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An Apatite for American Lobster

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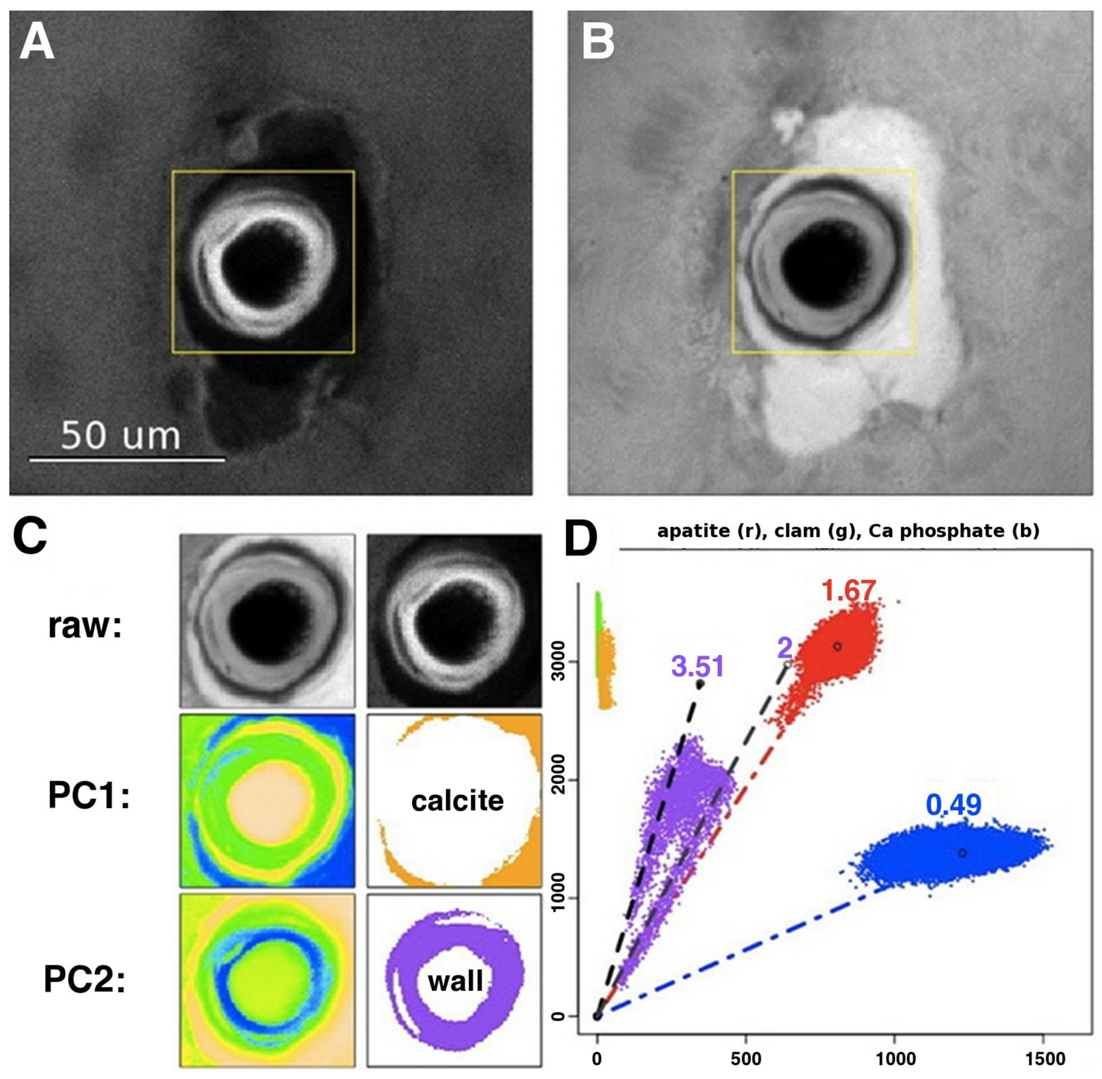
Carbonate Apatite Formulae

x	u	z	name	$Ca_{10-x+u}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x+2u} \cdot z\,H_2O$	Ca:P	Ca/P
		1	monocalcium phosphate	$Ca\,(H_2PO_4)_2 \cdot H_2O$	1:2	0.5
0	0	1	hydroxyapatite	$Ca_{10}(PO_4)_6$ … $(OH)_2 \cdot H_2O$	10:6	1.67
0	1	1	hydroxyapatite	$Ca_{11}(PO_4)_6$ … $(OH)_4 \cdot H_2O$	11:6	1.83
1	1	1	carbonate apatite	$Ca_{10}(PO_4)_5\,CO_3\,(OH)_3 \cdot H_2O$	10:5	2.0
2	1	1	carbonate apatite	$Ca_9(PO_4)_4(CO_3)_2(OH)_2 \cdot H_2O$	9:4	2.25
2	2	1	carbonate apatite	$Ca_{10}(PO_4)_4(CO_3)_2(OH)_4 \cdot H_2O$	10:4	2.5
3	1	1	carbonate apatite	$Ca_8(PO_4)_3(CO_3)_3\,OH \cdot H_2O$	8:3	2.67
3	2	1	carbonate apatite	$Ca_9(PO_4)_3(CO_3)_3\,(OH)_3 \cdot H_2O$	9:3	3.0
4	1	1	carbonate apatite	$Ca_7\,(PO_4)_2\,(CO_3)_4 \cdot H_2O$	7:2	3.5
4	2	1	carbonate apatite	$Ca_8(PO_4)_2(CO_3)_4(OH)_2 \cdot H_2O$	8:2	4.0
4	3	1	carbonate apatite	$Ca_9(PO_4)_2(CO_3)_4(OH)_4 \cdot H_2O$	9:2	4.5
5	2	1	carbonate apatite	$Ca_7PO_4(CO_3)_5OH \cdot H_2O$	7:1	7.0
5	3	1	carbonate apatite	$Ca_8PO_4(CO_3)_5(OH)_3 \cdot H_2O$	8:1	8.0

Table I. A variety of Ca:P ratios are possible following the Carbonate Apatite Formulae. Several are often seen in one polished slice of lobster cuticle e.g. (Kunkel et al. 2012) where Ca:P 1:2, 2:1, 7:2 are seen, sometimes in adjacent sectors of a structure such as the organule wall, panel 2.

In canal sectors close to the environment the Ca:P ratio approaches that of apatite itself, 10:6. Further away from the environment, last to be deposited, it is also furthest from the apatite ratio at 7:1 Ca:P.

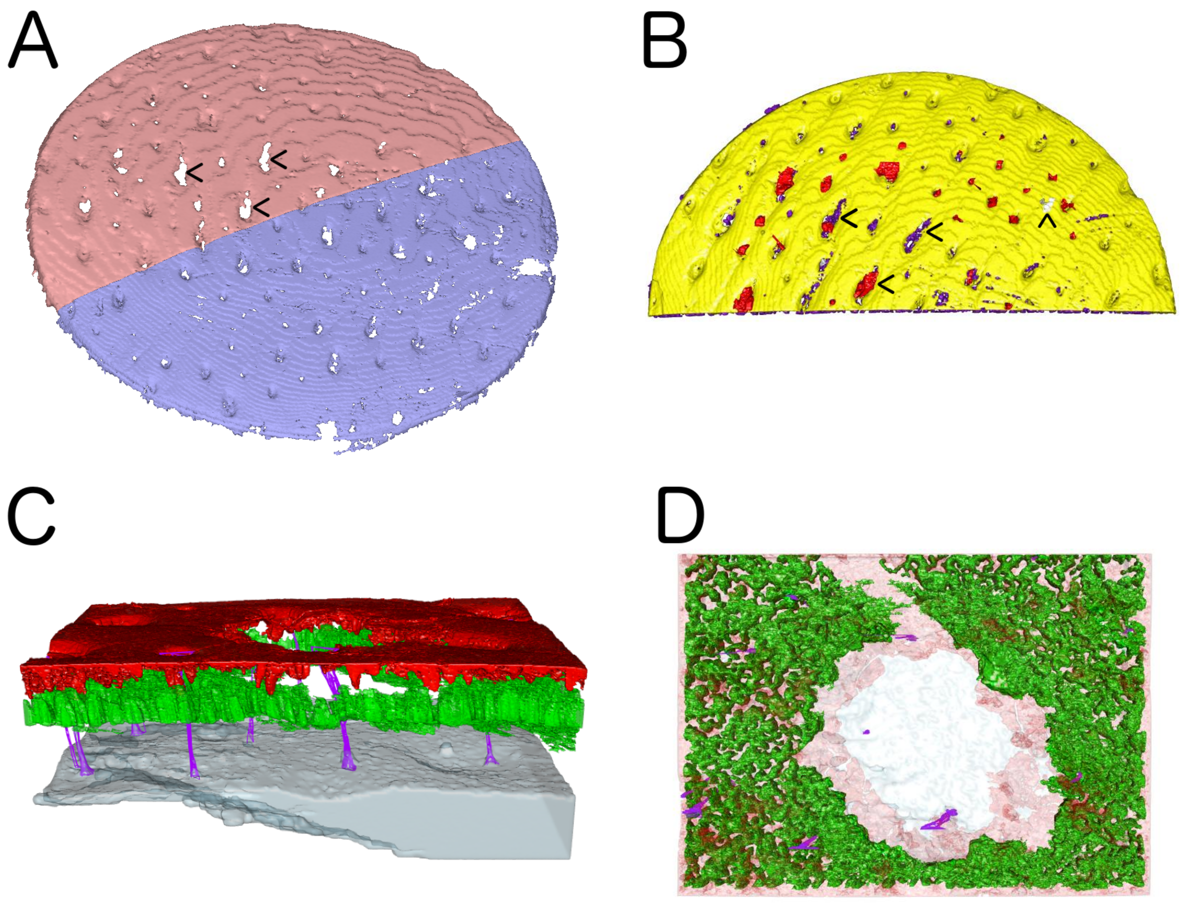
Kunkel, Nagel & Jercinovic 2012



A *tangentially polished* cuticle surface shows an organule canal perpendicular to its long axis. The Calcite collar is devoid of PO_4 and CAP lines the canal. (A) Phosphorous (Ka) X-ray map. (B) Calcium (Ka) X-ray map. (C) Rows top to bottom—raw: selected areas of Ca, P. PC1: Calcite PC used to choose calcite pixels. PC2: Wall PC used to choose wall pixels. (D) Calcite and Wall pixel Ca and P contents are plotted. Slopes extrapolated through zero show the Ca:P ratios relative to clam calcite (green, no P), HAP (red, Ca:P 1.67), and monocalcium phosphate (blue, Ca:P, 0.49). The brightness of images (A), (B), and (C-raw) scales linearly with X-ray intensity.

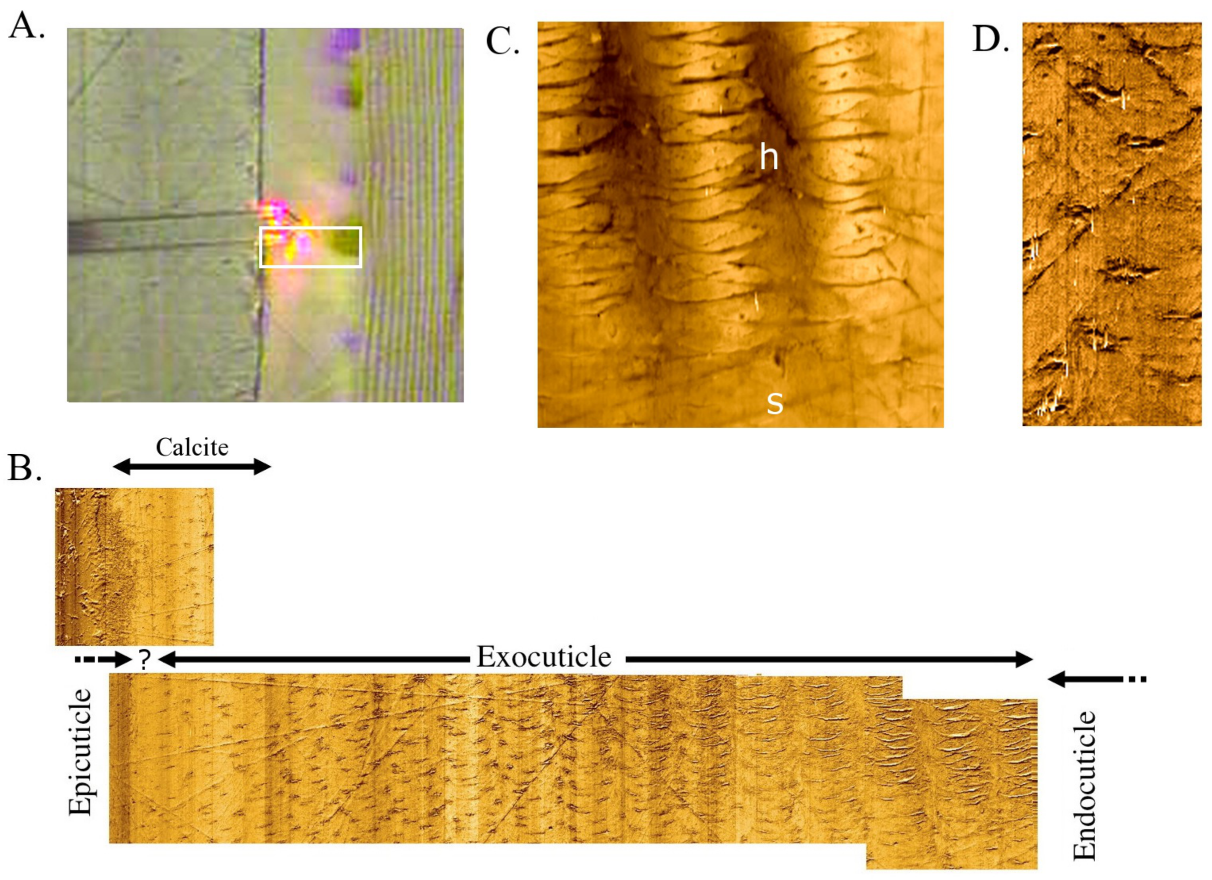
3D-Xray-tomography of lobster shell carbonate apatite trabeculae.

Fig 8 of Kunkel et al. 2016.



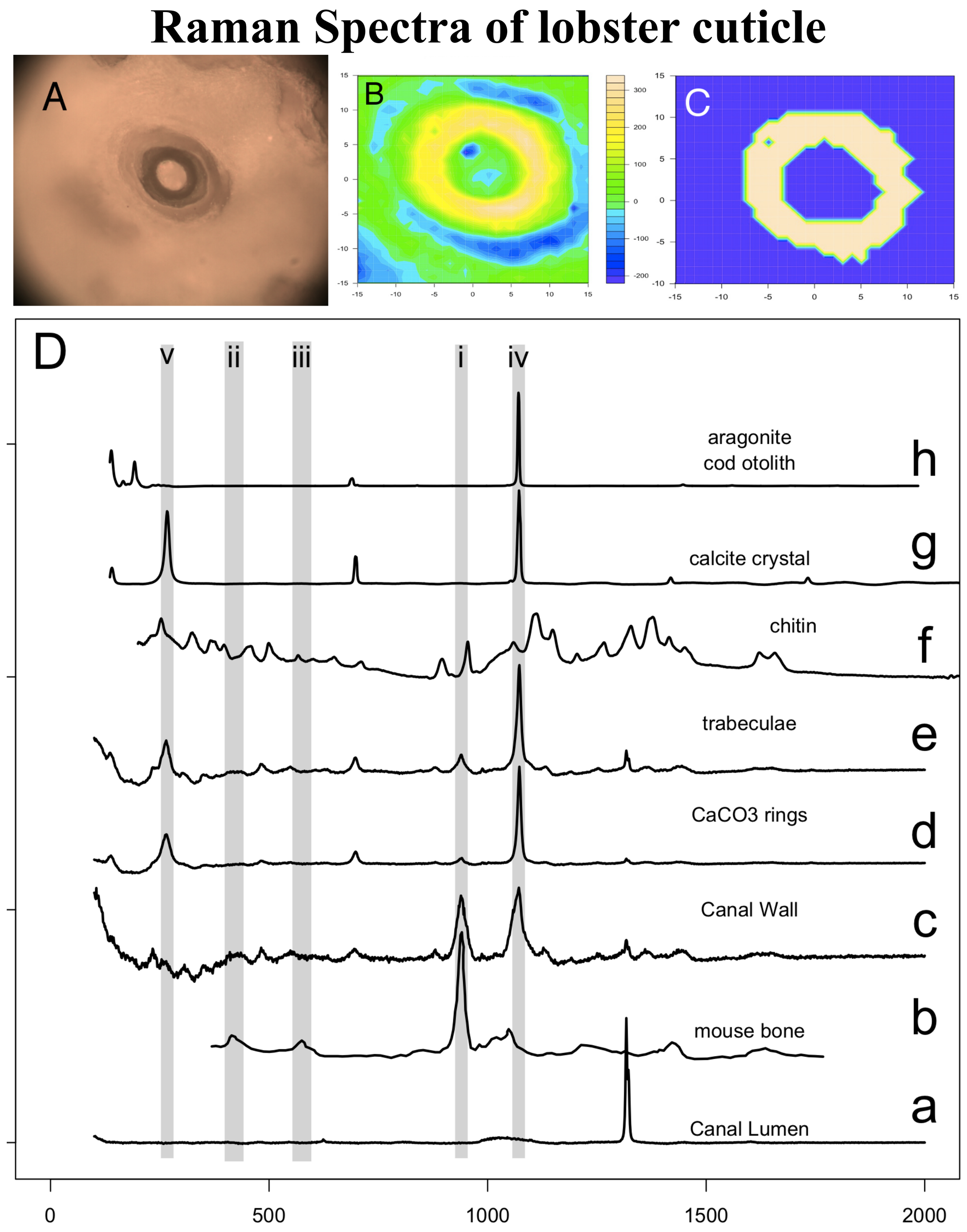
Placement of a trabecular structure (green in C and D) in the exocuticle of the lobster. One of these cuticle medallions (shown in C and D) has an ESD lesion which goes through the calcite and exocuticle layer dissolving them. The trabeculae (in green) are seen somewhat reorganized at the periphery of the lesion in the D tangental view, video link:
http://www.bio.umass.edu/biology/kunkel/3D/Ha4_ESDlesion.avi
With Skyscan 1272 uCT 6 mm diameter medallion, ~0.5um pixel size.

Atomic force microscopy of lobster cuticle.



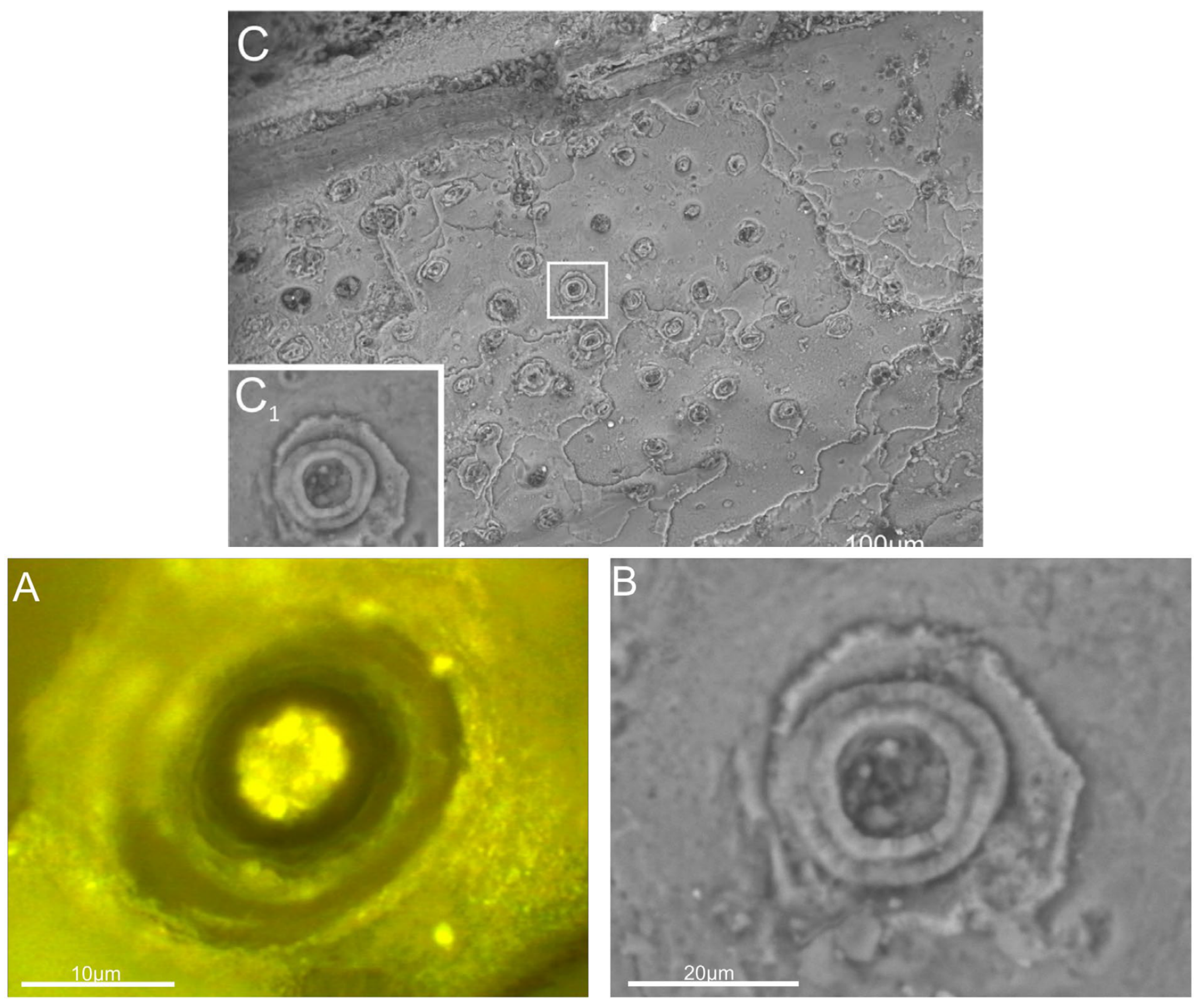
Atomic force microscopy finds the trabeculae to be harder (h) than its surrounding matrix (s). The trabeculae seem to be composed of plates but need higher resolution to evaluate their properties **(Kunkel 2013).**

Raman Spectra of lobster cuticle



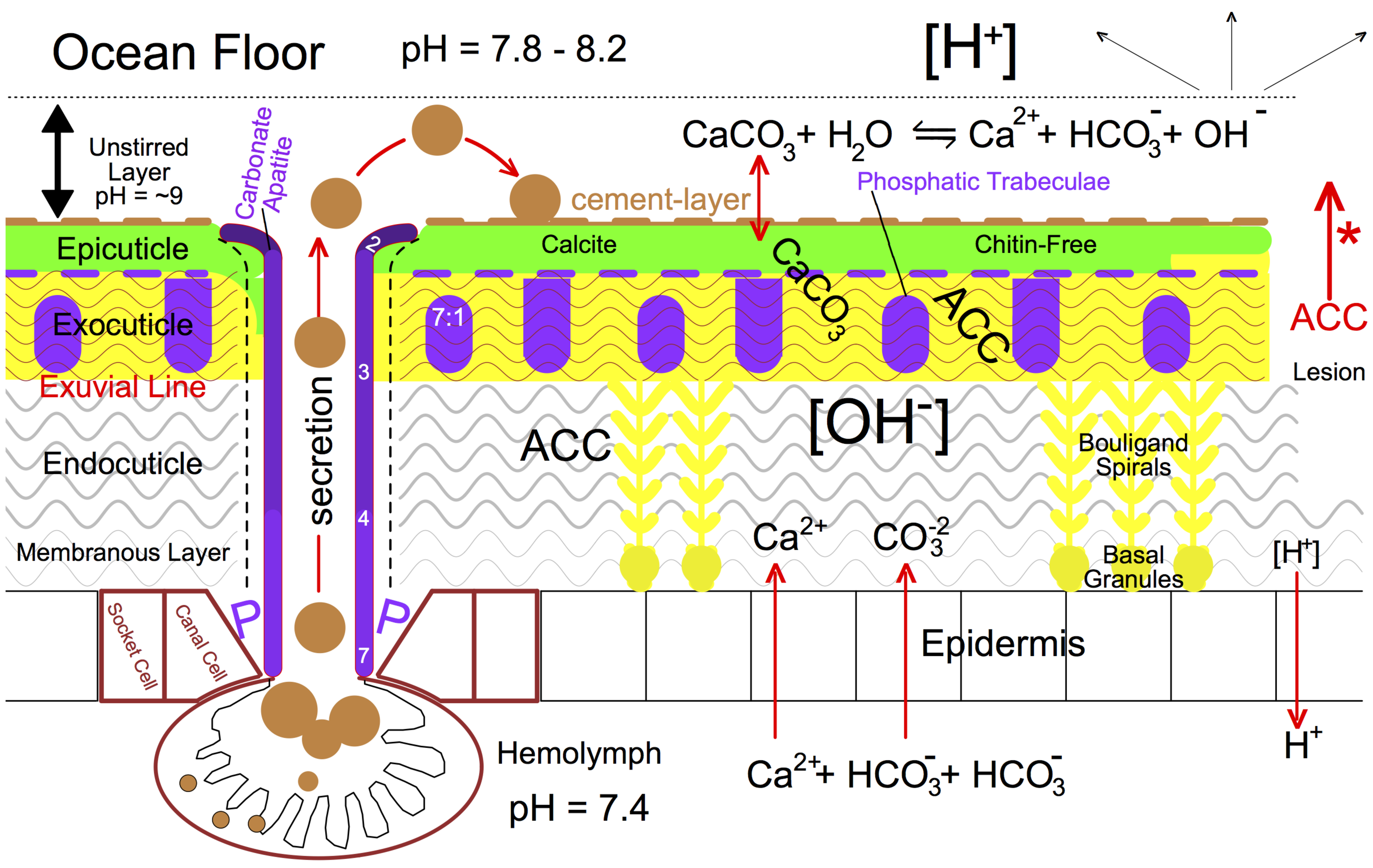
In Kunkel et al. (2018) these spectra show that the $CaCO_3$ is calcite not aragonite and that the carbonate apatite is a lower grade carbonite-apatite than vertebrate bone.

Fossil Thylocephalan organules.



Lobster, *Homarus* Late Devonian Thylocephalan
Broda & Zatoń (2017)

Latest model of the lobster epidermis and cuticle (Kunkel et al. 2018)



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http://www.bio.umass.edu/biology/kunkel/pub/reprints/