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THE INFLUENCE OF THE INTERNAL STRUCTURE OF PEARLS ON LAUEGRAMS

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INTRODUCTION

Among other possibilities, two types of x-ray methods are used for the examination of pearls. They are direct radiography (the shadow method) and the Laue method (x-ray diffraction). Both methods are of restricted use if applied exclusively, since each of them gives specific information which may not be conclusive for certain types of pearl. Thus in each case of a pearl test one has to decide on which method to place the greater reliance when deciding upon whether a pearl is natural or cultured. This study deals with the factors which influence the patterns of lauegrams.

Doing authenticity tests for the trade, we often found that lauegrams resulted in which neither a clear pseudohexagonal pattern nor a two-fold symmetry pattern showed, which is what an unprejudiced observer would expect from the pictures shown in textbooks. Most of these pearls deviated more or less from the ideal shape of a sphere. It is the purpose of this study to investigate any correlation of pearl shape and direction of the primary beam in respect of the resulting laue pattern. Furthermore it is of interest to evaluate the effects produced by a relatively thick overgrowth on the bead of a cultured pearl. To understand the pseudohexagonal spot patterns, the questions of the presence and type of aragonite twins and the arrangement of aragonite tablets are investigated.

DIRECT RADIOGRAPHY

The direct radiography method utilizes the fact that x-rays are weakened to varying degrees by the differing forms of matter they penetrate. The extent of the weakening depends on the thickness, the density and the chemical composition of the object being investigated. When x-raying a pearl, a shadow image is produced behind it on a photographic film. This image indicates the conditions of thickness and density as an effect of this absorption. In pearls, the relatively darker areas deriving from the conchyolin-rich parts are considered valuable in respect of diagnosis. These

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zones enriched with organic matter have a lower x-ray density than the surrounding calcium carbonate, and are thus weakening the radiation to a lower degree. Such zones may be situated in the centre of the pearl or in the form of single or repeated arcs or circles approximately concentric to it. In most cases, direct radiographs of natural pearls show such features. In addition to this, a typical, discontinuous course of darkness from the centre to the rim may be observed. In cultured pearls with a bead, usually one dark ring near the periphery is seen, which represents the conchyolin-rich shell around the bead. In non-nucleated cultured pearls, besides the mostly irregular external shape, an irregular shaped cavity lined with conchyolin is resolved in the radiograph as a quite striking dark irregular area at or near the centre of the pearl.

In some cases it is unfortunately not possible to make visible such fine growth inhomogeneities. These pearls show us the limitations of direct radiography. References for the technique and interpretation of this method are Webster (1975), Brown (1979), Anderson (1980) and Farn (1980).

TECHNICAL DETAILS

The lauegrams needed for his investigation were produced by the author in the x-ray laboratory of the Institute of Mineralogy and Petrology of Basel University. Since there is no specialized Laue camera, a precession camera with a 0.7 mm diaphragm was used instead. The molybdenum tube was operated with a Philips generator (40 kV/20 mA). The radiation was used unfiltered, for a continuum is required. The pearls were placed directly on the diaphragm, leaving an interspace of 4.5-6 cm to the film (plastic wrapped dental film). Exposure time, according to the thickness of the pearl, ranged between 4 to 10 hours.

The photographs of pearl surfaces were made by means of scanning electron microscopy (SEM) with a Stereoscan mark IIA instrument (Cambridge). It was operated with an acceleration voltage of 20 kV. The samples were coated with an approximately 20 nm thick gold layer.

LAUEGRAMS (X-RAY DIFFRACTION)

The German physicist Max von Laue succeeded in 1912, with his colleagues, in proving the wave character of x-ray radiation and the lattice character of crystalline matter. With this knowledge,

W. H. Bragg and his son, W. L. Bragg,* started to investigate crystal structures. Since at latest 1924 the Laue method has been applied in pearl testing (Galibourg & Ryziger, 1927; B. W. Anderson, pers. com., 1982). The Laue method is used to show the intrinsic symmetry of a crystal. If a narrow beam travels through a crystal parallel to a symmetry axis, it will deviate from this primary direction. It is diffracted (i.e. it will follow all directions in which the conditions of Bragg's law, $n.\lambda = 2d.\sin\theta$, are fulfilled). In total these diffracted rays will form a spot pattern on the film behind the crystal. This spot pattern or lauegram exhibits the symmetry which the crystal possesses in the selected direction.

Natural pearls are more or less good ordered aggregates of microscopic crystals. Their regulation follows a concentric or radial structure respectively. This is also evident from cross sections (Alexander, 1977). The tiny tabular crystals consist of Aragonite ($CaCO_3$, orthorhombic), but in some cases, (after Alexander, 1977), Calcite ($CaCO_3$, trigonal) is also found involved as a pearl material. The dominant faces of aragonite tablets or platelets are always set tangentially to the surface of the sphere. Their main symmetry axes (*c*-axes) point towards the centre of the pearl. Therefore, from whichever direction the x-ray beam passes through the centre of a spherical pearl, it will meet the same conditions. It will follow the symmetry axes of thousands of crystallites. Because of the pseudohexagonal symmetry pattern, Webster (1975) supposed the crystals to be twinned repeatedly (cyclic twinning). For orthorhombic minerals in the untwinned state, the resulting spot pattern should exhibit at the most two-fold symmetry. Other orthorhombic minerals show a tendency to form cyclic twins (e.g. chrysoberyl, cerussite) and thereby obtain a higher state of symmetry.

Thus, if a spherical natural pearl is struck centrally by an x-ray beam, an apparently hexagonal pattern or a ring (halo) will appear on the film.

Cultured pearls with nacreous beads are well ordered aggregates of microscopic crystals, too. But the type of arrangement is different. The cultivated layer consists of a skin with considerably varying thickness from pearl to pearl, from less than 10% up to possibly more than 70% (Scarratt, pers. com.,

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*Respectively Presidents of the Gemmological Association from 1937 to 1942 (Sir William Bragg) and from 1954 to 1972 (Sir Lawrence Bragg).—Ed.

1982). This outer skin has the same built up structure as described for natural pearls. If cultured pearls have a core of mother-of-pearl, as they do in most cases, the aragonite platelets of this core are arranged in more or less even, parallel layers. Their main symmetry axes are all oriented approximately parallel to each other. The resulting lauegram is produced mainly by the set of crystals forming the core, since this inner bead normally represents the main part of the pearl. It now depends upon the angle at which the x-ray beam hits the layered structure of the bead. Oriented lauegrams of a cultured pearl with a thin skin illustrate this directional dependence (Figures 1a-d). If the beam direction coincides with the main symmetry axes (*c*-axes), i.e. is perpendicular to the layers of tablets, the well known six spot pattern arises. In all other directions patterns with a lower symmetry appear, since the crystallites are struck obliquely or perpendicular to their *c*-axes. Such a pattern shows at most two-fold symmetry and has been used to prove the presence of a nucleated cultured pearl (Webster, 1975; Anderson, 1980), (Figures 1b-d, 17).

INVESTIGATIONS BY SCANNING ELECTRON MICROSCOPY (SEM)

With a 10× lens lines are already visible on the surface of pearls which resemble contour lines. They bound relatively extended aragonite tablets or scales which overlie each other in a terrace or tile-like manner. To obtain more information on these structures, we produced photographs by means of a SEM. The advantage of this instrument lies in the high degree of sharpness and the better resolution compared with the conventional light microscope, even at low magnification. Figure 2 shows the structure in cross section of a broken piece of the cultivated layer of a cultured pearl. In this strictly speaking authentic part the aragonite tablets follow the curved surface of the sphere (see also Figure 5). The surface of this cultivated layer is illustrated in Figure 4. The tile-like and displaced aragonite tablets are clearly seen. Less clearly visible is a polygonal honeycomb-like pattern within these platelets. In Figure 3 a cross section of the spherical bead of a nucleated pearl is shown. Most beads are worked out of mother-of-pearl from the shell of an American river mussel. The beads are implanted into the mantle tissue of a pearl oyster to induce pearl

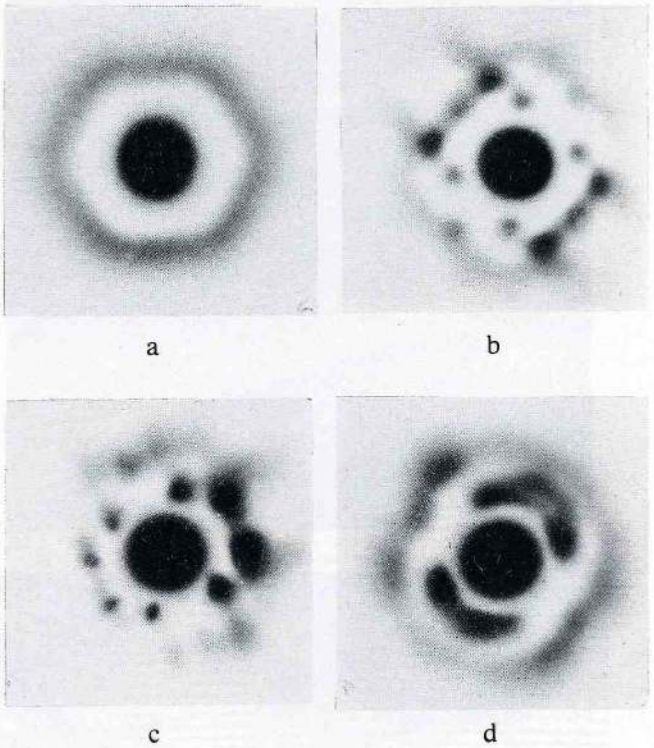


FIG. 1. Lauegram of a cultured pearl with bead, round, Ø 7 mm, with a thin overgrowth.
a: perpendicular to the aragonite layers of the core.
b: parallel to the aragonite layers of the core and perpendicular to the direction of a.
c: perpendicular to the directions in a and b.
d: oblique to the three preceding directions.

Scanning Electron Microscopic pictures of structures in pearls.

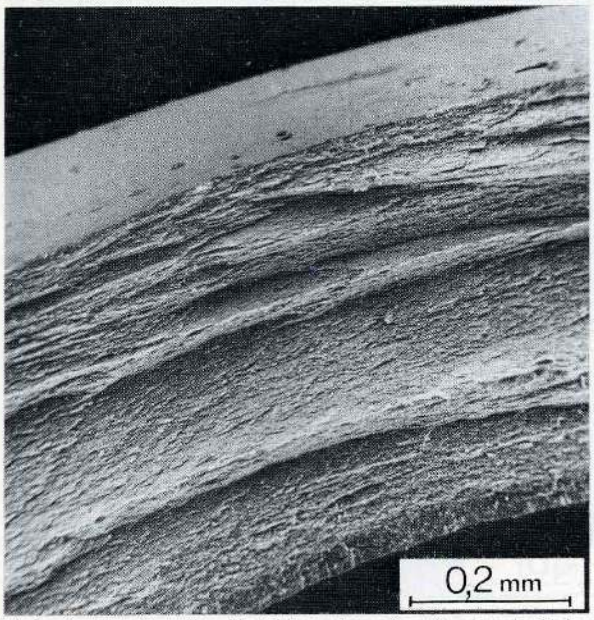


FIG. 2. Broken surface of a cultivated layer of a marine cultured pearl, with bow-structures. (SEM photograph)

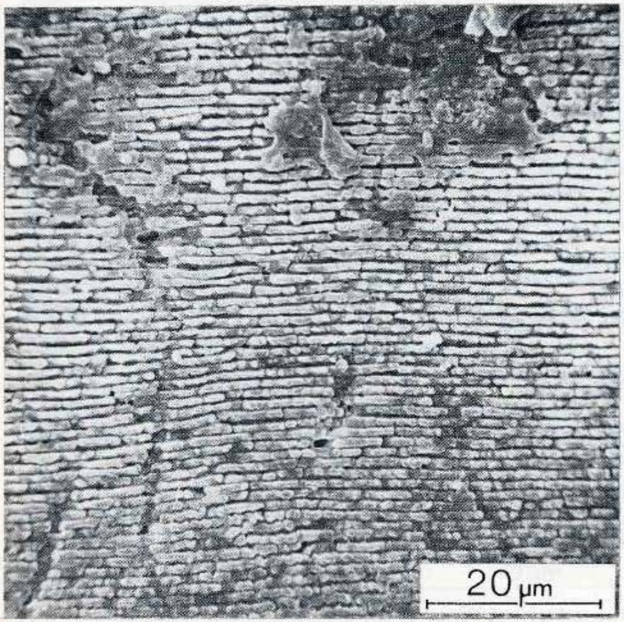


FIG. 3. Cross section through an etched bead of a cultured pearl, with brick-wall-like arrangement of the aragonite platelets. (SEM photograph)

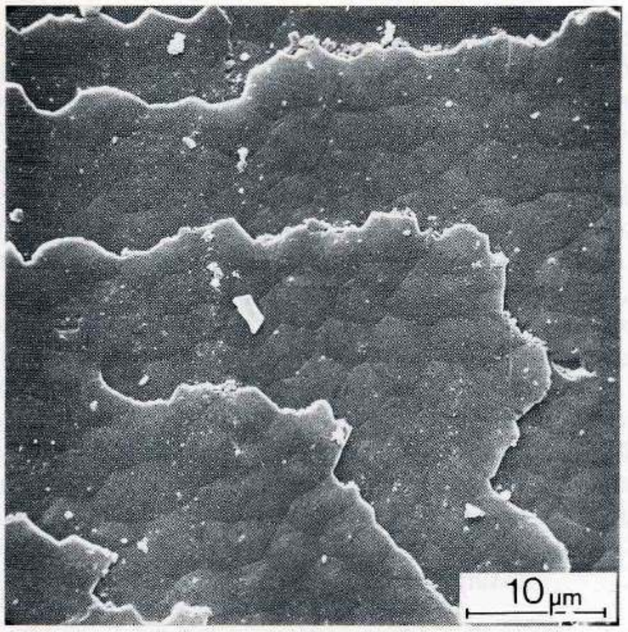


FIG. 4. Terrace or tile-like arrangement of aragonite platelets at the surface of a pearl. Honeycomb structures are visible. (SEM photograph)

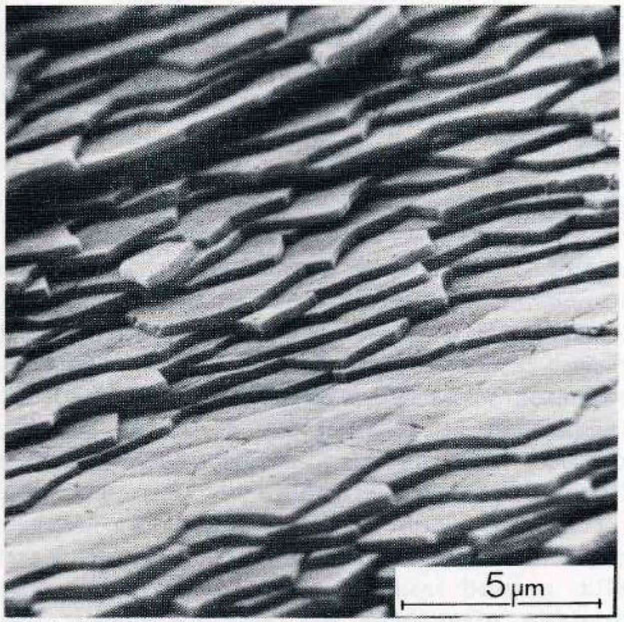


FIG. 5. Section out of Figure 2, with stacked aragonite platelets which show a polygonal split-up. (SEM photograph)

growth, i.e. to be overgrown by a pearly substance. These cores of mother-of-pearl have an even, layered structure, in contrast to the natural overgrowth which has a concentric build up. Figure 3 shows clearly the brick-wall-like arrangement of the plates which do not follow any curves of the pearl surface.

The honeycomb structure on the individual tiles of pearls deserves special attention (Figure 4). In search of twin structures which might prove the expected cyclic twinning, the surface was etched with dilute formic acid before inspection with the SEM, but no boundary lines between any twin individuals became visible, as expected according to the results of Mutvei (1977). He investigated different shells of moluscs, which showed after treatment with acid a strange type of regular intergrowth of aragonite. In Figure 6 different possibilities for twin formation are presented (Ramdohr & Strunz, 1967; Mutvei, 1977). The individual plates of the pearls are composed of a mosaic of polygons (honeycombs). In some places they are nearly regular hexagons; in other places, which are less ordered, distorted squares or pentagons are recognized.

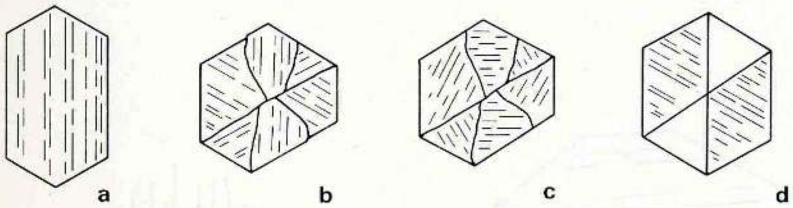


FIG. 6. Twin formations of aragonite. a: untwinned crystal. b&c: penetration-twins and repetition-twins respectively. d: twins according to Mutvei (1977). The *c*-axes of all individuals are perpendicular to the paper. The marked areas correspond to identically oriented individuals.

THE ARRANGEMENT OF ARAGONITE AGGREGATES IN PEARLS

To investigate the mutual crystallographic orientation of the polygons in the plates, the boundary angles were measured. The assumption that three preferred orientations existed, each being rotated 120° to the next, could not be confirmed for the time being. The verification of such a rule failed at the impossibility to orientate the individual polygons or domains with respect to the others. Such a statistical order within a plate would yield the effects of juxtaposition twinning and triplet-forming (Figure 7). The triplet state is also reached if, instead of an ordered arrangement embracing an entire plate, an arrangement between different 'floors' or in stacking is present. The 'honeycombs' which overlie each other and belong to different plates, i.e. different levels, may be rotated 120° from one to another (or a whole number of times of 120°). This arrangement would yield the effects of twinning in superimposition and triplet-forming (Figure 8). Both the first model of juxtaposition-triplets as well as the model of superimposition give an explanation for the pseudohexagonal Laue symmetry pattern. But it is not clear if, in the strict mineralogical sense, such formations are allowed to be named triplets, since the individual plates are separated from each other by organic membranes. They are thus not intergrown directly.

A pearl aggregate of aragonite plates possesses a maximum of regulation, if both principles of ordering are fulfilled. It is interesting to note that in our SEM investigations no prismatic layers became visible. Former authors (Smith, 1972; Eppler, 1973; Hurlbut & Switzer, 1979) may have interpreted stacked plates as prisms.

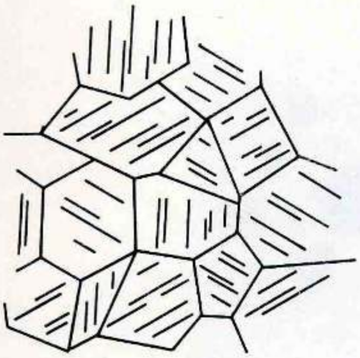


FIG. 7. A statistically ordered planar triplet aggregate, regulated after three directions (Triplet in juxtaposition).

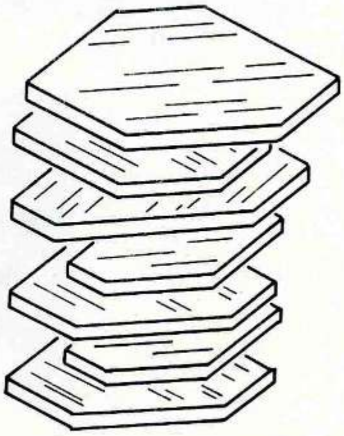


FIG. 8. A statistically ordered vertical triplet aggregate, regulated after three directions (Triplet in superimposition).

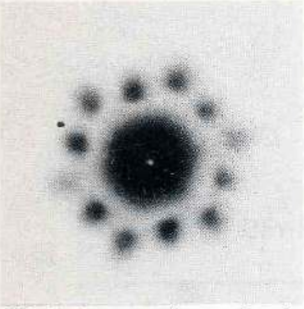


FIG. 9. Lauegram of a natural pearl, round, Ø 10 mm.

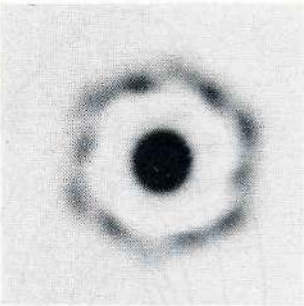
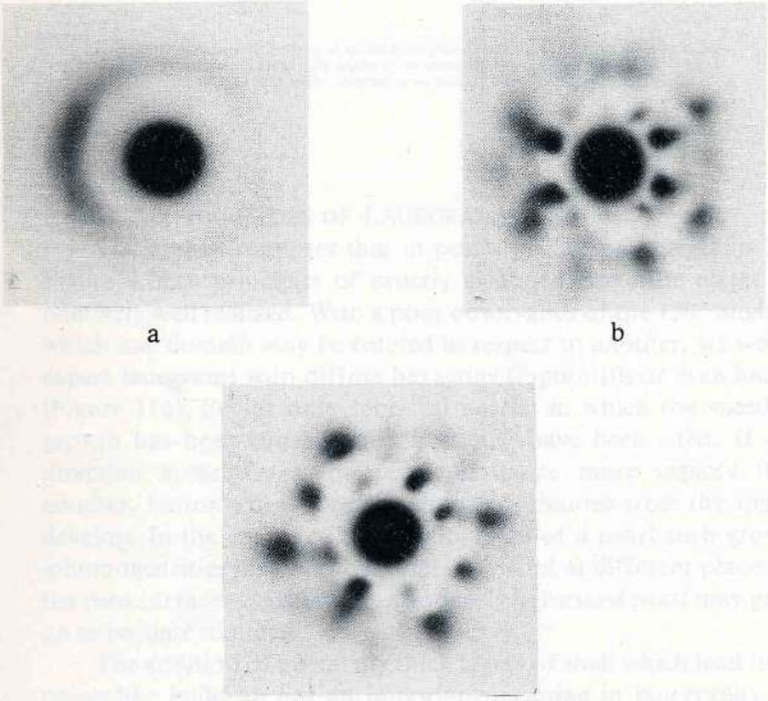


FIG. 10. Lauegram of a natural pearl, drop shape, 21 × 11 mm, taken through the short axis.



a b

c

FIG. 11. Lauediagrams of a natural pearl, bouton shape, 8 × 9 mm.
a: perpendicular to the flat region.
b: through the thickest place, perpendicular to a.
c: 2 mm eccentric, parallel to b.

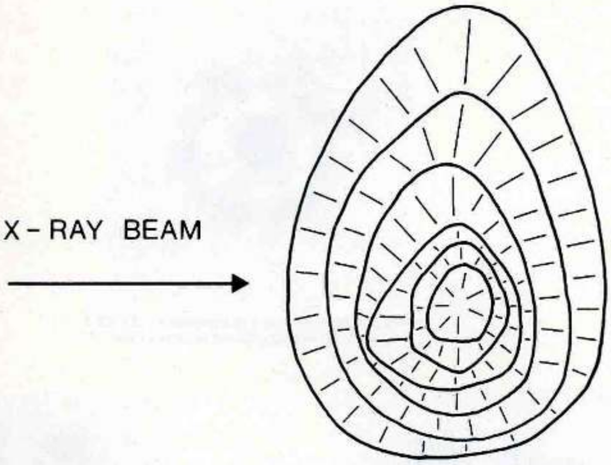


FIG. 12. Schematic built-up of an unround pearl. The small lines indicate the directions of the *c*-axes, which are at right angles to the platelets. The x-ray beam hits the crystallites under various angles, depending on how the pearl is situated/placed.

PRACTICAL EXAMPLES OF LAUEGRAMS

The author supposes that in pearls producing lauegrams like Figure 9 both principles of orderly arranged aragonite plates are relatively well realized. With a poor observance of the 120° angle to which one domain may be rotated in respect to another, we would expect lauegrams with diffuse hexagons (Figure 10) or even haloes (Figure 11a). So far only spherical pearls, in which the speed of growth has been equal in all directions, have been cited. If one direction accumulates the pearl substance more rapidly than another, button-, pear- or drop-shaped deviations from the sphere develop. In the course of the development of a pearl such growth inhomogeneities may occur several times and at different places on the then surface. Occasionally a formerly deformed pearl may grow on to become rounded.

The addition of unequally thick layers of shell which lead to an onion-like build-up has an important meaning in lauegraphy. In this way formations originate, which offer differing circumstances to a fixed x-ray beam (Figure 12). Frequently the beam will meet many crystals obliquely to their main symmetry axes. It will pass along a direction of two-fold symmetry. The resulting lauegrams

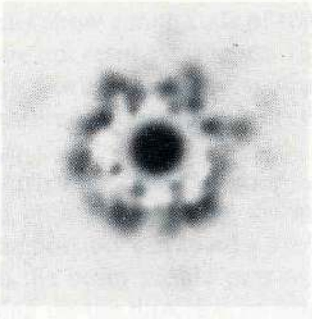


FIG. 13. Lauegram of a natural pearl, drop shape, 19 × 12 mm, in the direction of the short axis.

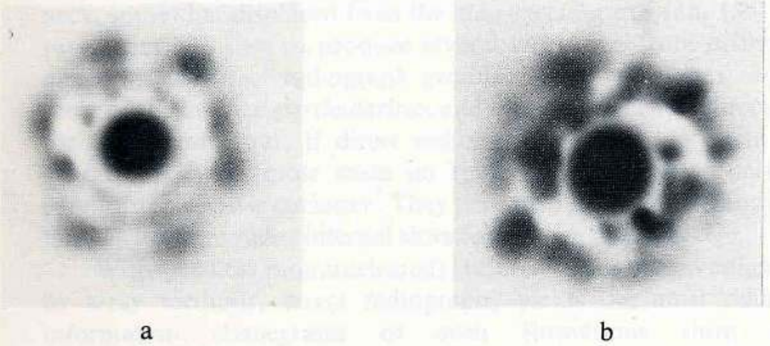


FIG. 14. Lauegram of a natural pearl, pear shape, 12 × 9 mm. a: through the short axis. b: obliquely, on the thin side.

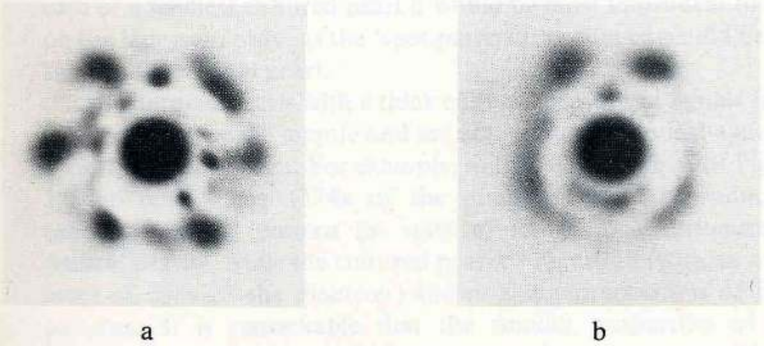


FIG. 15. Lauegram of a Natural pearl, drop shape, 20 × 11 mm. a: through the short axis. b: 2 mm above the short axis.

from such examples show a multitude of spots among which the six 'real' refections are not resolved (Figures 13, 14b). Sometimes even mixed pictures arise, where the four spot pattern which is typical for nucleated cultured pearls may get through quite strongly (Figures 11b, 15b).

The most intriguing pictures arise from button- or drop-shaped pearls. In both shapes, from the outside it is not clear in which position the possibly displaced nucleus is located, and for a decisive lauegram the beam should pass through the centre of the nucleus. Depending on the direction of the primary beam, mostly very complex lauegrams are produced (Figure 14). A directly misleading picture occurs if the beam strikes a drop pearl at the neck, somewhat displaced from the long axis (Figures 14b, 15a). In such cases it is best to produce several lauegrams from differing directions. A direct radiograph produced in advance may reveal some of the internal particularities and may recommend a direction for a lauegram, but, if direct radiography is informative in its characteristics, in most cases no further lauegrams are needed except for scientific curiosity. They then help us to understand the influence of a complex internal situation in such pearls.

When seedless (non-nucleated) cultured pearls are investigated by x-ray methods, direct radiography yields the most reliable information. Lauegrams of such formations show the pseudohexagonal symmetry of natural pearls, or a halo. These lauegrams are somewhat diffuse and characterized by fine radiating lines (Figures 16a, 16b) which are not yet explained. Thus in the case of a seedless cultured pearl it would be most imprudent to rely on the lauegram only, as the 'spot patterns' produced would be the same as for natural pearl.

In cultured pearls with a thick cultivated layer the signals from the kernel pierce the mantle and are able to put the four diagnostic spots on the lauegram. For example, in the cultured pearl of Figure 17 the outer layer (37% of the diameter) cannot produce a pseudohexagonal pattern (in spite of its identical structure to natural pearls), while the cultured pearl of Figure 18 (with an outer layer of 59% of the diameter) shows a superimposition of both patterns. It is remarkable that the smaller proportion of the mother-of-pearl bead in this latter pearl gives a more prominent pattern than the very thick overgrowth. It is thus reassuring that the diagnostically valuable information is able to penetrate the

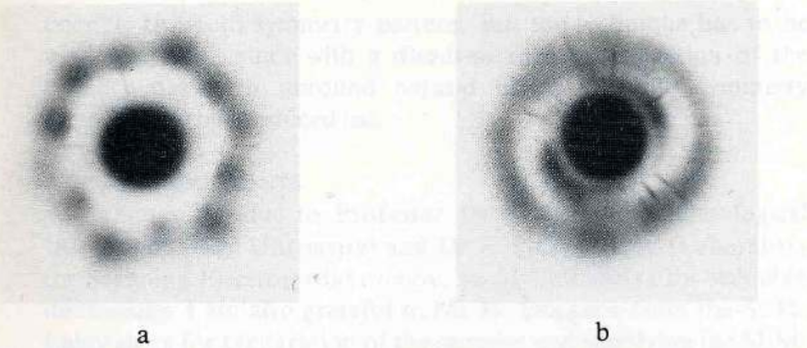


FIG. 16. Lauegram of a non-nucleated cultured pearl, baroque shape, 14 × 6 × 4 mm, a and b: two directions, at right angles to each other.

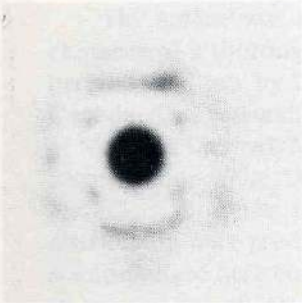


FIG. 17. Lauegram of a cultured pearl with nacreous bead, round, ⌀ 13 mm, thickness of the cultured layer 2 × 2.4 mm.

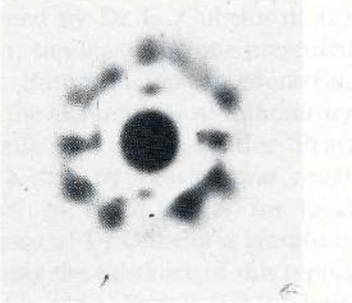


FIG. 18. Lauegram of a cultured pearl with nacreous bead, oval, 16 × 13 mm, thickness of the cultured layer 2 × 3.9 mm.

cultivation layers even if the coatings are very thick. It is therefore important to observe the central part of the lauegram (Figures 17, 18), looking for a strong four spot pattern.

CONCLUSIONS

Lauegraphy therefore yields indications for answering the question whether a pearl contains a mother-of-pearl bead or not. Lauegraphy is not the appropriate means to prove the authenticity of a pearl in general (e.g., seedless cultured pearls). Normally two lauegrams taken at 90° to each other are sufficient to demonstrate a possible two-fold symmetry pattern. But the technique has to be used with skill, since with a disadvantageous conduction of the primary beam on unround natural pearls two-fold symmetry patterns may be produced too.

ACKNOWLEDGEMENTS

Thanks are due to Professor Dr S. Graeser (Mineralogical Institute of Basel University) and Dr R. Guggenheim (Laboratory for Scanning Electron Microscopy, Basel University) for valuable discussions. I am also grateful to Mr M. Düggelin from the SEM-Laboratory for preparation of the samples and supplying the SEM-pictures. Furthermore my thanks go to Mr K. Scarratt (The Gem Testing Laboratory of the London Chamber of Commerce and Industry) for his important professional advice and critical reading of the manuscript.

The author was recently informed by Dr E. Gübelin of the existence of a thorough investigation, similar to the one presented here, carried out by Dr William H. Barnes in 1944 in Montreal, Canada. This research was done for the Gemmological Laboratory of Mappins Limited, Montreal, Canada. The report, entitled 'Pearl Identification: The Diffraction of X-rays by Pearls', was never published; however a small number of typed copies for local distribution were produced. The interest of Dr Gübelin is gratefully acknowledged here both for mentioning the existence of this report to me and for giving me access to his copy. Barnes treated both natural pearls and mother-of-pearl as being similar to fibrous aggregates. His results with respect to identification however are more or less identical to the results presented in this paper.

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