AFM-Raman coupling to study mesocrystal polymorphism in nacre

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Nacre has a multiscale ordering as shown on Fig. 1 (Rousseau, 2005). On the pluri-micrometer scale, nacre tablets exhibit a 'brick and mortar' ordering as shown on SEM fracture surfaces, Fig 1a. The tablet of nacre, the biocrystal, diffracts as a single crystal but is made up of a continuous organic matrix (white in Fig 1b) which breaks the mineral up into coherent nanograins (~40 nm mean size). All the nanograins share the same crystallographic orientation as documented by electron diffraction (inset in Fig 1b). Each nanograin has the structure of aragonite (orthorhombic structure, Fig. 1c). The growth of such nanograined-crystals does not proceed through ion-by-ion or atom-by-atom attachment but rather by attachment of nanograins. This growth mechanism was proposed as the Voronoi tilling model of nacre in 2005 (Rousseau, 2005b) and confirmed by a dynamic approach to the study of nacre growth using NanoSims (Rousseau, 2007). This type of structure is also known as 'mesocrystal'.

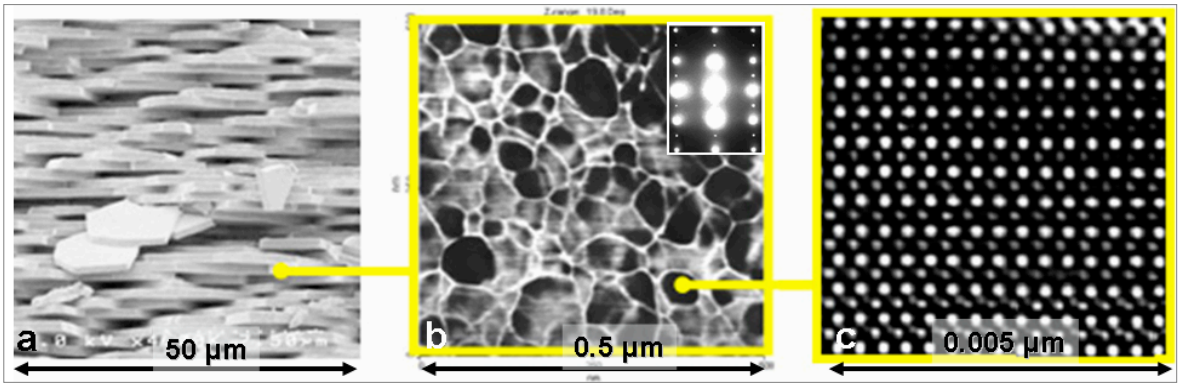

Fig 1 Multiscale structure of nacre : (a) pluri-micrometer scale 'brick and mortar' ordering of tablets (SEM) ; (b) nanograined structure of the tablets (AFM in tapping mode, inset is the TEM electron diffraction pattern of aragonite single crystal, same area) and (c) orthorhombic ordering of aragonite atoms inside the nanograin (HR-TEM image).

In the present study we documented a growth defect that retains the size and orientation of nacre tablets in which the mineral forms is vaterite, the hexagonal polymorh of calcium carbonate (Le

Bail et al., 2011). Polymorphism was most clearly demonstrated through the Raman spectral analysis and mapping (Fig 2, WITec Alpha500 RA, 532 nm,). Figure 2a is the optical transmission image of the defect. Aragonite and vaterite maps are obtained using the 1090cm^{-1} and 152cm^{-1} peaks area respectively. The background level image (Fig 2e) superimposes on that of the vaterite but exhibits unexplained intensity variations. The variations in background intensity can be explained by fluorescence related to the excess of organic matrix in vaterite, as previously observed by a pyrolysis technique (Bourrat, 2012). A similar contrast is observed by cathodoluminescence (Fig 2b).

In conclusion, this study shows that the coupling between AFM and Raman spectroscopy is ideally suited for studying mesocrystals and their polymorphic growth.

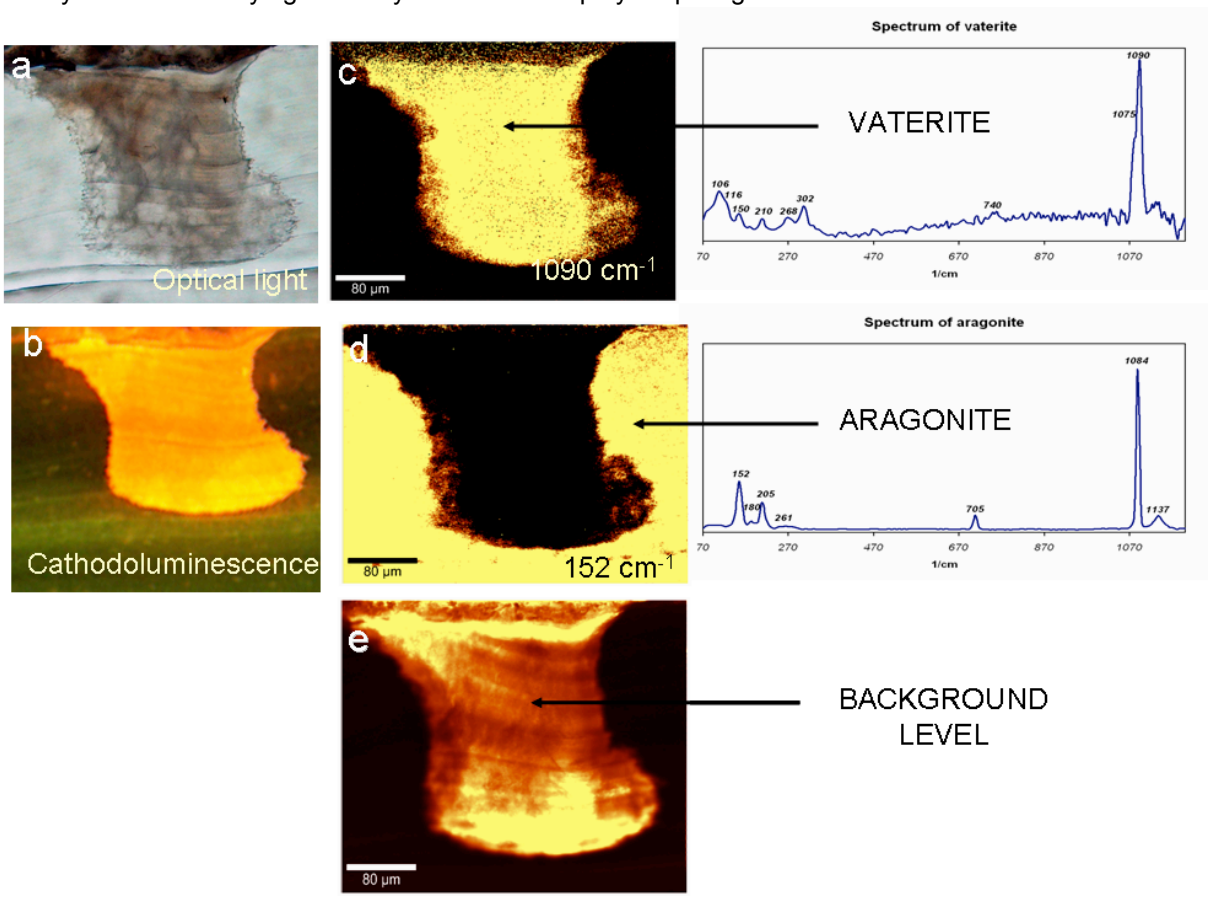

Fig 2 Raman mapping to study the polymorphism of calcium carbonate in a mesocrystal of nacre : (a) optical appearance of the defect ; (b) contrast of the defect in cathodoluminescence; Raman maps of (c) vaterite (1090 cm^{-1} peak area); (d) aragonite (152 cm^{-1} peak area) and (e) background level.

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