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Silicification of low-magnesium mollusc shells from the Upper Oligocene of Antigua, Lesser Antilles

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ABSTRACT. Silicified molluscs, namely the oyster *Hyotissa* and the scallop *Aequipecten*?, are commonly preserved as silica in the carbonate successions on the island of Antigua. These fossil assemblages are located within the Antigua Formation, above and adjacent to a variety of volcanic and volcaniclastic rocks, suggesting, on geological grounds, an igneous source for the silica. Energy dispersive spectroscopy (EDS) and cathodoluminescence (CL) have been applied to characterise the silcification and its conditions of formation which may have been associated with hydrothermal activity.

Keywords: Antigua Formation, limestone, EDS, cathodoluminescence, *Aequipecten*?, *Hyotissa*.

1. INTRODUCTION

Silicification is a relatively common mode of preservation in the fossil record. It generally occurs along thin zones within the fossil as the original calcium carbonate is dissolved and replaced by silica. The process of silicification (see **Butts, 2014**, for a comprehensive review) can occur through permineralization (precipitation of silica into voids), entombment (precipitation on external surfaces) and replacement (or silicification sensu stricto), that is, dissolution of skeletal material virtually concurrent with the precipitation of silica. The process is controlled by shell mineralogy, including the amount and location of organic matter, and the availability of silica. Thus, silicification of fossils in limestones can be considered an indication of early diagenetic conditions whereby there is a source of excess dissolved silica and the replacement mechanism is the likely one where monomers bond directly with organic material (**Butts, 2014**) rather than by force of crystallization (**Maliva and Siever, 1998**). The sources of silica can be many and various (e.g., **Upchurch et al., 1980**).

Cathodoluminescence (CL) is a tool for determining the nature and distribution of luminescence in quartz. These data may reflect specific conditions during the formation of quartz. Cathodoluminescence is the result of photon emission in the visible range resulting from excitation of high-energy electrons (**Ségalen et al., 2008**). The intensity of CL is dependent on the density of intrinsic and extrinsic defects within the band gap of the mineral. These defects are usually structural imperfections in the quartz crystal due to vacancies within the crystal lattice, and include point and planar lattice defects, radiation damage, shock damage, melt inclusions and fluid inclusions (**Frelinger et al., 2015**). These defects can provide information on the conditions during mineralization, and subsequent post-mineralization events such as deformation and metamorphism. The combination of scanning electron microscope (SEM) and CL data highlighting textural features allows distinction of different quartz types more easily than with conventional microscopy or colour CL analysis (**Bernet and Bassett, 2005**). Studies have shown that CL textures such as zoning, microcracks and deformation fractures can remain preserved in sedimentary rocks, withstanding processes such as uplift, sediment deposition and diagenesis (**Seyedolali et al., 1997**; **Bernet and Bassett, 2005**; **Götze, 2012**). This has made the textures a useful tool, because comparison with published CL data of specimens from well-typified settings enables the identification of the provenance of minerals and their conditions of formation. To the best of our knowledge, previous CL studies on Recent and fossil shells have focussed only on those with a carbonate composition, to determine, for example, growth trajectories, and the luminosity of calcite has

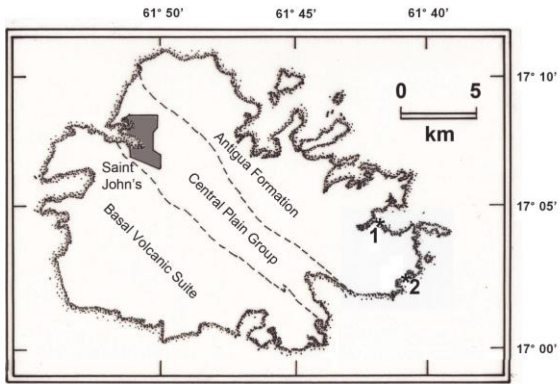

Figure 1. Outline map of Antigua (redrawn and modified after Weiss, 1994, fig. 3), showing the principal geological subdivisions and the city of Saint John's. The regional dip is towards the northeast. Localities 1 (Hughes Point) and 2 (Half Moon Bay) are marked.

been used to decide whether a shell is modern or ancient (see, for example, **Barbin and Gaspard, 1995**; **England et al., 2006**; and references therein). The application of using CL to determine information from silicified shells is therefore a new approach.

Herein, we characterise the silica prevalent in bioclasts of the Antigua Formation (upper Oligocene) of Antigua using a number of spectroscopy techniques. The island of Antigua (**Figure 1**) is characterised by an abundant and diverse Oligocene fossil fauna. Locally, these fossils are beautifully preserved, albeit silicified.

2. Geological Setting

The Caribbean island of Antigua lies towards the northern end of the Lesser Antilles volcanic arc. It is a Limestone Caribee, an island of volcanic origin capped by carbonates (**Wadge, 1994**; **Donovan et al., 2014a, b**). As such, it is a perfect field laboratory to investigate the relationships between a volcanic arc and the evolution of its carbonate cover succession. The rock record of the entire island is late Oligocene in age (**Weiss, 1994**), with the exception of some minor upper Quaternary sediments. The regional dip of the strata is towards the northeast, with the oldest rocks, the Basal Volcanic Suite, cropping out and exposed in the western and southern regions of the island. The stratigraphical succession can be defined in terms of three conformable units, in ascending order: the Basal Volcanic Suite; the Central Plain Group; and the Antigua Formation. The Antigua Formation is a succession of diverse limestones with minor siliciclastic and volcaniclastic, commonly tuffaceous, horizons that are exposed in the north and east of the island (**Figure 1**).

3. Localities

The specimens analysed herein were collected from two localities in the Antigua Formation.

3.1. Locality 1. Hughes Point

Oysters were collected from float and in situ from limestone beds in the Hughes Point area on the south coast of Nonsuch Bay, parish of St. Philip, eastern Antigua (Locality 1). Large gryphaeid oysters assigned to Hyotissa antiguensis (**Brown, 1913**) are locally common both in situ in an extensive coastal exposure, and reworked as float in adjacent shallow water, the latter associated with common bored clasts of limestone (**Donovan et al., 2014a**). A measured section of part of the coastal exposure appeared in **Collins and Donovan** (**1995**, fig. 2; **Figure 2** herein). Oysters are common and were noted in all beds identified in this illustration.

3.2. Locality 2. Half Moon Bay

Scallops, including *Aequipecten*? sp., were collected from the northeast point of Half Moon Bay, parish of Saint Philip, southeast Antigua (Locality 2). Here the section exposes over 8 m of the Antigua Formation. These limestones have yielded a diverse fauna (**Donovan et al., 2015**), including calcareous algae, articulated sponges, brachiopods, crinoid columnals, asteroid marginal ossicles, echinoids, rare oysters and other benthic molluscs, including scallops. Foraminiferans from these beds include flat *Lepidocyclina canellei* Lemoine and Douville and inflated *Eulepidina* sp. cf. *E. undosa* (Cushman). A measured section was published in **Donovan et al.** (**2015**, fig. 3; **Figure 3** herein).

4. Materials and Methods

Samples were studied for texture and composition using the SEM. Thin sections were cut at regular 10 mm transverse intervals perpendicular to the direction of growth through the samples to create cross sectional views. Thin sections were coated in Epo Tek 301 two-part epoxy resin and polished with diamond. Samples were then coated with c. 20 nm carbon to avoid charging during analysis. Imaging and analysis by SEM was carried out using the Hitachi SU-70 FEG SEM in Durham University using secondary electron and backscattered electron detectors at 12 kV. Both primary and secondary backscatter techniques were used to produce general images prior to SEM-EDS and SEM-CL analysis. Energy dispersive X-ray analysis was carried out

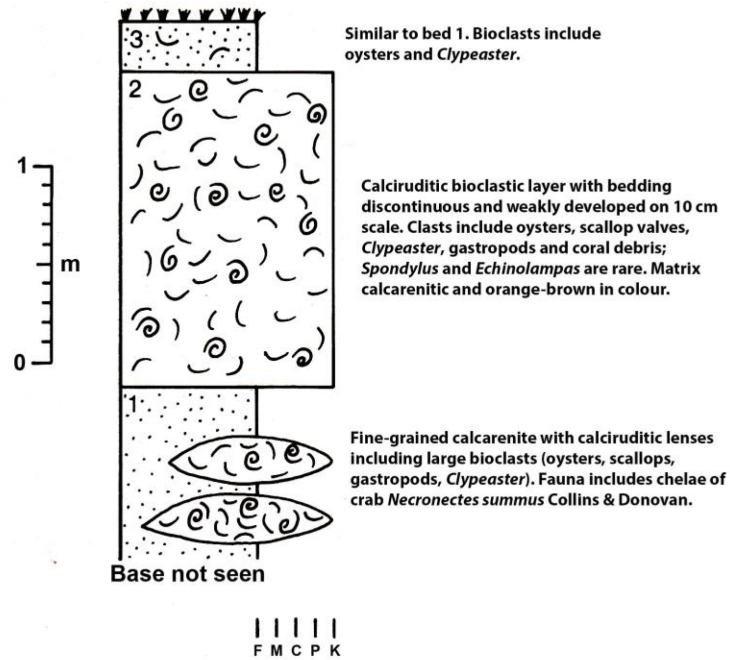

Figure 2. Measured section in the lower part of the cliff at Hughes Point (Locality 1), Nonsuch Bay, Antigua Formation (modified after Collins and Donovan, 1995, fig. 2). Key: F, M, C = fine-, medium- and coarse-grained calcarenite, respectively; P = pebble calcirudite; K = cobble calcirudite; all rocks are limestone.

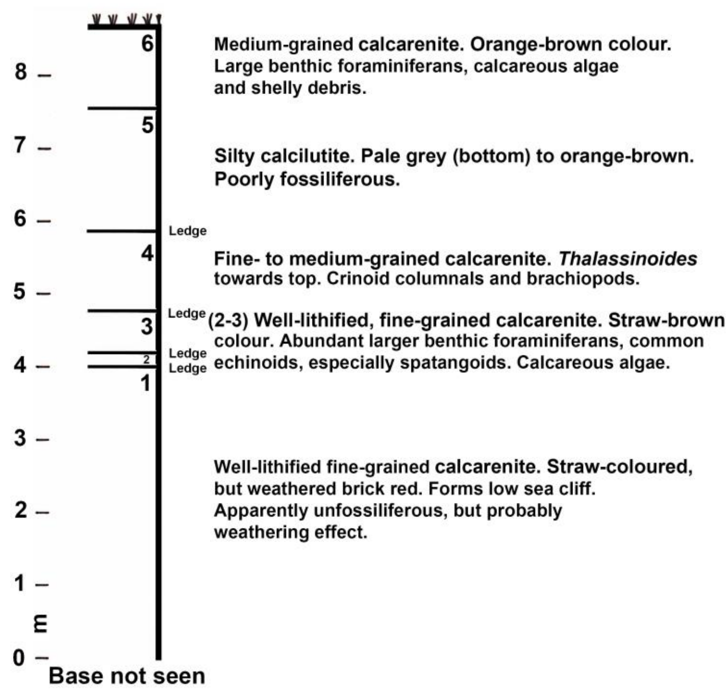

Figure 3. A measured section of the north-east point of Half Moon Bay (Locality 2), parish of Saint Philip, south-east Antigua; Antigua Formation (Upper Oligocene) (after Donovan et al., 2015, fig. 3). Crinoid columnals and a brachiopod were collected from bed 4; crinoid columnals are present, but rare, higher in the section.

using the backscatter detector and the same voltage settings were used for imaging. Results were processed using the QUANT software and running the standard several times to ensure maximum accuracy (100 ± 5%).

A mirror-type detector (Gatan Mono-CL) was used for SEM-CL analysis. The machine was set to low magnification with a 10 kV voltage to allow the site of interest to be determined. The working distance was set to 20 mm and then adjusted as necessary to allow focusing of the sample. Results were obtained using the panchromatic mode (clear filter) with both mirrors adjusted to panchromatic mono-CL settings. Working distance was set to 16.2–16.7 mm and CL luminosities collected. Grey-scale pictures were produced using mono-CL, due to the increased speed and smaller scale resolution achievable from grey scale CL imaging. Various studies have been carried out which show that quartz grains display a variety of luminosity intensities dependent on their provenance. The characterization of the distinctive CL fabrics and methods were adapted from **Seyedolali et al.** (**1997**). A more recent study suggests that textural features can provide additional support to investigations of colour and CL wavelength in determining provenance of quartz (**Schieber et al., 2000**).

5. Results

5.1. Locality 1: Hughes Point

Data using EDS show that the gryphaeid oysters are composed predominantly of silica (>80 %) intermixed with calcite (**Table 1**), lacking any correspondence to the original growth lamellae or shell ultrastructure (**Figure 4A**). Under the backscatter detector (BSE), the silica grains in the samples appear relatively uniform with no visible distinguishing features (**Figure 5A**). The silica studied by SEM-CL shows a range of grey scale luminosities ranging from dark grey to white (white being the strongest luminescence) with the majority of grains appearing mottled in texture (**Figure 5B**). These varying intensities highlight features in the silica such as zoning. This distinct zoning appears as varying shades of grey, with the outer rim showing almost no luminescence; however, zonation is not uniform. An emission spectrum was produced using the intensity of counts against wavelength. The emission band of this silica lies between 540 – 740 nm (**Figure 6**), indicated neoformed silica (e.g., **Aparicio and Bustillo 2012**), which correlates with a possible hydrothermal source (**Götze et al., 2001**).

Table 1. EDS data for specimen from Hughes Point (Locality 1). These data (wt.100%) are normalised to 100 and are calculated using the oxide option in QUANT software.

Spot Sample A	CaO	MgO	SiO	Total
1	0	0	100.00	100.00
2	0	0	100.00	100.00
3	98.61	1.39	0	100.00
4	100.00	0.00	0	100.00

5.2. Locality 2: Half Moon Bay

Scallops (pectinid bivalves) from Half Moon Bay share the same composition as the oysters (**Table 2**) from Locality 1, composed of silica and calcite; this pattern, similar to that of the oysters from Hughes Point, does not conform to the original growth lines or shell ultrastructure (**Figure 4B**). The optical BSE textures are homogenous, and there are no clear defects visible under normal SEM imaging (**Figure 5C**). However, SEM-CL again shows a distinct mottled texture and similar irregular distribution of luminosity intensities, as at Locality 1. This irregular distribution (**Figure 5D**) of luminosity helps distinguish neoformed silica from that of metamorphic origin (**Matter and Ramseyer, 1985**). There is also evidence of zoning present, with the overall texture similar to that found at Hughes Point.

Table 2. EDS data for specimen from Half Moon Bay (Locality 2). These data (wt.100%) are normalised to 100 and are calculated using the oxide option in QUANT software. Note – the value for MgO of 3.17 is probably an artefact.

Spot Sample B	CaO	MgO	SiO	Total
1	0	0.11	99.89	100.00
2	0	3.17	96.83	100.00
3	97.24	2.76	0	100.00
4	100.00	0	0	100.00

6. Discussion

Silicified fossils are common in the upper Oligocene limestones of Antigua. These rocks overlie and are regionally interbedded with a range of volcanic and volcaniclastic rocks, providing an obvious source of silica. The proximity of these extrusive igneous rocks to the fossils provides a key test of the efficacy of some of techniques available to identify the source of silica in diagenetically altered shells. In particular, those molluscs with low magnesium shells, oysters and scallops, seem particularly prone to silicification. The technique of studying patterns of variable-intensity mono CL in quartz grains has been applied to many provenance studies (**Seyedolali et al., 1997**; **Boggs et al., 2002**), but in this case we have focused on the conditions of formation of the silica. We infer that silica replacement in these fossils was a multi-stage process, indicated by the variety of textures and crystal sizes visible under CL. The minerals from both localities show a characteristic mottled texture with irregular zoning and fractures throughout (**Figure 5**). The emission band of this silica lies between 540 – 740 nm (**Figure 6**), suggestive of a possible hydrothermal source (**Götze et al., 2001**; **Götze, 2012**). This evidence is not incompatible with silicification driven by the hydrothermal products of a volcanic arc, much of which forms the basement of the Limestone Caribees.

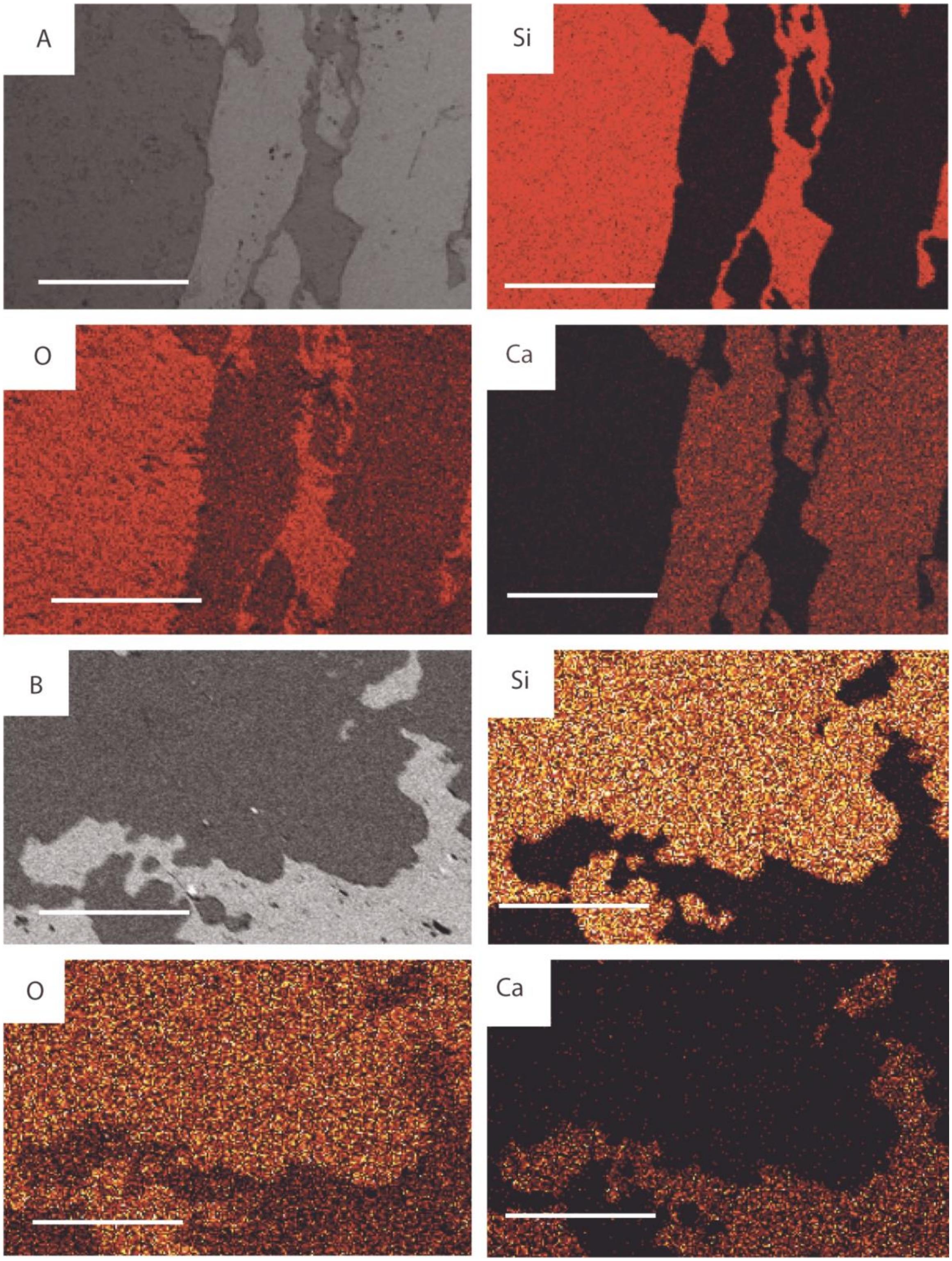

Figure 4. Elemental maps of specimens from both localities. A. Elemental maps showing the distribution of Si, Ca and O of a sample from Hughes Point of the oyster *Hyotissa antiguensis*. B. Elemental maps showing the distribution of Si, Ca and O of the Half Moon Bay sample of *Aequipecten*? sp. Scale bars represent 100µm.

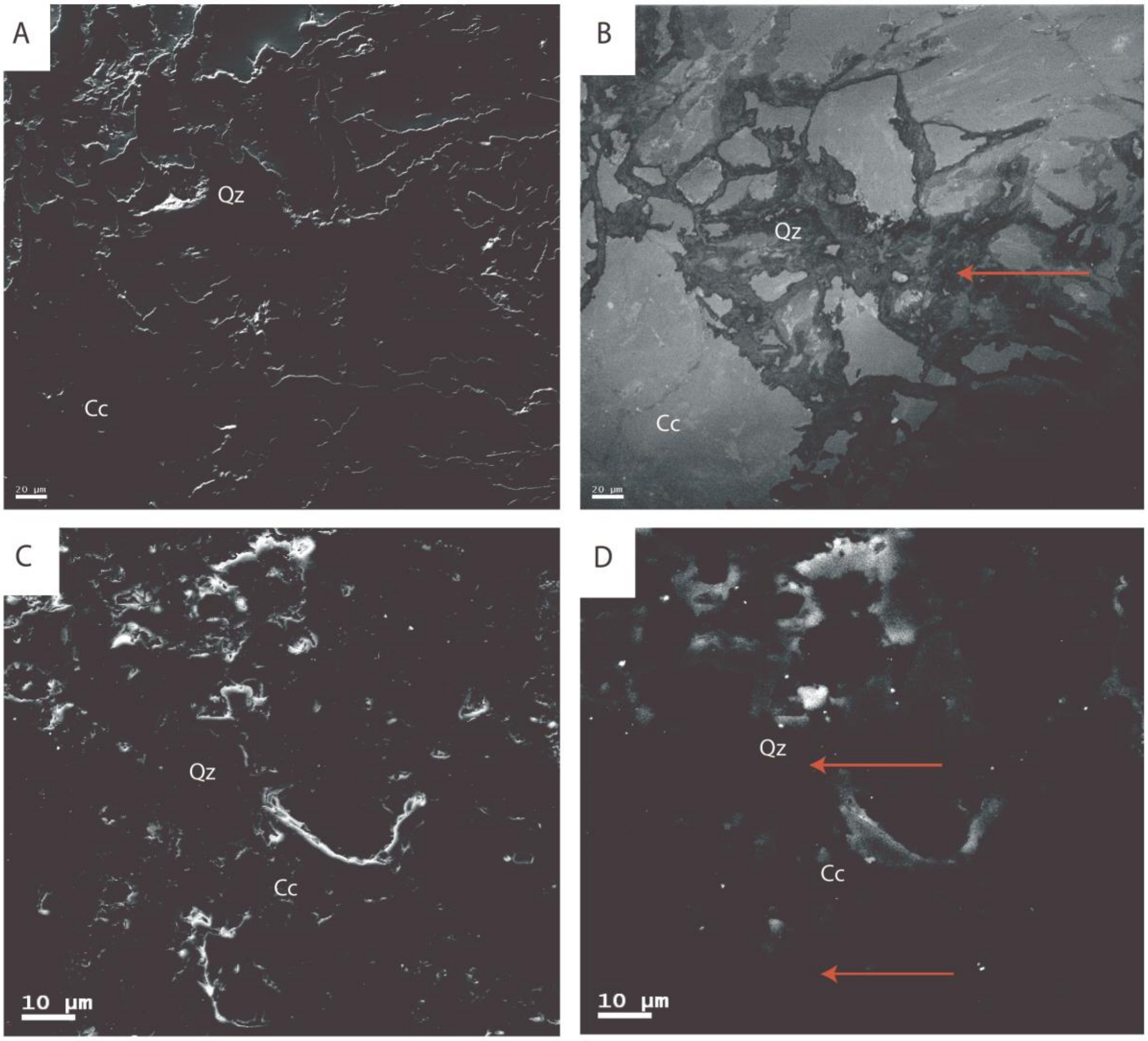

Figure 5. SEM and CL images of specimens from Hughes Point and Half Moon Bay. A. SE image showing the relationship of calcite to silica zones in the oyster Hyotissa antiguensis. B. SEM-CL of same area and specimen as (A), showing distinct mottled texture (red arrow). C. SE image of Aequipecten? sp. from Half Moon Bay, showing the distribution of calcite and silica zones. D. SEM-CL of same area and specimen as (C), showing differing luminosity in silica and mottled textures (red arrows). Scale bars represent 20 µm (above) and 10 µm (below). Abbreviations: Cc – calcite; Qz – quartz.

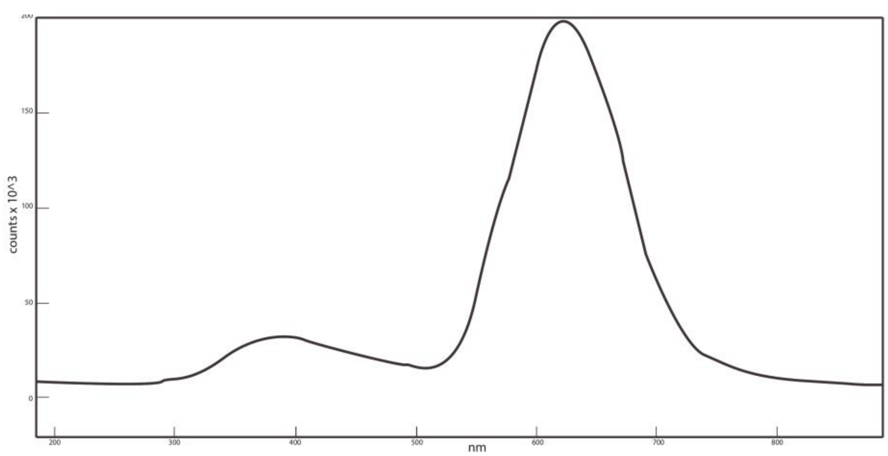

Figure 6. CL-SEM spectrum of quartz; emission band of this silica lies between 540 – 740 nm.

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