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The structure and optical behaviour of iridescent agate

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1. Introduction

It is well known that agate exhibits a banded structure. One explanation of the banding which has been put forward is that the agate is the result of the deposition of silica in an intermittent manner from liquids containing the material in solution. The assumed manner of formation is, however, clearly hypothetical and it leaves the question of the physical nature of the banding resulting therefrom unanswered. A different explanation that has been suggested and received with some favour is the so-called silica-gel theory. This regards the banded structure of agate as analogous in its nature to the periodic precipitates formed in gelatinous substances in certain circumstances. We may remark, however, that the characteristic structure of agate is observed even in the absence of any material other than silica in its composition. Further, it is to be noted that the microscope shows agate to be a coarsely crystalline material and not a colloid. The explanation of its banded structure as a Liesegang phenomenon in a colloidal gel appears in the circumstances to be rather far-fetched.

The question of the nature of the banded structure of agate presents itself in a particularly interesting form when we consider the case of the specimens exhibiting iridescence. It has long been known that the stratifications in agate may be so close and so regularly spaced as to enable a polished plate of the material to function as a diffraction grating when traversed by a beam of light. It is natural to suppose that a structure exhibiting such a high degree of regularity with strata following each other some 10,000 times in a centimetre is a consequence of some special feature in the aggregation of the crystallites of quartz of which agate is composed. The fact that we had at our disposal two examples of iridescent agate encouraged us to undertake a careful study of this question by optical and X-ray methods. The investigation has revealed several interesting facts, and besides elucidating the particular problem under consideration has also thrown fresh light on the structure and optical behaviour of non-iridescent agate and chalcedony.

2. Some general observations

Enlarged photographs of our two specimens are reproduced as figures 1 and 2 respectively in plate I. They exhibit a banded structure over the entire area of the plates except in a region adjacent to the irregular upper edge of specimen I where it is definitely absent, while in the case of specimen II, the banding gradually fades off and becomes inconspicuous as we approach the triangular tip of the plate at its lower end. In both cases the banding meets the surface in a series of curved lines running parallel to each other and exhibiting several sharply defined changes of direction. The iridescent area in each case is a strip about a centimetre in width running parallel to the banding and traversing the entire specimen from one side to the other. In figure 2 it appears as a series of conspicuous bands running across the middle of the specimen, while in figure 1 the strip appears perfectly dark in its first segment on the right, faintly banded in the middle segment, and quite bright in the third segment towards the left.

Figures 3 and 4 in plate II are photographs of a small section of the iridescent area on specimen II greatly enlarged. The two photographs were recorded respectively by transmitted and by diffracted light, and it will be recognised at once that they are complementary, the areas appearing bright in one picture, appearing dark in the other and *vice versa*. The photographs exhibit other features of interest to which we shall revert later. It may be remarked here that the complementarity which they exhibit is a feature which is noticeable with both of our specimens over the entire area exhibiting a banded structure, those regions which appear bright by diffracted light appearing dark by transmitted light, and *vice versa*. Viewed obliquely to the direction of the illuminating beam, both specimens in the non-iridescent areas show a bluish-white opalescence.

3. Polarisation of the transmitted light

Our specimens I and II were respectively 3 and 2 millimetres thick. They are both noticeably transparent, but much more so in the case of the thinner specimen. In other words, a light-source such as an open window or the dome of an electric lamp could be seen through the agate with full definition in all its details, though overlaid by a field of diffuse radiation. As is to be expected, the areas exhibiting iridescence are much less transparent than the rest and they also impart a distinctly reddish tint to the light passing through them. *Per contra*, the non-banded areas near the upper edge of specimen I are distinctly more transparent than its banded areas, the yellowish-red tint of the transmitted light being however very conspicuous.

It is noteworthy that the intensity and colour of the light transmitted by our specimens are largely influenced by varying the inclination of the specimen with respect to the rays of light traversing it; the effect is very conspicuous when the specimen is so tilted that the plane of incidence remains normal to the planes of banding of the material. The maximum transmission is observed when the light rays are parallel to the planes of banding; the light transmitted diminishes rapidly in intensity and at the same time becomes a deeper red in colour when the light rays make increasingly larger angles with the planes of banding, until finally it is lost altogether in a notably strenghthened background of diffuse light. A tilt of the specimen in the same plane as the banding layers produces an effect of the same nature which however is much less conspicuous.

A remarkable observation made by us is that *the light transmitted by our specimens is completely polarised when observed through the areas exhibiting a banded structure.* This is the case even when the banding is inconspicuous. Further, a tilt of the specimen with respect to the light rays which notably alters the intensity and colour of the transmitted light does not affect the totality of its polarisation. The direction of electric vibration in the transmitted light lies in a plane normal to the planes of banding in the specimen. When the area of observation is moved to another adjacent position in which the planes of banding have taken a sudden turn, the direction of vibration in the transmitted light takes a similar sudden turn. Likewise, as we move along the curved areas which represent the banding planes, the direction of vibration in the transmitted light swings round in the same fashion. It should finally be remarked that for those areas of our specimen I where no banding is visible and which allow a transmitted light of an yellowish-red colour, a marked though incomplete polarisation of the same is observable, the direction of vibration being approximately the same as in the neighbouring banded areas.

4. The diffusion of light accompanying transmission

When a small intense source of light is viewed through the banded non-iridescent areas of our specimens, we observe a phenomenon which is illustrated in figure 5 in plate III. On either side of the light source as seen through the specimen we notice a fairly intense but a narrow bundle of diffused light stretching out in a direction parallel to the planes of banding. Further away, this spreads out both longitudinally and transversely into a diffuse brush of light of rapidly diminishing intensity.

As mentioned above, the image of the light source seen through the banded areas of our specimens is completely polarised. This effect is demonstrated by figure 6 in plate III which represents the light source as viewed through a non-iridescent area of the agate coupled with a double-image prism of quartz. Of the two images produced by this combination seen side by side in the figure, the one on the right hand has the electric vibration normal to the banding planes while for the one on the left, the vibration direction is parallel to these planes. It will be noticed that the image of the source appears only in the former and is totally absent in the latter. The vertical brush of light passing through the image is however seen in both images but is less intense in the latter, indicating that the brush is partially polarised in the same sense as the transmitted light. The farther away we move from the image of the light source in either direction, the less conspicuous becomes the difference in intensity between the two images. Owing to their overlap in the photograph, it is not possible to make a definite statement whether or not there is a reversal of the state of polarisation in the more distant parts of the brush.

5. The diffraction spectra

From figures 1 and 2 in plate I it is evident that the iridescent strips in our specimens do not form a single continuous diffraction grating over their entire width but consist of several distinct gratings with intervening gaps. The photographs reproduced as figures 3 and 4 in plate II show this very clearly; the strip contains six different gratings separated by intervals which are not iridescent and hence appear bright by transmitted light and dark by diffracted light. That the six gratings in the agate are dissimilar is apparent from the fact that the colours which they exhibit when it is viewed obliquely are not identical. That each individual grating is nearly perfect however is proved by the observation that when a source of monochromatic light is viewed through it, a series of well-defined and regularly spaced images formed by the diffracted light is seen; with a mercury arc lamp as source the two sets of images formed respectively by the green and yellow radiations are seen well separated. No images formed by the λ4358 Å radiations are visible owing to the strong diffusion and lack of transparency of the agate in that region of the spectrum.

The spectra formed by the agate are not simply a series of images of the source. Actually, each spectrum including that of zero order is a diffusion pattern exhibiting the features already described and illustrated in figure 5 of plate III with their specific polarisation characters. The geometric images of the source appearing in the spectra are completely polarised with their vibration directions perpendicular to the lines of the diffraction grating, while the vertical bundle of diffused light accompanying each image exhibits a partial polarisation in the same sense. The diffuse brush appearing further out however exhibits a partial polarisation in the reverse sense, having its vibrations parallel to the lines of grating. These features are evident to inspection in figure 7 of plate III which was recorded with a mercury arc as source and a double-image prism of quartz superposed on the agate to exhibit the two components of polarised light in each spectrum separately.

It may be remarked that the diffraction phenomena described above are notably influenced by tilting the grating with respect to the incident light rays in one plane or the other, as could have been anticipated from the observations of the same nature already reported for the non-iridescent areas. We may also make a brief reference to the diffraction phenomena which are observed when a light source is viewed through certain non-iridescent but conspicuously banded areas of the agate. They are of a much less striking character than those exhibited by the iridescent areas and will not here be described in detail.

6. Significance of the results

The optical phenomena described above enable us to derive the following conclusions regarding the structure of the agate in the areas exhibiting the diffraction spectra:

I. The crystallites of quartz composing the agate arrange themselves in fibres along a direction normal to the planes of banding.
II. The principal axis of the quartz in the individual crystallites lies in the planes of banding.
III. Each fibre exhibits along its length a periodicity in the orientation of the principal axis of the quartz, such periodicity being the same for all the fibres.

The first proposition stated above follows directly from the nature of the diffusion patterns reproduced in plate III.

The second proposition finds its justification in the observed fact that the light regularly transmitted by the banded regions is completely polarised with its vibrations normal to the planes of banding. Had the optic axis of the quartz in the crystallites been orientated *at random*, the birefringence of the quartz would have resulted in the agate not transmitting any part of the incident light but merely diffusing it. On the other hand, had the optic axes all been *normal to the planes of banding*, the light regularly transmitted would have exhibited both components of polarisation. If, however, as indicated, the optic axes of all the crystallites lie *in the planes of banding*, the effective refractive index for a vibration normal to the planes of banding would be the same for all of them, while the index for a vibration in a transverse direction would vary from crystallite to crystallite. Hence the former component would be regularly transmitted, while the latter would be diffused and totally excluded from the transmitted light, in agreement with what is actually observed.

The third conclusion stated above follows inevitably if an aggregate of individual fibres is to function as a diffraction grating exhibiting the optical effects illustrated in figure 7 of plate III. In the circumstances of the case, the only type of periodicity in optical properties which could be admitted is that the optic axis lies in different directions along the length of the fibre, repeating themselves at corresponding points in the diffraction grating.

7. The X-ray diffraction patterns

As both of our specimens had sharply defined edges intersected by the banded structure, it was found easy to obtain X-ray diffraction patterns of the agate in selected regions. A narrow pencil of X-rays was allowed to graze the edge at the chosen region and the diffraction pattern was recorded with a flat-film camera. Figures 8, 9 and 10 in plate IV reproduce the patterns obtained in this manner using our specimen II and unfiltered X-radiation from a molybdenum target. Figure 8 is the record for the region exhibiting strong iridescence, figure 9 for a region further down which was non-iridescent but exhibited visible banding and figure 10 at the triangular tip where no banding was visible at all. We have obtained very similar records with our other specimen, but these have not been reproduced. The striking differences observed in the X-ray patterns of different regions in the same specimen are a clear demonstration that the structure of agate is a consequence of the grouping of the crystallites in specific orientations along the planes of banding. The X-ray pattern of the iridescent area reproduced as figure 8 in plate IV is readily identifiable as due to an aggregate of crystallites having one of the crystallographic *a*-axes as a common direction while the principal or *c*-axis assumes all possible orientations. This result is in full accord with the conclusions derived from the optical studies set forth earlier in the paper. The patterns reproduced in figures 9 and 10 show a less well-defined state of orientation of the crystallites. Indeed, in the latter, there is hardly any specificity of orientation indicated. This is not surprising since the banded structure of the agate is invisible near its extremity.

8. Some further observations

In the enlarged photographs of the iridescent agate (specimen II) reproduced in plate II, it is possible to recognize a good deal of visible structure in the material. Of particular interest are the curious wavy patterns seen in some of the strips, both in transmitted and by diffracted light. Similar patterns are seen over the entire iridescent area of our specimen I by merely holding it up against a window and viewing it through a magnifier of moderate power. These patterns are best examined by placing the agate on the stage of a low-power binocular microscope and viewing it either by direct or by oblique illumination from below the stage. Very interesting effects are observed if between the agate and the objectives of the microscope a polaroid sheet is interposed and turned round in its own plane. *The wavy patterns are vividly seen when the polaroid has its vibration direction parallel to the planes of banding of the agate. But they disappear completely when the polaroid is set with its vibration direction perpendicular to the planes of banding.*

The significance of the results stated above becomes evident when one recognises the patterns as being of the same nature as those seen when two similar diffraction gratings which are not perfectly in register are held together and viewed against a source of light. In the present case, we are dealing with a single grating which extends through a considerable depth of the material. Hence, unless the structure is of extraordinary perfection, superposition patterns of the nature observed would necessarily arise. In the light of these remarks, the disappearance of the patterns when the light vector is normal to the planes of banding is highly significant. Such disappearance is to be expected if the grating has its origin in a periodicity of the orientation of the principal axis of the quartz along the length of each fibre. For, such periodicity would influence the retardation of light waves having their vector parallel to the planes of banding, but would leave unaffected the propagation of light having its vector normal to those planes.

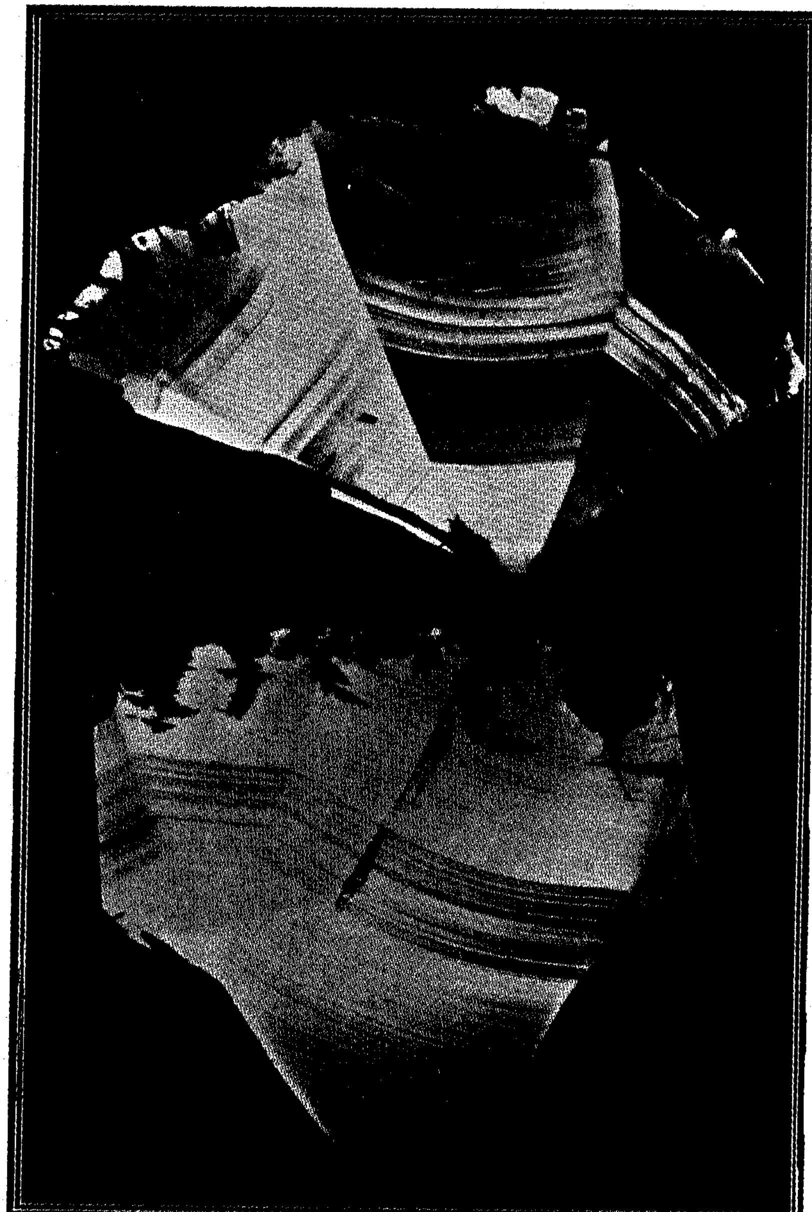
9. Concluding remarks

The ideas regarding the structure of iridescent agate set forth in section 6 are thus independently supported by the X-ray patterns and by the optical evidence. It remains now to find a reason why the principal axis of quartz exhibits a periodicity in its setting along the length of the fibres in the iridescent regions. We wish here tentatively to put forward a suggestion regarding this matter. It is known that quartz exhibits a type of twinning in which the principal axis in the two components of the twin are nearly at right angles to each other—more exactly make an angle of 84° 33′ with each other. It seems to us that the fibres of quartz in iridescent agate may be described as polysynthetic twins in which the alternate elements are related to each other presumably in the same manner as in the twins of the kind referred to.

10. Summary

A detailed study has been made by optical and X-ray methods of two plates of banded agate which display iridescence over part of their area. The light transmitted by the banded areas is found to be completely polarised with the vector normal to the planes of banding. On the other hand, the wavy superposition patterns exhibited by the iridescent areas disappear for the same vibration direction. From these facts and the observed optical characters of the diffusion and diffraction phenomena it is deduced that the crystallites of quartz form fibres elongated in the direction of a crystallographic *a*-axis, while their principal or *c*-axes lie in the planes of banding but are orientated in a periodic

manner in these planes so as to build up a structure which functions as a diffraction grating. The X-ray results support these findings. More generally also, they indicate that the banding of agate is a consequence of the presence in it of groups of crystallites of quartz having common specific orientations.


(1)
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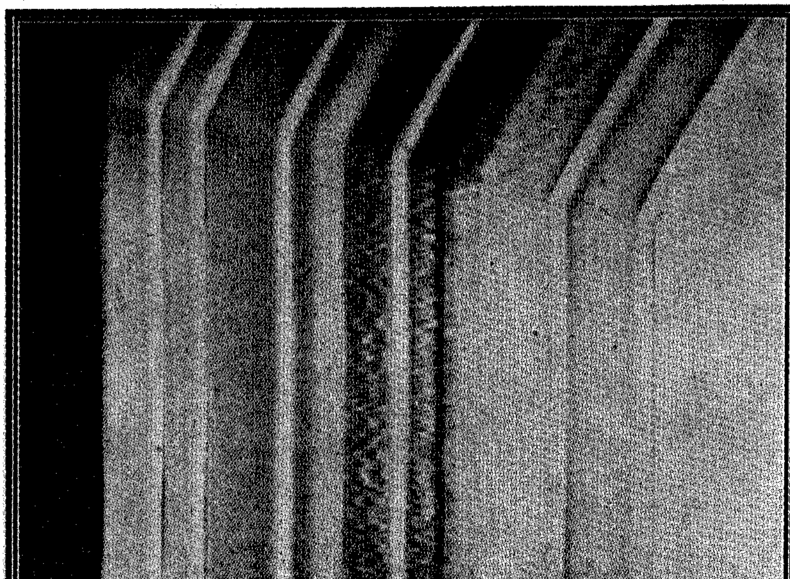
Figures 1 and 2

Plate I



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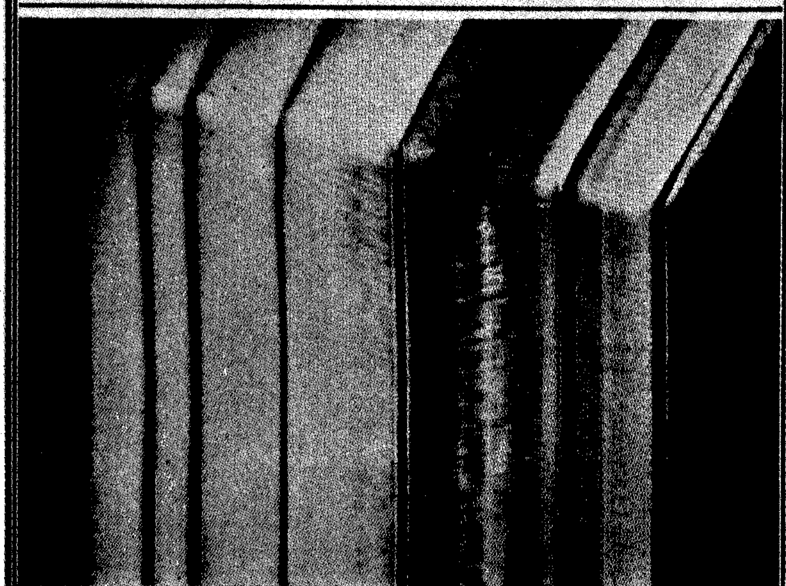

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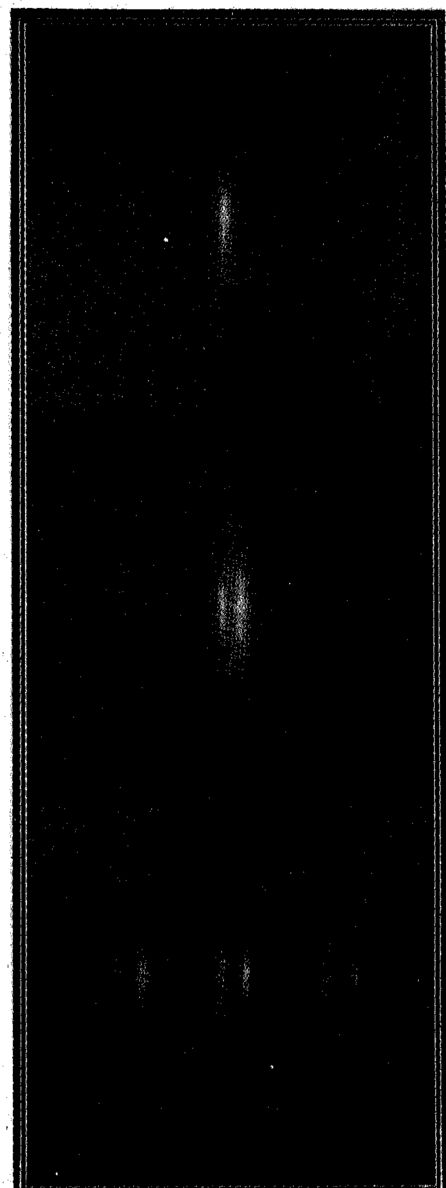
Figures 3 and 4

Plate II



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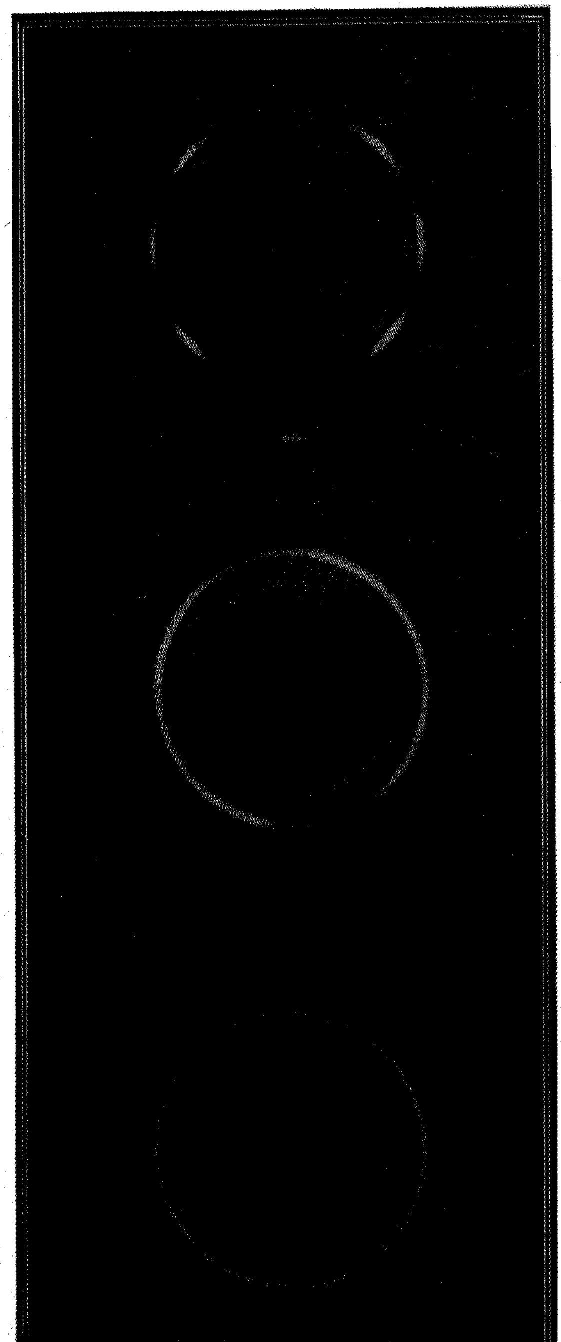
Figures 5–7

Plate III



(8)

(9)

(10)

Figures 8–10

Plate IV