



Coexistence of three calcium carbonate polymorphs in the shell of the Antarctic clam *Laternula elliptica*

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[1] We analyzed shell cuts of five individuals of the Antarctic bivalve *Laternula elliptica* from three locations along the Antarctic Peninsula by means of Confocal Raman Microscopy (CRM) as well as Electron Microprobe (EMP). The shell of *L. elliptica* has been previously described as being composed of aragonite exclusively. Now, CRM mapping reveals that three polymorphs of calcium carbonate – aragonite, calcite, and vaterite – are present in the chondrophore region of the examined individuals. Annual shell growth layers continue through aragonite and vaterite, suggesting simultaneous mineralization of both polymorphs. Spatially congruent EMP scans showed that the calcium carbonate polymorph affects the distribution of magnesium and strontium within the chondrophore. This is, to our knowledge, the first report of the coexistence of these three calcium carbonate polymorphs within the mineralized structures of a marine calcifying organism. Particularly the presence of vaterite is unexpected, but shows striking similarities to some fish otoliths. The strong effect of the calcium carbonate polymorph on trace element incorporation restricts the suitability of magnesium and strontium based proxies for the chondrophore area of *L. elliptica*.

Components: 4300 words, 4 figures.

Keywords: *Laternula elliptica*; Raman; aragonite; biomineralization; calcite.

Index Terms: 0419 Biogeosciences: Biomineralization; 3934 Mineral Physics: Optical, infrared, and Raman spectroscopy.

Received 6 December 2011; **Revised** 18 April 2012; **Accepted** 18 April 2012; **Published** 24 May 2012.

Nehrke, G., H. Poigner, D. Wilhelms-Dick, T. Brey, and D. Abele (2012), Coexistence of three calcium carbonate polymorphs in the shell of the Antarctic clam *Laternula elliptica*, *Geochem. Geophys. Geosyst.*, 13, Q05014, doi:10.1029/2011GC003996.

1. Introduction

[2] Many organisms produce mineralized calcium carbonate (CaCO₃) structures, ranging from small platelets formed by coccolithophorides to the shells

of mollusks and skeletons of reef forming corals. Calcite and aragonite represent the main mineral phases among these marine biogenic CaCO₃ [Lowenstam and Weiner, 1989; Watabe, 1974]. Only in a few cases the polymorphs vaterite and amorphous calcium carbonate (ACC) have been

found [e.g., *Beniash et al.*, 1997; *Lowenstam and Abbott*, 1975; *Watabe*, 1974]. Moreover, most marine biogenic CaCO_3 structures consist of just one mineral polymorph, albeit some marine organisms produce aragonite and calcite [see, e.g., *Carter*, 1980].

[3] During the last decades interest in understanding biomineralization processes leading to the formation of biogenic structures of CaCO_3 is growing for several reasons: (i) The extent to which elements like e.g., magnesium (Mg) or strontium (Sr) substitute Ca in biogenic CaCO_3 depends on their concentration in the surrounding water and is species dependent. However, the incorporation of some elements also correlates to the environmental conditions, e.g., salinity or temperature [*Dissard et al.*, 2010; *Nürnberg et al.*, 1996], during formation. I.e., such elements can serve as proxies in climate reconstruction. (ii) “Ocean acidification” (OA), i.e., the decreasing ocean pH caused by increasing atmospheric CO_2 concentrations, leads to lower saturation levels with respect to the different CaCO_3 phases. Apparently, some marine calcifying organisms may be restricted in their ability to calcify at such lowered saturation levels [e.g., *Langer et al.*, 2009, 2011] which in turn could affect marine ecosystem functioning and the global carbon cycle [*Caldeira and Wickett*, 2003; *Hoegh-Guldberg et al.*, 2007]. (iii) Biogenic carbonates show unique properties that make them interesting for possible industrial applications [e.g., *Estroff and Hamilton*, 2001].

[4] These investigations demonstrated that biogenic CaCO_3 represent complex composites of one or more mineral phases and organic molecules. This complexity is visible at the macroscopic level and manifests down to sub-micrometric structures which are only revealed by micro analytical techniques [e.g., *Cuif et al.*, 2011, 2012]. Understanding to what extent and how organisms can control the formation of these structures, the major aim of biomineralization research, requires identifying the mineral and organic phases and their spatial organization. During the last decades, advances in micro-/nano-analytical techniques such as Atomic Force Microscopy (AFM), synchrotron based micro X-Ray Diffraction (XRD) and Confocal Raman Microscopy (CRM) facilitated the analysis of biogenic minerals distinctly [*Nehrke and Nouet*, 2011].

[5] One interesting finding was that in some cases during the biomineralization process a less stable CaCO_3 precursor such as amorphous calcium carbonate (ACC) is precipitated initially which

subsequently (partially) transforms into a more stable polymorph, e.g., into calcite during sea urchin larval spicule growth [*Beniash et al.*, 1997] or into vaterite and aragonite during pearl formation [*Soldati et al.*, 2008]. *Jacob et al.* [2008] state that (page 5401): “Freshwater and marine cultured pearls form via identical processes to the shells of bivalves and can therefore serve as models for biomineralization of bivalve shells in general.” *Spann and coworkers* [*Spann et al.*, 2010] found that vaterite can occur in the usually fully aragonitic shells of the freshwater bivalve *Corbicula fluminea*. *Frenzel and Harper* [2011] demonstrated that the two polymorphs within *Corbicula fluminea* show distinct differences in the incorporation of elements like e.g., Mg and Sr. This polymorph dependent uptake is well known for CaCO_3 , but challenges the use of proxies based on different element/Ca ratios like Mg/Ca and Sr/Ca if a biogenic carbonate is comprised of different polymorphs.

[6] In the present study we investigated the shell of the clam *Laternula elliptica*, a prominent Antarctic bivalve that is present in coastal shallow water soft sediments throughout the Southern Ocean [*Ahn*, 1993; *Ahn et al.*, 2003; *Ralph and Maxwell*, 1977; *Urban and Mercuri*, 1998]. Owing to its wide distribution, large shell (up to >100 mm length) and an age of ≤ 40 years [*Philipp et al.*, 2005], *L. elliptica* is a potentially valuable bioarchive. The shell shows a distinct pattern of annual growth increments in the chondrophore [*Brey et al.*, 2011], enabling intraannual resolution analysis of morphological, mineralogical and chemical features. *Brey et al.* [2011] showed that annual shell growth of *L. elliptica* is an indicator of the warming trend at the Antarctic Peninsula over the last 50 years (“Distinct changes in shell growth pattern include a near doubling of specific growth rate, a 25% decrease in maximum size, and a shift in individual energy expenditure from production to respiration.” page 542). Previous studies on *L. elliptica* shell biogeochemistry, e.g., oxygen stable isotope ratios $\delta^{18}\text{O}$ [*Brey and Mackensen*, 1997; *Tada et al.*, 2006], trace element concentrations [*Dick et al.*, 2007] and effects of ocean acidification [*Cummings et al.*, 2011] all presumed (explicitly or implicitly) that the shell of *L. elliptica* is completely comprised of aragonite.

[7] In the present study we used CRM mapping to confirm aragonite as exclusive CaCO_3 polymorph throughout the shell of *L. elliptica* and Electron

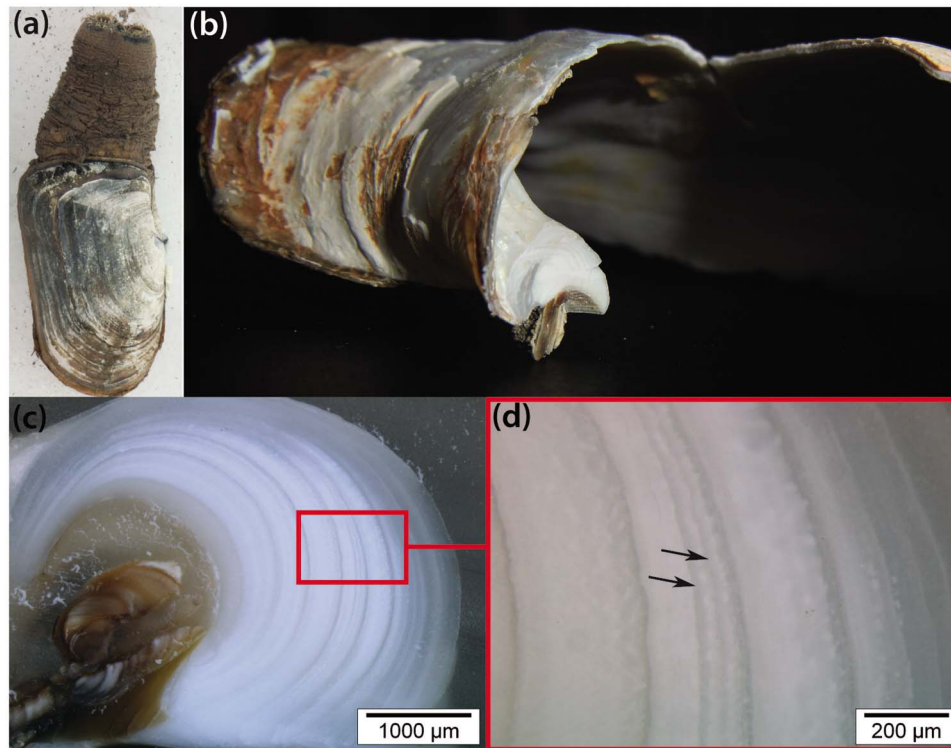


Figure 1. (a) *Laternula elliptica*, (b) cut through the shell and the chondrophore, (c) chondrophore including visible seasonal growth layers, (d) seasonal growth layers. The annual formation of the growth bands were validated by stable isotope analysis ($d^{18}\text{O}$ and $d^{13}\text{C}$) earlier [Brey and Mackensen, 1997]. Major dark bands were deposited during winter. However, a secondary pattern can occur too (see black arrows).

Microprobe (EMP) mapping of Mg and Sr to test its usability as proxy archive.

2. Materials and Methods

2.1. Sample Preparation

[8] Three *L. elliptica* (Figure 1a) were collected in Potter Cove, King George Island ($62^{\circ}14' \text{S}$, $58^{\circ}40' \text{W}$, 10 to 20 m water depth) in January 2010 by scuba diving, and one further specimen each at Collins Harbor, King George Island ($62^{\circ}11' \text{S}$, $58^{\circ}51' \text{W}$) in 1993, and at Rothera Station, Adelaide Island ($67^{\circ}34' \text{S}$, $68^{\circ}08' \text{W}$) in 2000. One clam sampled in Potter Cove was the major object of our analysis, whereas the other four shells served for confirmation of our findings.

[9] Air-dried shells were cut through the chondrophore (Figure 1b) with a diamond saw (Buehler, Isomet Low Speed Saw). Saw blade and samples were water cooled during cutting. One half of the chondrophore was embedded in resin (Araldite2020®, Huntsman International LLC., USA) and hardened under five bar pressure and 60°C for 16 h. The chondrophore surface of both halves was ground

using waterproof silicon carbide paper in the qualities of P1200, P2400, P4000 (Struers, Denmark). Finally, the sample surface was polished (Figure 1c) with a $3 \mu\text{m}$ diamond suspension (Dia Duo, Struers, Denmark) and with a $0.3 \mu\text{m}$ Al_2O_3 emulsion (Struers, Denmark) using an automated polishing machine (Logitech PM2A, Logitech, Great Britain).

2.2. Micro Analysis

[10] Mineralogical phase identification (mapping) was performed on a WITec alpha 300 R (WITec GmbH, Ulm, Germany) confocal Raman microscope (CRM), equipped with a diode laser (excitation wavelength 512 nm) and a $20\times$ objective (Zeiss EC Epiplan, Oberkochen, Germany). Raman signals were detected by a high throughput spectrometer (UHTS300, WITec, Ulm, Germany) including a DV401 CCD detector and a grating of $600 \text{ grooves mm}^{-1}$ at 500 nm blaze.

[11] The $6000 \times 2000 \mu\text{m}$ large area scan was performed on a motorized scan table. Spectra were acquired every $10 \mu\text{m}$ with an integration time of 0.2 s per spectrum. All measurements were conducted at room temperature. WITecProject software

(version 2.04, WITec GmbH, Ulm, Germany) was used for spectral analysis and imaging processing. The peak positions given are determined using the “Multipeak Fitting 2” routine of IGOR Pro (version 6.11, WaveMetrics, Inc. USA).

[12] The spatial distributions of Ca, magnesium (Mg) and strontium (Sr) were analyzed by means of Electron Probe Microanalysis (EPM) at the Institute of Geosciences of the Christian Albrechts University Kiel (Germany) using a JXA 8900 R Electron Probe Microanalyzer (JEOL Ltd., Japan). Parameter settings were: 15.0 kV accelerating potential, 50.2 nA probe current, 5 μm probe diameter and a dwell time of 120.0 ms.

3. Results and Discussion

[13] CRM analysis identified three different polymorphs of CaCO_3 within the chondrophore area of the *L. elliptica* shells, mainly aragonite, but also calcite and vaterite (Figure 2b). The Raman spectra of the different polymorphs (Figure 3) showed the typical vibration modes ν_1 (1085 cm^{-1} calcite and aragonite) and ν_4 (711 cm^{-1} calcite and 705 cm^{-1} aragonite) for CO_3 in a crystal lattice [Behrens *et al.*, 1995]. Further peaks of the lattice modes were located at 155 cm^{-1} (aragonite and calcite), 282 cm^{-1} (calcite), and at 206 cm^{-1} (aragonite). Vaterite was identified by the two doublets of the vibration modes ν_1 (1075 cm^{-1} , 1090 cm^{-1}) and ν_4 (740 cm^{-1} , 750 cm^{-1}). Raman lattice peaks of all three CaCO_3 polymorphs are very specific. Lattice mode frequencies of vaterite showed strong peaks at 105 cm^{-1} , 114 cm^{-1} , 267 cm^{-1} , and 300 cm^{-1} . The spectra were compared to in-house reference material and agree very well with the data reported by Behrens *et al.* [1995]. The reference materials have been natural calcite and aragonite from Spain and vaterite precipitated as described in Nehrke and Van Cappellen [2006] (all verified by XRD analysis).

[14] Figure 2b shows the spatial distribution of the three polymorphs within the chondrophore area. While aragonite (red) is present in the outer areas, vaterite (blue) dominates the inner area of the section plane shown. Calcite (green) is present in the innermost part and is surrounded by vaterite and aragonite. Annual growth layers are clearly visible within the areas comprised of aragonite and vaterite, suggesting simultaneous mineralization of both polymorphs. Raman point measurements on a further chondrophore that was not embedded and polished confirmed the presence of the three polymorphs,

i.e., sample preparation did not cause the formation of vaterite and/or calcite.

[15] After CRM analysis, an additional 1 mm of the sample surface was abraded to determine the mineral composition in deeper layers of the chondrophore. The new section plane (data not shown) showed a slightly larger aragonitic area at the expense of the calcite area. Extent and location of vaterite did not change. All five specimens examined contained the three polymorphs in the chondrophore area, albeit with varying spatial pattern and share of each polymorph. Even though all five examined individuals of *L. elliptica* from two distant sampling sites along the Antarctic Peninsula (Potter Cove, Marian Cove on KGI and at Adelaide Island) show the presence of different CaCO_3 polymorphs in the chondrophore area, at present our observation should not be generalized without further testing. The phenomenon seems, however, to be at least frequent across different *L. elliptica* populations.

[16] To evaluate whether or not the presence of different CaCO_3 polymorphs affects trace element distribution in the shell, we scanned Ca, Mg and Sr by means of EMP across the same area previously mapped by CRM (Figures 2c–2e). To estimate absolute concentrations in the different polymorphs a set of single point measurements were performed, two single point measurements in the aragonitic area (between seasonal growth layers) and ten measurements in the vateritic area (six measurements between seasonal growth layers and within winter growth bands). As major constituent of CaCO_3 , Ca shows a nearly homogenous distribution throughout all three polymorphs. Only layers deposited during winter are characterized by a depletion in Ca concentration (Figure 2c). Ca concentrations ranged from 35.0 weight% to 37.3 weight% in winter layers (vaterite: $V_{\text{a,winter}}$) and from 37.1 weight% to 42.1 weight% in summer layers (aragonite: $A_{\text{r,summer}}$; vaterite: $V_{\text{a,summer}}$). Mg concentrations are distinctly higher in the calcite/vaterite area, particularly in the layers deposited during winter ($V_{\text{a,winter}}$: 6160 – 11,000 ppm \gg $V_{\text{a,summer}}$: 1000 – 1630 ppm), while aragonitic structures show Mg concentrations close to the detection limit ($A_{\text{r,summer}}$: 96 – 110 ppm) (Figure 2d). Sr shows just the opposite distribution, it is distinctly enriched in the aragonitic regions ($A_{\text{r,summer}}$: 1840 – 2280 ppm $>$ $V_{\text{a,summer}}$: 180 – 650 ppm / $V_{\text{a,winter}}$: 340 – 550 ppm), particularly in the winter layers (Figure 2e). The polymorph dependent element incorporation is well known from inorganic data and is related to the difference in cation size and crystal structure [e.g., Finch and Allison, 2007].

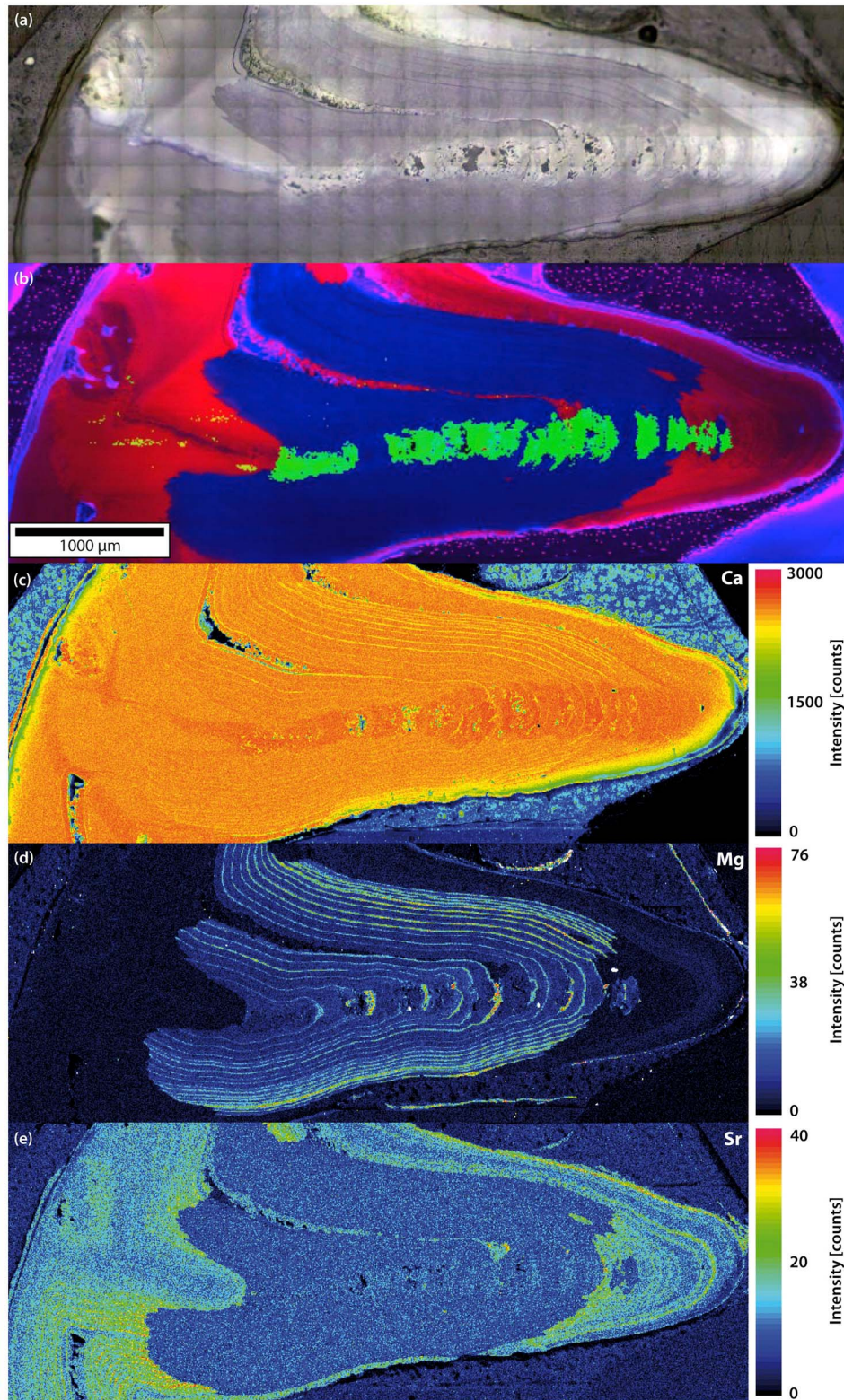


Figure 2. (a) Reflected light microscopy image of the investigated chondrophore. (b) Distribution of aragonite (red), calcite (green), and vaterite (blue) measured by CRM. Element distributions of (c) calcium, (d) magnesium, and (e) strontium within the chondrophore area of *L. elliptica* as measured by EMP.

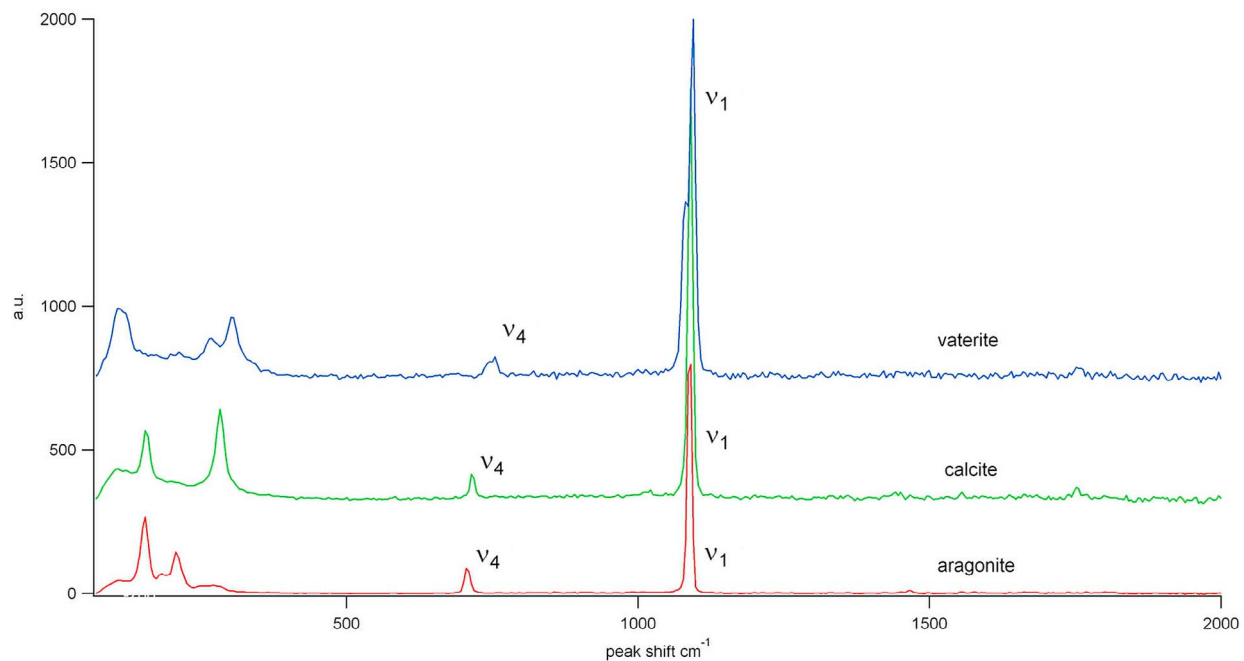


Figure 3. Raman spectra of the three CaCO_3 polymorphs aragonite, calcite, and vaterite.

[17] Our finding of three CaCO_3 polymorphs in the chondrophore area of *L. elliptica* contradicts the present view that the whole shell is aragonitic [e.g., Tada *et al.*, 2006; Cummings *et al.*, 2011]. Previous studies, however, may have been hampered by methodical limits. The chondrophore constitutes a relatively small part of the entire shell, and thus vaterite and/or calcite may not be detectable by XRD within a mainly aragonitic sample. Vaterite is quite rare in natural environments due to its relatively low stability under Earth's surface conditions, under which it normally transforms into aragonite or calcite within hours to days [e.g., Nehrke and Van Cappellen, 2006]. However, it is well documented that unstable polymorphs of CaCO_3 (especially vaterite and ACC) can be present in biogenic CaCO_3 [Beniash *et al.*, 1997; Weiss *et al.*, 2002; Wehrmeister *et al.*, 2011]. In such complex biogenic composites their transformation is probably inhibited by e.g., divalent cations and/or organic macromolecules [e.g., Aizenberg *et al.*, 1996; Loste *et al.*, 2003]. The possible function of these polymorphs is discussed controversially. Whereas ACC seems to play a crucial role in the initial nucleation within a biological system [Beniash *et al.*, 1997; Weiss *et al.*, 2002], the role of vaterite is less clear. Current hypotheses relate vaterite to repair structures in adult calcifying organisms [e.g., Watabe, 1983; Wilbur and Watabe, 1963] and to secondary shell thickening (e.g., in the freshwater bivalve *Corbicula*

fluminea [Spann *et al.*, 2010]. Even though *L. elliptica* is strongly affected by iceberg rafting [Philipp *et al.*, 2005; Smale, 2007], which can cause damage to their shells, none of the investigated individuals showed any injury in the chondrophore area and, furthermore, annual growth lines continue through all polymorphs (Figure 4), suggesting simultaneous mineralization. Neither does the

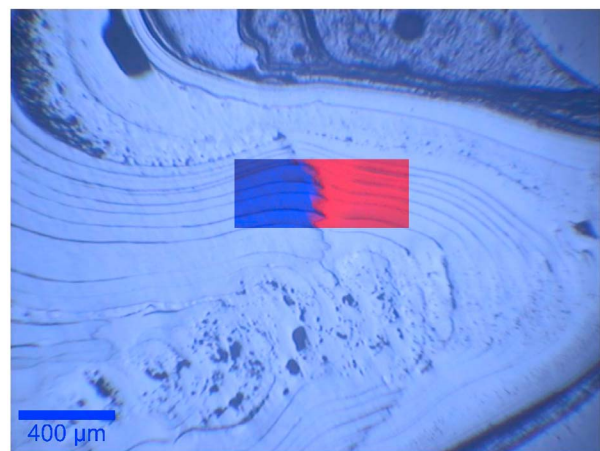


Figure 4. Overlay of a Raman mapping on a reflected light microscopy image (obtained on the same sample shown in Figure 2a but in a deeper horizon after re-polished following the EMP measurements), showing the growth lines continuing through the vaterite (blue) and aragonite (red) polymorph.

vaterite make the shell of the *L. elliptica* thicker; it is just part of the “normal” chondrophore structure.

[18] However, the polymorph composition of the chondrophore area of *L. elliptica* is strikingly similar to the aragonite-vaterite patterns in the otoliths of some fish species, e.g., *Oncorhynchus tshawytscha* (Chinook salmon) [Gauldie, 1996] and *Salvelinus namaycush* (lake trout) [Melancon et al., 2005]. As in the chondrophore of *L. elliptica*, distribution and amount of vaterite varied considerably between otoliths [Melancon et al., 2005]. And, as in the chondrophore of *L. elliptica* (Figure 2b), different polymorphs are present across annual growth bands, which is indicative of simultaneous precipitation. Furthermore, in both shell chondrophore and otoliths Mg is enriched in the vateritic (and if present calcitic) and Sr in the aragonitic areas. The polymorph dependent incorporation of Mg and Sr observed here (Figure 2) and in otoliths [Melancon et al., 2005] gives further support for simultaneous polymorph precipitation from the same fluid. e.g., the endolymph or hemolymph (please note that it is still controversially discussed from which fluid exactly the ions are transported to the site of calcification).

4. Conclusions

[19] We demonstrated that the shell of the investigated specimens of *L. elliptica* is not, as previously stated, completely comprised of aragonite, but is composed of the three polymorphs aragonite, calcite and vaterite, at least in the chondrophore area. The extent to which these polymorphs are present varies between specimens. To our knowledge this is the first observation of the coexistence of these three polymorphs in a marine biogenic carbonate. The polymorph specific incorporation of elements like Sr and Mg complicates the use these elements as proxy signals. The striking similarity of the *L. elliptica* chondrophore morphology and biogeochemistry to otoliths that show co-precipitation of vaterite and aragonite requires reconsidering the current view of vaterite resulting from irregular, incomplete or failed carbonate formation. It is difficult to imagine that a complex process like biogenic calcification that developed over millions of years will be so error prone, i.e., exhibiting the same malfunction in the growth of fish otoliths and bivalve shells. However, this study emphasizes the need for high resolution analytical techniques like CRM to determine the phase composition in biogenic structures prior to reconstruct paleo-environmental conditions from chemical signals. Further work is

necessary to identify the reason for the coexistence of different polymorphs of CaCO₃ in some biogenic structures.

Acknowledgments

[20] We would like to thank the divers and the crew of the Argentinean Antarctic Station Jubany for their logistic help, I. Y. Ahn (Korea Polar Research Institute, Incheon, Korea) and E. Philipp (Institute of Clinical Molecular Biology, Kiel, Germany) for providing sample material, Peter Appel and Barbara Mader of the Department of Geosciences of the University of Kiel (Germany) for electron micro probe measurements as well as Kerstin Beyer (AWI) for the support during sample preparation. This work was supported by the German Research Foundation (DFG) under grant AB 124/11–1 in the framework of priority program 1158 – Antarctic Research and is associated to the IMCOAST project. Financial support for was provided by the German Federal Ministry of Education and Research (BMBF, FKZ 03F0608, “BIOACID”), and the European Commission through grant 211384 (EU FP7 “EPOCA”). Gernot Nehrke and Harald Poigner have contributed equally to this work.

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