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Vaterite or aragonite observed in the prismatic layer of freshwater-cultured pearls from South China

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Abstract

A prismatic layer is present in both freshwater-cultured pearls and seawater-cultured pearls. The phase structure of the prismatic layer of freshwater-cultured pearls is investigated for the first time and novel findings are reported in this paper. X-ray diffraction (XRD), optical microscopy (OM) and micro-infrared (IR) spectroscopy were used to characterize the crystallized layers of high and low-quality freshwater-cultured pearls. Results show that there is no calcite in the prismatic layer of freshwater-cultured pearls, which is different from what was found for seawater-cultured pearls. We found that an aragonite phase was present in the prismatic layer of high-quality freshwater-cultured pearls and that a vaterite or aragonite phase was present in low-quality pearls. Based on this study an internal factor that influences the quality of freshwater-cultured pearls is discussed.

Keywords: Vaterite; Aragonite; Prismatic layer; Freshwater-cultured pearls

1. Introduction

Arajirou first reported in 1960 that the prismatic layer of seawater-cultured pearls is composed of calcite [1]. This theory has since been accepted widely around the world [1–9]. However, in 2007, Ma found that there were in fact three types of prisms in the prismatic layer of seawater-cultured pearls [10]. They are aragonite prisms, calcite prisms [1] and a combination of aragonite and calcite prisms. In this paper we investigated mineral phases of different quality freshwater-cultured pearls to determine if the freshwater-cultured pearls are the same as the seawater-cultured pearls.

2. Materials and methods

Two types of freshwater-cultured pearls were used. They were high quality high luster and low quality low luster pearls as determined by their general external appearance. The pearls used for this paper came from Zhejiang Province, South China and were rich in color (Fig. 1). Some pearls have good luster while some have no luster at all.

The samples were milled into a fine powder with agate for X-ray diffraction (XRD) (Gemerny Simens company D500, CuKα, 35 kV, 30 mA, and 2°/min).

Samples were produced as flakes for systematic observation by optical microscopy (OM) (Japan Nikon Company LV100POL/501) and infrared (IR) microscopy (American Nicolet Company Magna-IR 750). The pearls were cut into thin 0.02 mm sections and mounted on the glass slices with shell-lac.

3. Results and discussion

Observations of the cut samples revealed that freshwater-cultured pearls do not have a nucleus and seawater-cultured pearls do [10]. Distinct differences in the mineral and structural characteristics of high and low-quality freshwa-

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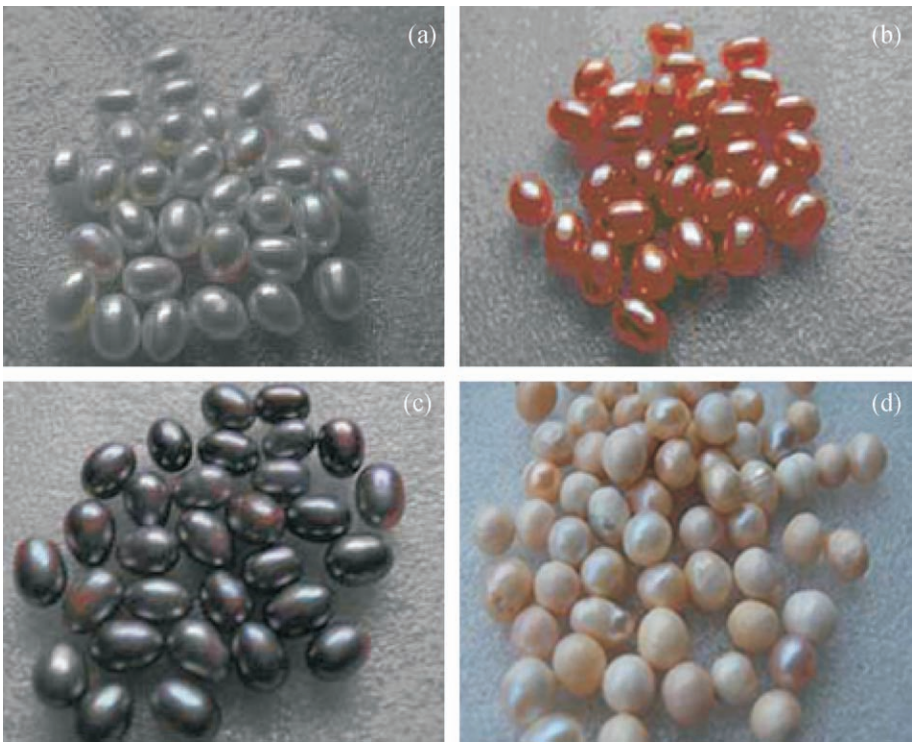

Fig. 1. Different quality freshwater-cultured pearls. High-quality freshwater-cultured pearls: (a) white; (b) pink; (c) purple; low-quality freshwater-cultured pearls: (d) lusterless pearls.

ter-cultured pearls are also found. XRD patterns for both types of freshwater-cultured pearls were obtained. High-quality freshwater-cultured pearls only contain aragonite with no calcite or vaterite present (Fig. 2(a–c)). Vaterite and aragonite are, however, present in low-quality freshwater-cultured pearls as seen in their XRD pattern (Fig. 2(d)).

Internal microcrystal biomineralization of high and low-quality freshwater-cultured pearls was observed by OM. Freshwater-cultured pearls with high luster have good structural uniformity. There is no or a very thin prismatic layer in this kind of pearl (Fig. 3). The thin prismatic layer shows parallel extinction and it is thus identified as aragonite. The absence of calcite and vaterite confirms the findings from the XRD analysis. Pearl sections appear colorless or extremely light yellow under the microscope. These sections have a compact structure composed of veined layers. Small mineral aggregations of about 0.3–0.5 μm can be distinguished under the optical microscope at 200 times magnification. It has a weak flash with high-grade white interference colors. In addition, a minor mineral shows parallel extinction at 400 times microscopic magnification. The sections show cross extinction under the optical microscope at 50 times magnification. Combined with the results from XRD, it is observed that aragonite is certainly present. Thin slices from low quality freshwater-cultured pearls without luster appear relatively dirty and yellowish-brown. It shows that plenty of organic material is mixed with the mineral in the prismatic layer. The layer structure is obvious from the center to the rim of lusterless freshwater-cultured pearls (Fig. 4). Based on distinctive shapes, a prominent remarkable flash, a high-grade white interference color and the absence of lumps in this mineral is identified as a third phase of calcium carbonate — vaterite rather than aragonite or calcite.

IR microscopy was used to analyze both kinds of freshwater-cultured pearls. Aragonite peaks are present from the center to the rim in high-quality freshwater-cultured pearls with peaks at 1485, 1082, 859, 712 and 699 cm^{-1} (Fig. 5(a)). IR from the thin prismatic layer in the high luster freshwater-cultured pearls shows that the prismatic layer is composed of aragonite. For the low-quality freshwater-cultured pearls without luster, vaterite peaks are present from the center to the rim with peaks at 1489, 1450, 1420, 1087, 1085, 876, 830, 762 and 743 cm^{-1} (Fig. 5(c)). Microregion IR spectra show that prismatic layers in the luster pearls are composed of aragonite and that vaterite or aragonite is present in the lusterless pearls. OM reveals that there is more organic material in low quality freshwater-cultured pearls than in high quality pearls. Based on the previous reports of calcium carbonate biomineralization [11,12], organic material seems to control the formation of calcium carbonate and stabilizes the vaterite in lusterless pearls.

4. Conclusions

No calcite was found in freshwater-cultured pearls. Aragonite is observed in the prismatic layer of high-quality freshwater-cultured pearls with high luster. Vaterite or aragonite is observed in the prismatic layer of lusterless freshwater-cul-

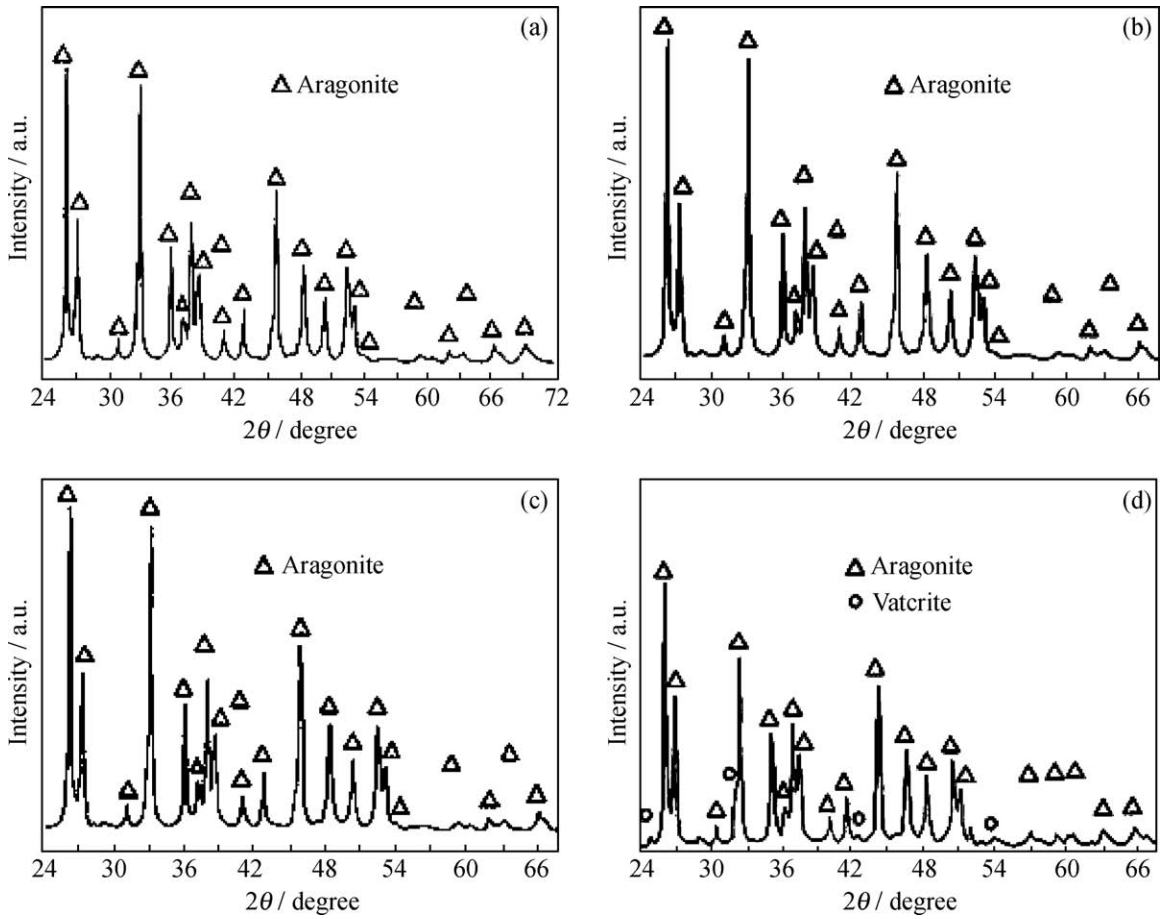

Fig. 2. XRD patterns of different quality freshwater-cultured pearls. High quality: (a); (b); (c); low quality: (d); (a) white; (b) pink; (c) purple; (d) lusterless.

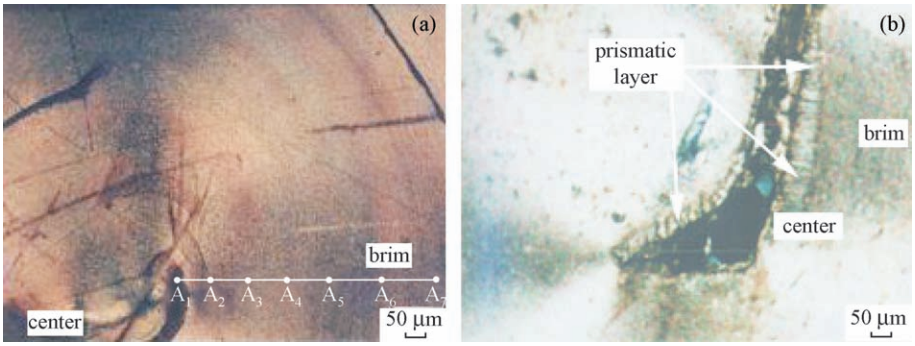

Fig. 3. Microtextures in the cross section of high-quality freshwater-cultured pearls without (a) or with a thin prismatic layer (b); all aragonite (a)(b).

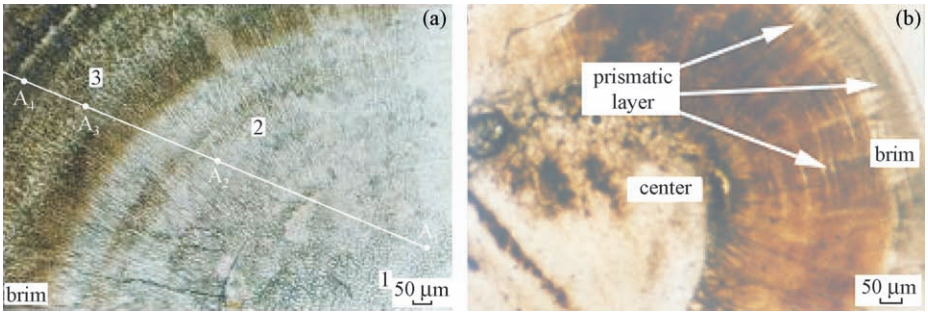

Fig. 4. Microtextures in the cross section of low-quality freshwater-cultured pearls with a thick prismatic layer. (a): 1. granular vaterite; 2. needle-shaped vaterite; 3. irregular vaterite mixed with organic materials; (b) all aragonite.

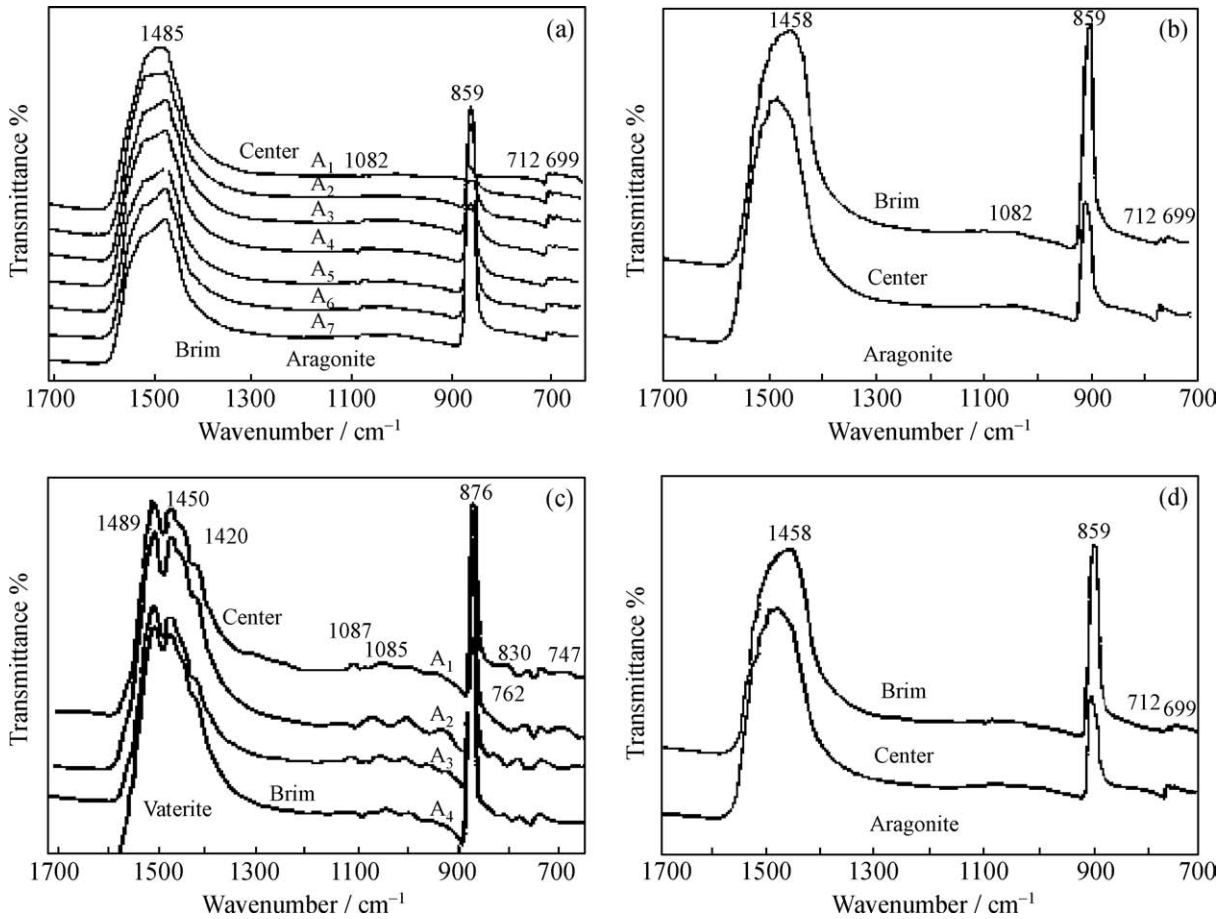

Fig. 5. The micro-IR of different quality freshwater-cultured pearls. (a) Aragonite presence from the center to the brim in high-quality freshwater-cultured pearls from Fig. 3(a); (b) aragonite presence from the center to the rim in high-quality freshwater-cultured pearls from Fig. 3(b); (c) vaterite presence from the center to the brim in low-quality freshwater-cultured pearls from Fig. 4(a); (d) aragonite presence from the center to the brim in low-quality freshwater-cultured pearls from Fig. 4(b).

tured pearls. Comparing mineral phases in the prismatic layer of different pearls we now have a new systematic understanding of the difference between seawater-cultured pearls [10] and freshwater-cultured pearls [this study]. No vaterite was observed in seawater-cultured pearls but aragonite and calcite are present. Freshwater-cultured pearls do not contain calcite and only vaterite or aragonite was found. OM observations clearly show that the thickness of the prismatic layer and the spatial distribution of the mineral phase in the prismatic layers are the principal factors that determine the quality of freshwater-cultured pearls.

Acknowledgements

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