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The unusual mineral vaterite in shells of the freshwater bivalve *Corbicula fluminea* from the UK

Nicole Spann · Elizabeth M. Harper · David C. Aldridge

Abstract Asian clams (*Corbicula fluminea*) with abnormally thickened shell valves were found in four rivers in the UK (Rivers Yare, Waveney, Thames and New Bedford River). The material making up these malformations was the rare calcium carbonate polymorph vaterite. Vaterite is seldom found in the natural environment because it is less stable than the other calcium carbonate polymorphs (aragonite and calcite). In the few reported cases of vaterite formation in molluscs, it is usually related to unusual biomineralisation events such as shell regeneration, pearls and initial stages of shell formation. We compared two populations from the Rivers Yare and Waveney in the Norfolk Broads, UK, one (River Waveney) displaying dominantly the normal *Corbicula* shell form with aragonitic shells. In the River Yare population, all individuals sampled had shell deformations to different extents. These deformations were apparent as bulges on the inside of the ventral shell margin. X-ray diffraction confirmed that the shell material in the bulges of recently collected clams was vaterite. Other parts of the deformed shells were aragonitic. The shell deformations alter the shell morphology, leading to higher and wider shells. The shell microstructure is fibrous in the vateritic parts and crossed-lamellar in the aragonitic parts of deformed or non-deformed shells. The cause for the malformations is probably a disrupted biomineralisation process in the bivalves. Fossil *Corbicula* specimens from the late Pleistocene had similar deformations, suggesting that this is not a response to anthropogenic causes, such as pollution.

Keywords Vaterite · Biomineralisation · Shell formation · *Corbicula fluminea* · Shell deformation

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Introduction

The mechanisms of calcium carbonate biomineralisation are of considerable interest not only for biologists but also for material scientists, geochemists and palaeontologists (Jacob et al. 2008). Calcium carbonate occurs in three different polymorphs: calcite, aragonite and vaterite. These polymorphs differ in crystal structure: Calcite has a trigonal, aragonite an orthorhombic and vaterite a hexagonal structure (Kamhi 1963; Behrens et al. 1995; Wang and Becker 2009). All can be grown in vitro and the formation of the different polymorphs is influenced by temperature (Vecht and Ireland 2000), proteins (Lakshminarayanan et al. 2005; Pokroy et al. 2006), ions or humic acids (Falini et al. 2009). Calcite is the most stable of the three polymorphs in ambient conditions, and aragonite is metastable at the Earth's surface (Lippmann 1973). Vaterite is considered to be unstable in these conditions (Lippmann 1973). Albright (1971) proposed that vaterite is stable only at low temperatures (below 10°C at 1 atm). It has a higher water solubility than the other two forms (Plummer and Busenberg 1982) and a lower density (Lippmann 1973). It rapidly transforms into calcite when exposed to water (Kralj et al. 1997) or at high temperatures (Perić et al. 1996).

Accordingly, calcite and aragonite are the two most common calcium carbonate polymorphs in nature. There

are only two sites where vaterite has been reported to precipitate from natural waters, Holkham Lake in Norfolk, UK, and a supraglacial sulphur spring on Ellesmere Island, Canada (Rowlands and Webster 1971; Grasby 2003), though the occurrence of vaterite for Holkham Lake could not be confirmed in a later study (Lucas and Andrews 1996). The majority of natural occurrences of vaterite are related to biogenic activity, and the assumption is that organic macromolecules allow stabilisation in living organisms (Rodriguez-Navarro et al. 2007), but even there aragonite and calcite are the dominant materials (e.g. hard parts of bivalves, corals, ascidians; Lowenstam 1981). Vaterite is seldom found in biomineralising organisms (Watabe 1983; Wilbur and Saleuddin 1983). It has been reported in only a few instances and there in just low amounts, e.g. during molluscan shell repair (Wilbur and Watabe 1963; Saleuddin and Wilbur 1969), in freshwater pearls (Ma and Lee 2006; Qiao et al. 2007; Wehrmeister et al. 2007) and in egg capsules and normal shells of some gastropod species (Hall and Taylor 1971; Meenakshi et al. 1974; Hasse et al. 2000). In other taxa, it occurs in spicules of ascidians (Lowenstam and Abbott 1975), in otoliths of fish (Gauldie 1993; Melancon et al. 2005; Morat et al. 2008) and in human gall stones (Sutor and Wooley 1968; Palchik and Moroz 2005).

Originally living in Southeast Asia, the freshwater bivalve *Corbicula fluminea* (Müller 1774) was introduced into the USA in the early part of the twentieth century, and it then spread to South America and Europe (McMahon 1983; Elliott and zu Ermgassen 2008). It was discovered for the first time in Britain in 1998, in the River Chet in the Norfolk Broads (Howlett and Baker 1999). Now it can be found in many rivers in this area, as well as in the Thames (Elliott and zu Ermgassen 2008) and the Great Ouse system (Willing 2007). Although *C. fluminea* is considered to be an invasive species in Europe, *Corbicula* fossils are known from late Pleistocene interglacial deposits in northwest Europe (Sparks and West 1970; Preece and Meijer 2000).

This study gives the first report and description of shell deformations in *Corbicula* from the UK, taking into account shell form, mineralogy and microstructure. We also record the presence of large volumes of vaterite in these deformed shells.

Material and methods

C. fluminea (living individuals) were collected by dredging in the Rivers Yare and Waveney in the Norfolk Broads, UK, in April and May 2008 (Yare: site 1 near Brundall, 52°36′52″ N, 1°26′38″ E (41 live clams) and site 2 long dyke to Rockland Broad 52°35′16″ N, 1°26′47″ E (49 live

clams); Waveney: site near Burg St. Peter 52°28′50 N, 1°40′12″ E (57 live clams)).

In addition, the recent *Corbicula* sp. specimens from the collections of the Natural History Museum (London) were also surveyed for shell deformations (around 130 samples, most containing multiple specimens, different species and locations: Southeast Asia, India and Pakistan, Northeast Africa, the Middle East, Australia, South Africa, Europe and South America). Samples from other collections by the authors (River Thames (83 live clams) and New Bedford River (33 live clams), Rivers Chet (338 live clams) and Ant (25 live clams), all UK; sampled in 2008 and 2009) were also checked. We also studied specimens of fossil *Corbicula* sp. from the Pleistocene of the UK, in the collections of the Sedgwick Museum (Cambridge University). These collections, of over 150 samples, include large holdings of *Corbicula* from a classic study of the fauna of Wretton (Norfolk) from the Ipswichian Interglacial (Late Pleistocene) by Sparks and West (1970) and also from sites in Cambridgeshire.

Shell form

For the clams (Waveney: $n=57$; Yare, site 1: $n=41$), shell length, height and width (to the nearest 0.1 mm with vernier calipers), shell volume (displacement method; Rodhouse 1977) and whole animal volume (shell volume plus volume inside the valves, measured by filling shells with salt) were determined. These values were used to calculate three shell morphometric parameters for each animal: heightening as shell height/shell length, obesity as shell width/((shell length + shell height)/2) and thickness as shell volume/ animal volume. A principal component (PC) analysis (PCA) was performed on these three parameters and each PC was tested for differences between the two sites (unequal variance t test, normal distributed data).

X-ray diffraction analysis

In order to investigate the mineralogy of the unusual shell material, a small amount of the translucent calcium carbonate material was scraped off with a scalpel from the inner ventral margin of eight heavily deformed shells from the River Yare and six individuals from the Waveney in which there was no sign of deformation or translucent material. Samples were then analysed by X-ray diffraction (Bruker D8 Room Temperature Diffractometer, Department of Earth Sciences, Cambridge).

Shell microstructure

Shells were embedded in polyester resin, cut along the axis of maximum growth, polished and etched in 1% hydro-

chloric acid (20 s). In addition, another set of shells was fractured approximately along the line of maximum growth. Specimens were mounted on stubs and gold-coated for investigation by SEM (Jeol 820, Department of Earth Sciences, Cambridge).

Shell density and shell organic matter content of *C. fluminea*

Five undeformed shells and five deformed shells were chosen from the Waveney and Yare, respectively. Shell density was determined by weighing fragments from the ventral shell margin and measuring their volume by displacement. The same fragments were used to work out the insoluble organic matter (OM) content by slowly dissolving them in 1% hydrochloric acid (Dame 1972) and calculating the quotient of weight of dried organic matrix (72 h at 75°C) and fragment weight. By using fragments, we ensured that only deformed or undeformed parts of the shell were used without the periostracum. Differences in shell density and shell organic matter content between the two sites were tested with two sample non-parametrical tests (Mann–Whitney *U* test).

Results

Shell morphology

All 90 individuals of *C. fluminea* from the two sites at the River Yare had deformed shells, irrespective of their size, and the deformations occurred to different degrees (see Fig. 1). The clams originating from the River Waveney displayed predominantly the normal shell form; only seven out of 57 (12%) had tiny (1–3 mm) deformed spots on the inner shell surface. Usually shells have a smooth and lustrous inner surface which may be white or purple (Fig. 1a). Deformations occurred to different extents; in some shells (12% in River Waveney, 19% in River Yare), they consisted of only small rounded or elongated spots about 1 to 3 mm wide that protrude from the otherwise smooth inner shell surface. In other shells (37% of River Yare specimens), the deformations were more widespread and appear as bulges at the ventral shell margin (Fig. 1b). In addition, a thickening of the shell near to the umbo can often be seen. In a third group, the whole shell margin was strongly thickened and nearly always the part towards the umbo as well (Fig. 1c; 44% of River Yare *Corbicula*). The valve hinges are frequently also deformed (Fig. 1b, c). Very often the deformations are asymmetric between shell valves. The deformed parts are beige-green, translucent and not as lustrous as the rest of the shell. Shells which have bulging inner deformations are often deformed on the outside as well with the shell margin drawn in at the site of the inner bulge (Fig. 1b).

A radial section through a shell showed that the translucent material was laid down on the inside of the normal more opaque shell, and the transition between the two shell structures is abrupt (Fig. 2). At the ventral margin, the translucent material was deposited directly on the periostracum.

The survey of *Corbicula* species from a wide range of geographic locations in the Natural History Museum (London, UK) revealed only one site in Egypt where

Fig. 1 Shells of *C. fluminea*, inside views. **a**–**c** Recent shells (*scale bar* is 1 cm). **a** Undeformed shell from the River Waveney population. **b** Deformed shell with one thickened bulge at the shell margin (River Yare). **c** Deformed shell having a completely thickened shell margin (River Yare). **d**–**f** Fossil *Corbicula* shells from the Ipswichian interglacial deposits from Barnwell Abbey (Cambridgeshire), UK (CASM D.2482; *scale bar* is 1 cm). Note the loss of shell material around the ventral shell margins
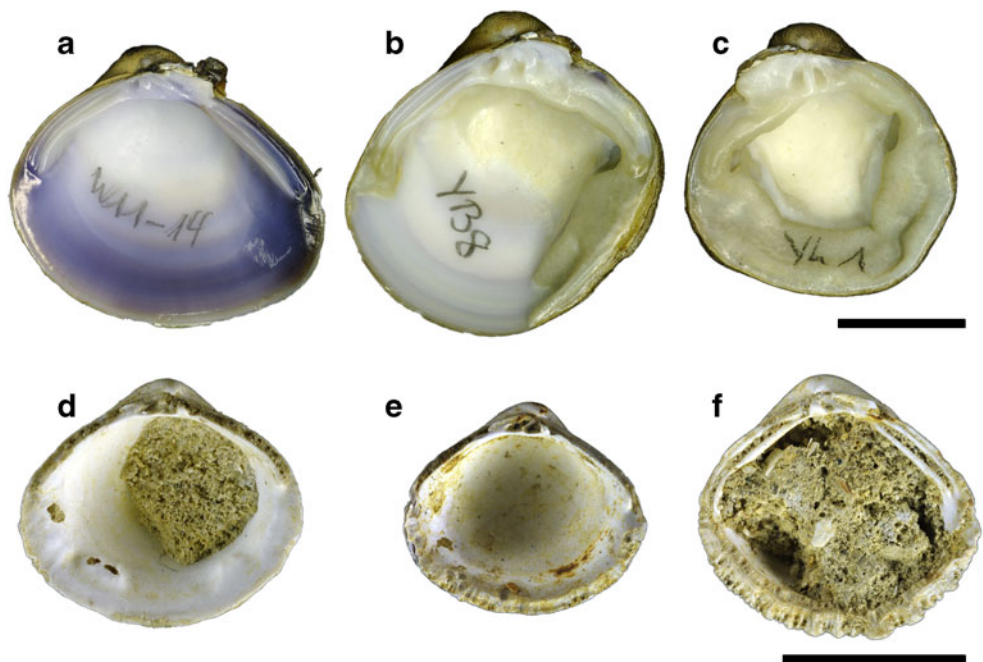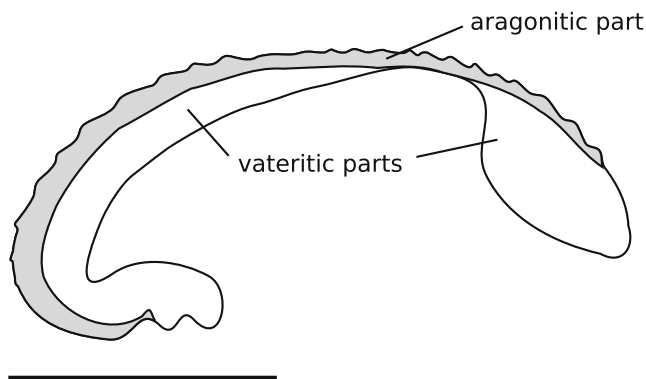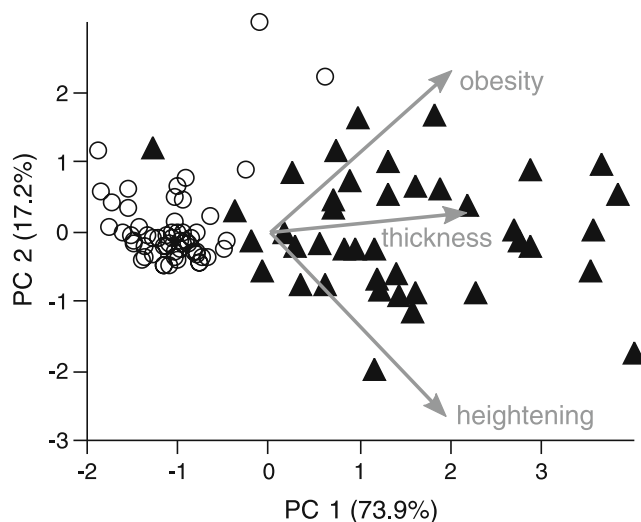
Fig. 2 Schematic drawing of a section through a deformed *C. fluminea* shell. SEM pictures taken in this section are shown in Fig. 5b, d. The *grey part* is the normal aragonitic shell which is opaque. The *white parts* consist of the translucent vaterite material that has been deposited on the inner shell surface (*scale bar* is 1 cm)

Fig. 3 Distance biplot of a principal component analysis of three shell parameters of *C. fluminea* (heightening, obesity and thickness). *Circles*: individuals from the River Waveney (*n*=57), *filled triangles*: individuals from the River Yare (*n*=41). *Values in parentheses* are the percentage of variation in the data that can be explained by each axis (principal component)

similar shell deformations in *Corbicula artini* were present (two out of three shells had thickened spots at the ventral shell margin). All the other examined specimens (different *Corbicula* species from various locations, around 130 samples) showed no deformations. In the UK, the shell deformations are common in some *C. fluminea* populations (Rivers Yare, Thames, Waveney and New Bedford River), but in other rivers, where *Corbicula* is abundant, deformed shells have not been found so far (Rivers Chet and Ant). In addition, many of the fossil *Corbicula* specimens (Late Pleistocene) from the sites at Wretton (Norfolk) and Barnwell Abbey (Cambridgeshire) in the UK had 'frayed' shell margins (Fig. 1e, f), and in some specimens, there were protruding spots on the inner shell surface (Fig. 1d) which were often hollow. These observations indicate the loss of some shell material during the taphonomic (postmortem) history of the shells. Close examination of these surfaces reveal that they correspond to sharp boundaries in the original microstructure of the shells rather than physical breakage.

Quantitative shell morphometric parameters

The effect of the deformations on overall shell form is seen in the PCA utilising the three shell form parameters heightening, obesity and thickness (Fig. 3). A size effect (cubed root of animal volume) on these shell parameters could be neglected because animals in both samples had similar sizes (normal distributed data; unequal variances *t* test: $t=1.2$, $df=69.5$, $p=0.25$). The two *Corbicula* populations from the Yare and the Waveney form two separate groups along PC1 in the PCA plot. PC1 explains a substantial amount of the variance in the dataset (74%). River Yare shells were significantly different in shape to those from the River Waveney ($t=12.3$; $df=47$; $p<0.001$), with Yare shells showing greater thickness, obesity and

heightening (Fig. 3). The remaining two PCs do not distinguish between the two river populations. The spread of values for the River Yare population along PC1 shows the different degrees of deformation. *Corbicula* species can have very different shell forms depending on the habitat they are living in, which has led to some confusion in the taxonomy of this genus. Therefore, the difference between populations due to shell deformations in our PCA can only be regarded as descriptive for our sample sites (lowland rivers) and not generalised to other habitats.

X-ray diffraction analysis

Figure 4 shows examples of the typical XRD traces produced by both undeformed shell and the deformed material. As reported by previous studies, all areas of undeformed shell examined produced only the traces characteristic of aragonite (Fig. 4a), while each of the eight analyses of deformed material produced different traces, characteristic of vaterite (Fig. 4b), although it is clear that this sample also contains some aragonite.

Shell microstructure

Normal shell areas of *C. fluminea* showed to be aragonitic with a crossed-lamellar or complex crossed-lamellar microstructure (Fig. 5d). In contrast, the microstructure of the patches of vaterite in the deformed areas lacks these microstructures. SEM of fractures through these regions show a fibrous structure (Fig. 5a). Individual fibres are approximately 20 μm in width and 60 to 100 μm in length
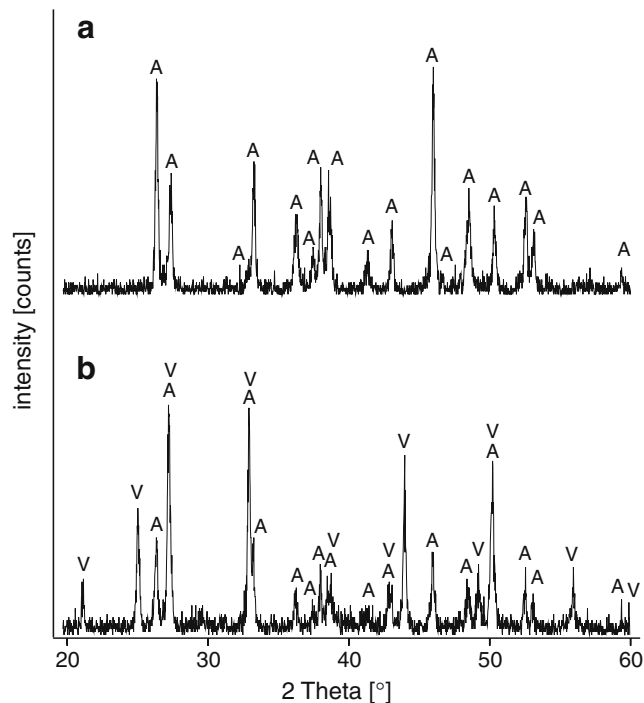
Fig. 4 Examples of typical XRD spectra of **a** material from an undeformed *Corbicula* shell (River Waveney) and **b** material from the margin of a deformed *Corbicula* shell (River Yare, site 2). *A* and *V* identify aragonite and vaterite peaks, respectively. The spectra are displaced along the *y*-axis

and are arranged in parallel bundles. In an etched section of a deformed shell (Fig. 5b), it becomes visible that these fibres are made of irregularly organised round-shaped crystals. It is apparent that, embedded within the vaterite areas, there are patches of 'normal' aragonite, clearly discernible by their crossed-lamellar microstructure (Fig. 5c). The boundaries between aragonite and vaterite microstructures are sharp (Fig. 5c, d).

Shell density and organic matter content

The density of deformed shell fragments was 2.52 g/ml (median; range 2.50–2.56 g/ml), which is significantly lower than the one of undeformed fragments (2.78 (2.75–2.86) g/ml; $n_1=n_2=5$, $U=0$, $p=0.008$). The organic matter content in deformed fragments was significantly higher, 2.12% (1.14–2.31%), compared to undeformed ones (0.47% (0.10–0.78%); $n_1=n_2=5$, $U=0$, $p=0.008$).

Discussion

The XRD analysis revealed that the translucent material deposited in the deformed parts of *C. fluminea* shells is vaterite. Biogenic vaterite is rare. Ascidians produce vateritic hard parts in their normal state (Lowenstam and

Abbott 1975), and it is present in the albumin gland and egg capsules of some snail species (Hall and Taylor 1971; Meenakshi et al. 1974; Hasse et al. 2000). For other animals, it is considered to be a precursor phase for aragonite or calcite (Mayer 1931; Kessel 1933; Wilbur and Watabe 1963; Watabe et al. 1976) or the product of a malfunctioning biomineralisation process (Gauldie 1993; Soldati et al. 2008).

Usually, *C. fluminea* has a shell consisting entirely of aragonite (Taylor et al. 1973; Mackie 1978; Prezant and Tan-Tiu 1985). The shell microstructure can be divided into an outer crossed-lamellar layer and an internal complex crossed-lamellar one (Taylor et al. 1973; Counts and Prezant 1982; Prezant and Tan-Tiu 1985). These two layers are separated by the prismatic pallial myostracum. The microstructure we found in the vaterite is completely different to these undeformed aragonitic *Corbicula* shells. Vaterite crystals have been reported to occur in a wide variety of forms. In our samples, we found fibrous crystals. In vitro, vaterite often grows as spherules (Kralj et al. 1990; Vecht and Ireland 2000; Lakshminarayanan et al. 2005; Hayashi et al. 2008; Falini et al. 2009). Spherules also occur in biomineralised vaterite of mollusc shells (Wilbur and Watabe 1963; Meenakshi et al. 1974), but fibrous and botryoidal structures have been documented for fish otoliths (Gauldie 1993). Soldati et al. (2008) reported that, in freshwater pearls, vaterite displays the same structural units as the adjacent aragonite parts, prisms and tablets. The structure of crystals formed in organisms is controlled by the organic matrix (Lowenstam 1981; Addadi and Weiner 1985). Boundaries between different calcium carbonate polymorphs in bivalve shells are sharp. This has been reported for aragonite and calcite (Carter 1980; Wilmot et al. 1992), as well as aragonite and vaterite (Qiao et al. 2007; Soldati et al. 2008). These sharp boundaries were also seen in the *Corbicula* shell sections.

We have found no previous reports of the occurrence of either vaterite or the associated deformations in the shells of *Corbicula* and discovered no previous unpublished awareness of them (B. Morton and R. McMahon, personal communication). The survey in the Natural History Museum (London) revealed only one site in Egypt out of a wide range of geographic locations, where similar shell deformations in *C. artini* were present. In UK *Corbicula* populations, the deformations are common in some rivers (Rivers Yare, Waveney, Thames and New Bedford River), but not present in other populations (Rivers Chet and Ant), where *Corbicula* is abundant. The evidence from the fossil material (where the diagenetically unstable vaterite portions have been lost during taphonomy) suggests that this condition was shared by congenerics during the last interglacial. The deformations we have observed must have fitness consequences, by

Fig. 5 SEM pictures of portions of deformed *Corbicula* shells. **a** Fractured shell showing vaterite crystals organised in fibres (*scale bar* is 5 μm). **b** Radial cut and etched section taken in the vaterite part of a deformed shell (*scale bar* is 5 μm). **c** Fractured section showing the ventral part of a deformed shell. Embedded in the vateritic material (*V*) is some aragonite shell material (*A*) showing the difference between the microstructure of the two calcium carbonate polymorphs (*scale bar* is 200 μm). **d** Radial cut and etched section of a deformed *Corbicula* shell showing the boundary between the crossed-lamellar microstructure (*A*) which consists of aragonite and the fibrous structure in the vaterite part (*V*; *scale bar* is 20 μm)
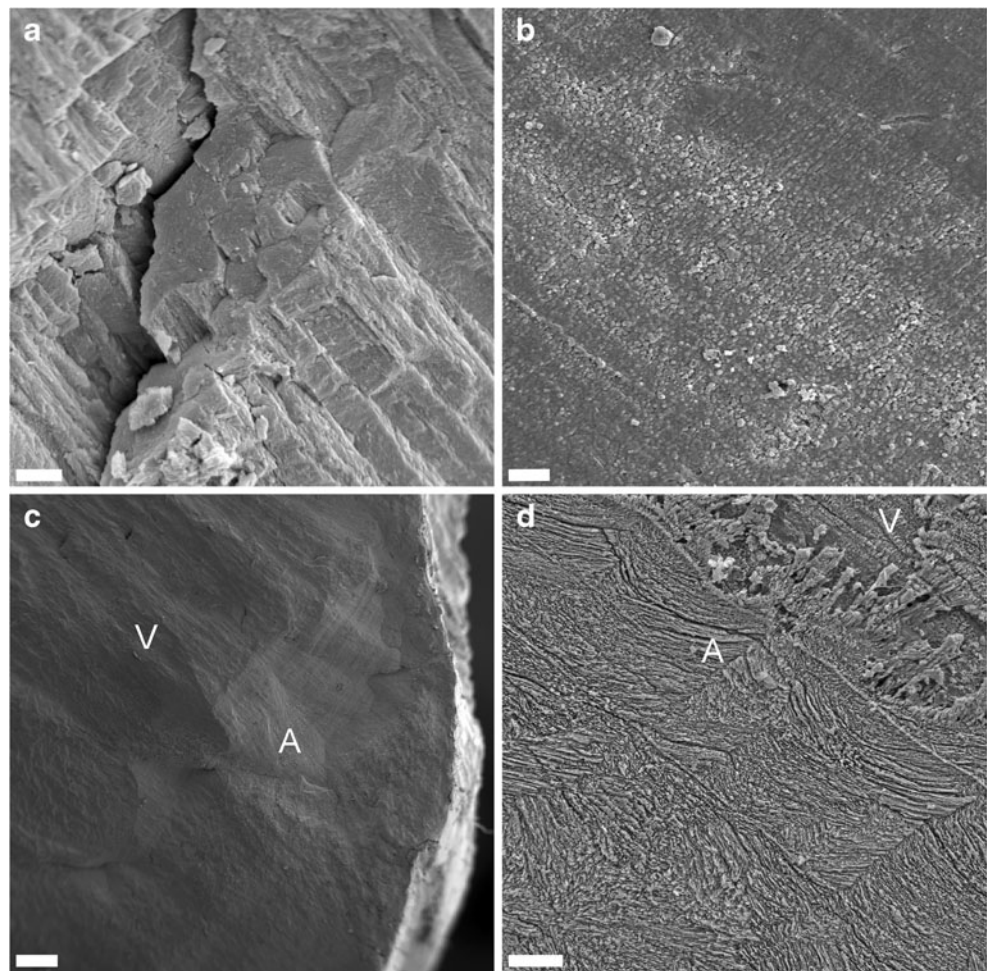
altering the outer shell morphology to higher and wider shells and increasing shell thickness, thereby reducing the volume inside the shell and thus the available space for the soft tissue. Bivalve shell morphology is typically adapted to meet local habitat conditions (Zieritz and Aldridge 2009) and so deformity may result in suboptimal phenotypes. We have also noted that, in some instances, the deformation is so great as to prevent the valves from shutting properly, which may increase exposure to predation.

The lower density of the deformed shell fragments in our study can be explained by the lower density of pure vaterite (2.65 g/ml) compared to pure aragonite (2.93 g/ml; Lippmann 1973) and the higher organic matter content of deformed shell. Simon et al. (1994) measured 0.28% OM content in aragonite crossed-lamellar marine shells which is in the same range as the 0.44% measured in the normal aragonite *Corbicula* shells in our study. Biogenic vaterite in other studies was found to contain a higher amount of organic materials than aragonite (Ma and Lee 2006; Soldati et al. 2008; Ma et al. 2009).

Considering that vaterite is unstable compared to the other two polymorphs (Lippmann 1973), there needs to be

a stabilisation mechanism present in the deformed *Corbicula* shells. In other instances, it was shown that organic molecules induce or stabilise vaterite formation in vitro (Falini et al. 2005; Lakshminarayanan et al. 2005; Pokroy et al. 2006; Rodriguez-Navarro et al. 2007; Hayashi et al. 2008). The same mechanisms have been proposed to preserve biomineralised vaterite (Ma and Lee 2006; Soldati et al. 2008). Results from Falini et al. (1996) suggest that shell macromolecules are also involved in the formation of either aragonite or calcite in vivo. Qiao et al. (2008) reported that vaterite from lackluster pearls has a lower dissolubility and higher thermal stability than inorganic vaterite and is therefore able to coexist with aragonite. The organic matrix might be responsible for the stabilisation of vaterite in *Corbicula* as well, which might explain the slightly higher amount of OM in vaterite shell fragments compared to aragonite ones. It is apparent from the fossil shells that vaterite is diagenetically less resistant than the adjacent aragonite and is lost relatively easily, perhaps related to the degradation and loss of the protective organic matrix (Glover and Kidwell 1993).

In our *Corbicula* shells, as well as in other studies with fish otoliths or pearls (Melancon et al. 2005; Soldati et al.

2008), vaterite and aragonite usually appear in very close proximity with growth lines crossing both crystalline structures. In the deformed shells, we found patches of 'normal' aragonite embedded in the vaterite areas. This implies that both polymorphs can be formed simultaneously by different parts of the mantle tissue responsible for hard part mineralisation (Melancon et al. 2005; Soldati et al. 2008). This observation probably also explains the co-occurrence of aragonite with the vaterite discovered in the XRD samples (Fig. 4b).

We have not been able to investigate the causes for the abnormal shell formation observed here and are able only to speculate on possible reasons. For molluscs, the appearance of vaterite is usually associated with unusual hard tissue formation (pearls, shell repair, initial stages of shell formation; Wilbur and Watabe 1963; Saleuddin and Wilbur 1969; Meenakshi et al. 1974; Hasse et al. 2000; Ma and Lee 2006). Also for fish, the occurrence of vaterite otoliths appears to be related to stress (Melancon et al. 2005). Stress in the form of anthropogenic chemical pollution has been implicated in altered shell forms in some bivalves (Sokolowski et al. 2002; Strayer 2008). Especially deformations as a thickening of the shell valves have been described for some species as a reaction to poisoning by the antifoulant paint ingredient tributyltin (TBT; Alzieu et al. 1982; Machado et al. 1989; Page et al. 1996; Coelho et al. 2006; Higuera-Ruiz and Elorza 2009). Chambering of the shell valves filled with a gelatinous mass is responsible for the thick ball-like shaped shells in oysters exposed to TBT (Alzieu et al. 1982). TBT levels at our study sites in the Norfolk Broads are relatively elevated in the sediments, especially in close proximity to marinas (Waite et al. 1989; Dowson et al. 1992; Hoare 2007). Already in 2003, Müller incidentally found Corbicula individuals with the same type of shell deformations as described by us in the River Yare between Surlingham and Langley Dyke when he collected Corbicula specimens for another survey. Similarly deformed clams were recognised nowhere else in the Norfolk Broads at this time. Müller (2003) suggested not only the elevated concentrations of especially mercury but also other heavy metals in the sediment (Bubb et al. 1991a, b, c; Birkett et al. 2002), as the cause for these deformations. In our case, however, the occurrence of similar deformations in fossil Corbicula shells rules out the possibility of solely anthropogenic influences, such as pollution with TBT or mercury, as a cause. Some bivalve species develop a thicker shell in response to exposure to predators, such as crabs (Leonard et al. 1999; Trussell and Smith 2000). However, these thickenings are different because they simply involve greater production of normal shell microstructures. Because the Corbicula deformations are irregular, not strengthening the whole valve and often cause the valves not to close, predator-induced defence

seems an unlikely explanation. Deformations occurring during shell repair of deep burrowing bivalves after attack by shore birds and abnormal shell growth around parasites have been reported by Lomovasky et al. (2005). Yet, neither of these two cases involved similar structures and a change in mineralogy as in the case reported for Corbicula. Vaterite vesicles have been proposed as a storage or excretion mechanism in molluscs (Meenakshi et al. 1974; Prince et al. 2006), but the large amount of excess shell produced by Corbicula and the possible detrimental effects also make this improbable.

The ultimate explanation for the occurrence of vaterite in some populations of Corbicula remains unresolved. It is possible that a number of stressors may be responsible, but more work is needed to better understand this unusual, but striking, phenomenon.

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