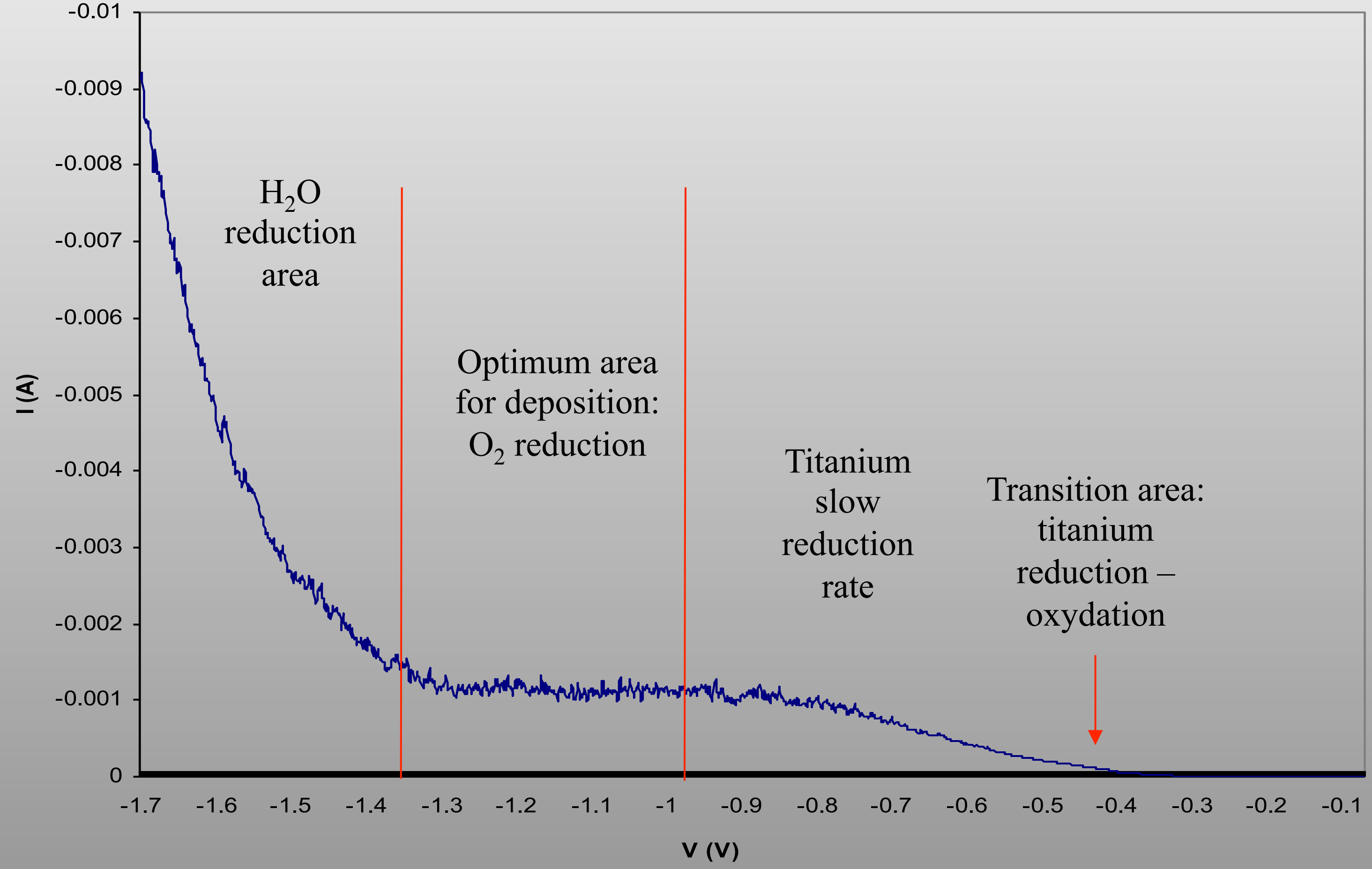
Without $MgCl_2$: vaterite +calcite+aragonite



$[MgCl_2, 6H_2O] = 2{,}73.10^{-2}M$ pure aragonite

- Excluding vaterite and calcite
- Magnesic calcite less stable that aragonite

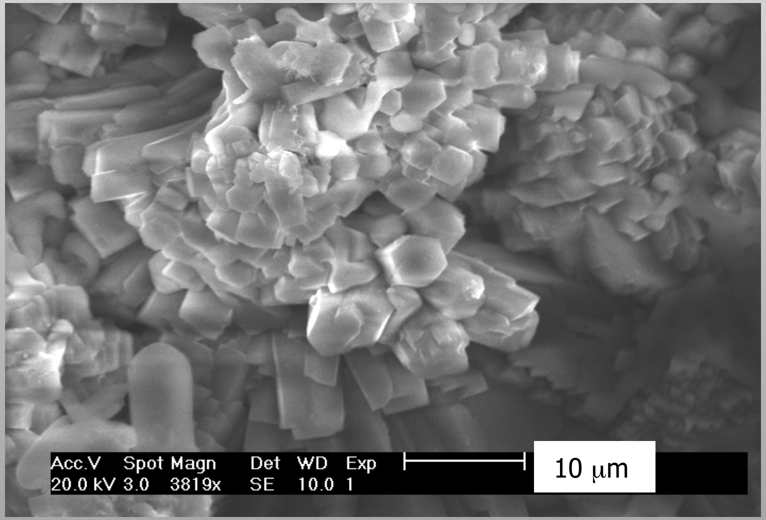
Results: Potential induction



Results: Potential

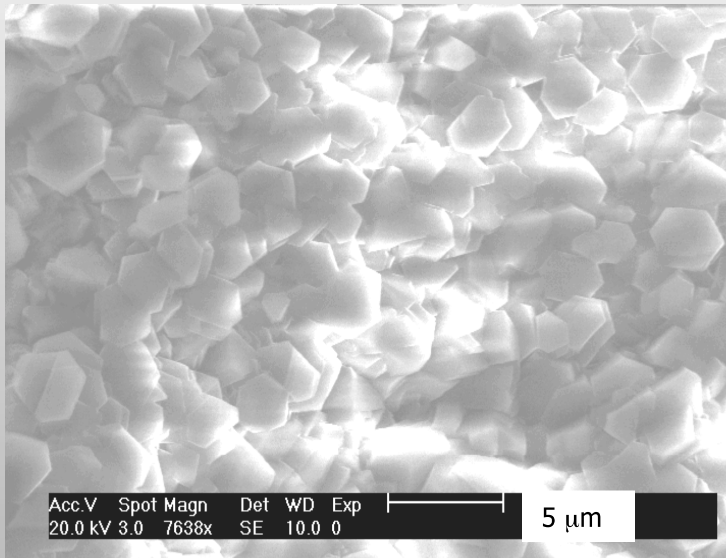
<u>-1.1V</u>

F^2 = 1.2 m.r.d.^{2}
e = 4.7 μm



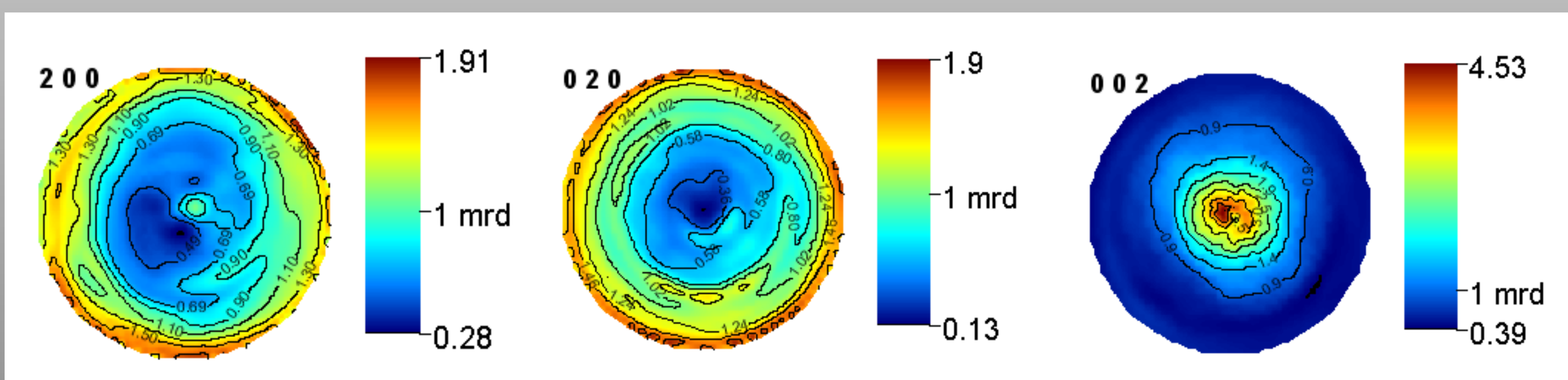
At not enough reducting potential, shape and texture differ from natural nacre: **c** ⊥

Results: Potential



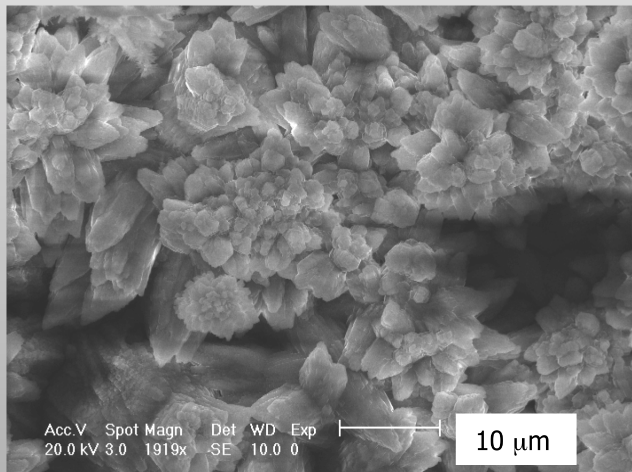
-1.4V

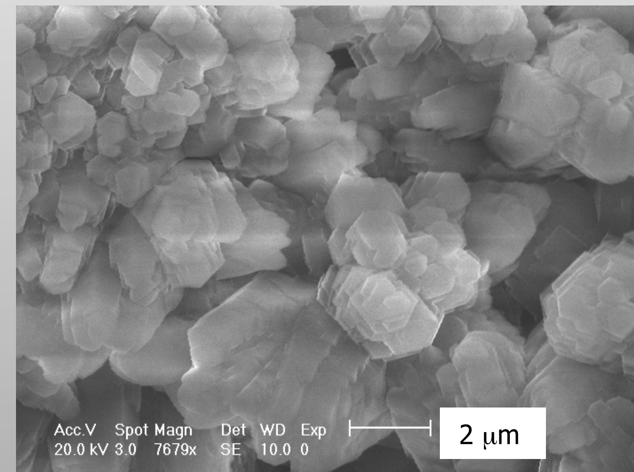
F^2 = 1.7 m.r.d.^{2}
e = 1.9 µm



Results: # Potential

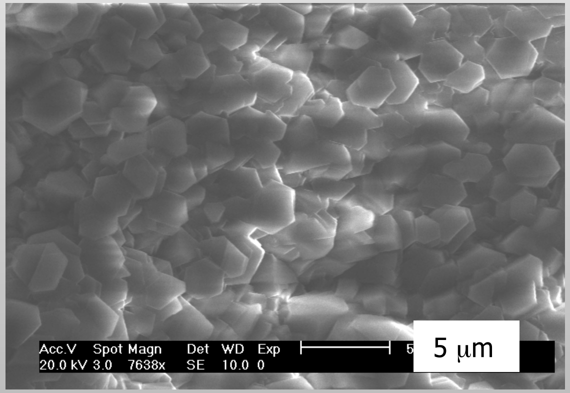
-1.5V



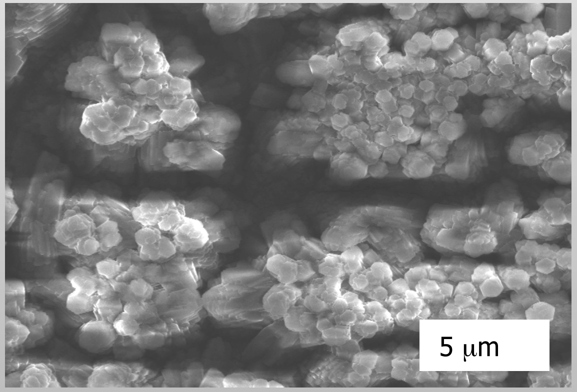


At too much negative potential; gaseous H_2 induces porous deposit and size, orientation inhomogeneity

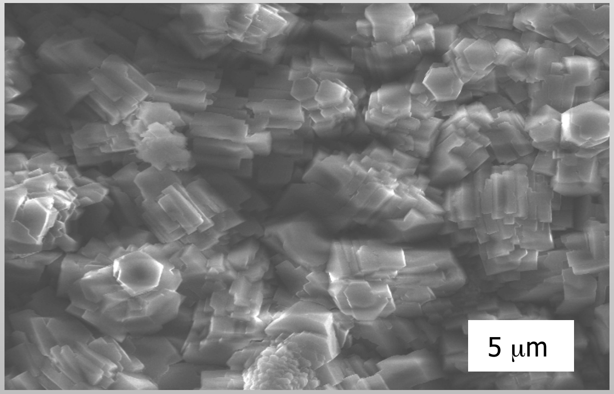
Results: # Temperature, at -1.4V



40°C



50°C



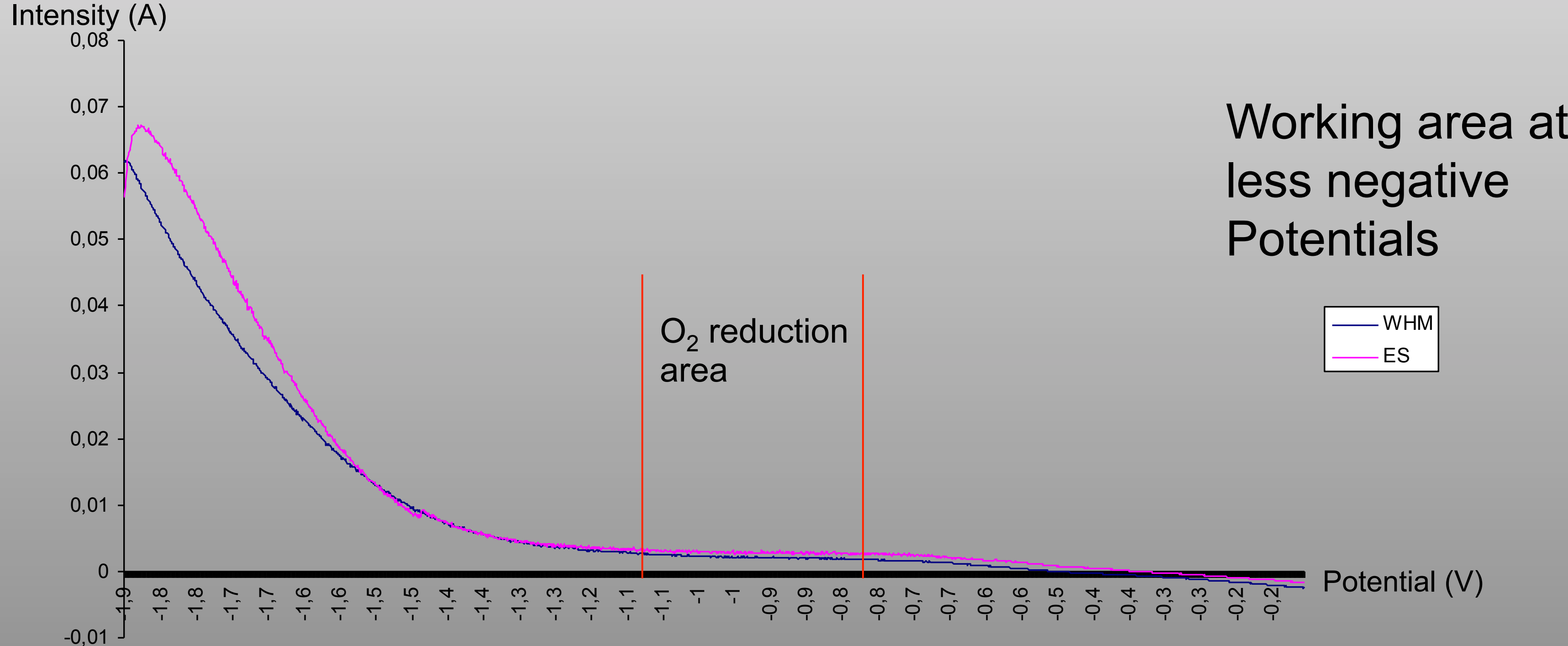
60°C

Too much high temperature induces inhomogeneous growth of crystallites

Results: Organic phase induction

Used organic phases: Nacre powder of *Pinctada maxima*
Extracted by 2 different ways:

- WSM: water soluble, polar phase
- ES: ethanol soluble, non-polar phase



Results: **Organic phase induction**

WSM phase

ES phase

Cauliflower features,
calcite and vaterite reapearance:
New parameters to adjust.

Perspectives

Crystallites and texture force to be improved:

- Layer optimization (Pot., T°, [C], polyacrylic acid …)
- Layer adhesion (chitosan,…)

Titanium surface (surface treatments)

… Titanium foam