

The structure and optical behaviour of iridescent opal

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1. Introduction

The remarkable and very beautiful effects exhibited by iridescent opal have long been known and have made it one of the most admired of gems. In the finest specimens, the play of colour takes the form of localised internal reflections exhibiting hues of extraordinary brilliance and saturation which vary from place to place over the area of the gem and change in a surprising manner with the angle of incidence of the light. Not the least part of the beauty of a fine opal is the orange-red colour of the transmitted light which may be seen reflected back by the rear surface of the gem and then appears all the more vivid by reason of its contrast with the greens and blues so frequently seen in the iridescence. Spectroscopic examination reveals that the internal reflections and the corresponding extinctions in the transmitted light are highly monochromatic. From this, it is evident that they are consequent on the presence within the material of regularly stratified layers in great number. Indeed, the existence of such stratifications is not just a hypothesis. When a gem-opal is examined through a microscope which has arrangements for illuminating the object from above the stage and viewing it by the internally reflected light, the lamellar structure of the material becomes immediately evident. In not a few cases, geometric patterns of a very striking character are observed (see figures 1 to 4 in plate I).

A reasonable hypothesis which would fit the observed character of the stratifications as well as the optical effects to which they give rise is that iridescent opal consists of alternate layers of two crystalline modifications of silica of slightly different refractive index. In a recent paper¹ in these *Proceedings*, we presented evidence which supports this hypothesis derived from a study of the X-ray diffraction patterns of hyalite which is a material having a composition similar to that of gem-opal and exhibiting optical phenomena of a similar nature. Further studies have since been carried out by us in which X-ray cameras of higher resolving powers were used and the resulting photographs were precisely measured. They have enabled us to reach the definite conclusion that the *two modifications of silica present in hyalite are respectively low-tridymite and high-*

crystalite. X-ray studies have also been made by us with common opal which occurs in massive form with a waxy lustre. These have led to a similar conclusion regarding the nature of the latter material.

The X-ray patterns of gem-opal are diffuse, thereby making it less easy than in the case of the crypto-crystalline materials hyalite and common opal to identify the nature of the atomic groupings which appear in the alternating layers of its lamellar structure. Nevertheless, a careful examination of the patterns leaves little room for doubt that, as in the case of the iridescent hyalite, we are concerned with two modifications of silica present side by side in it, one of them having a structure resembling that of low-tridymite and that the other that of high-cristobalite. Comparative studies of the optical behaviour of hyalite and of gem-opal made by us confirm this finding and establish this as the origin of the iridescence exhibited by these materials.

2. The crypto-crystalline forms of silica

As is well known, agate and chalcedony are massive forms of silica which X-ray studies show to consist of crystallites of quartz. The latter are frequently grouped together in specific orientations, thereby giving rise to the characteristic banding of the material, as has been shown by us in a recent paper.² *Prima-facie*, one may expect that two other crypto-crystalline forms of silica should also be forthcoming in nature consisting respectively of low-tridymite and low-cristobalite. The latter expectation, at least, is found to be fully justified. Some years ago, a white and compact porcelain-like material was collected by one of us on the open terrain not far from Indore in Central India. It was usually found associated with agate, but occasionally also appeared as separate masses. The density of the material has been determined and lies between 2.32 and 2.35, thus excluding the possibility of its being chalcedony. The density approximates closely to the known value for low-cristobalite, and examination by X-ray diffraction methods confirms this identification. On heating the substance to about 300° C, it transforms completely to high-cristobalite, and on cooling reverts again to low-cristobalite. These findings are illustrated in figures 12(a) and (b) in plate IV which show respectively the X-ray patterns of the material at the low and at the high temperature. The pattern was first recorded at the high temperature and later at the room temperature. Measurement of the photographs confirms the identification of the material with cristobalite.

It is clear from the X-ray patterns that the cristobalite is present in the material

randomly orientated. The most significant result that emerges is that high-cristobalite is unstable at ordinary temperature even when in a fine state of subdivision and reverts immediately to low-cristobalite.

3. The structure of common opal

Another material examined by us in detail is common opal with a waxy lustre, two large lumps of which were purchased from a mineral dealer in New York. The material is translucent in thick layers, but in smaller thicknesses of the order of a millimeter transmits light freely. The density of the material is 2.02 and its refractive index 1.440. On heating to about 800° C, it becomes opaque and white and also loses about 10% of its weight, presumably due to the loss of adsorbed water. An X-ray diffraction pattern was recorded in the usual manner, using a fine rod prepared from the material with a cylindrical camera of 3 cm radius. This is reproduced in figure 13(b) in plate V. Figures 13(a) and (c) in the same plate are X-ray diffraction patterns respectively of high-cristobalite and low-tridymite, recorded under identical conditions. The low-tridymite was taken off a burnt-out silica brick and then finely powdered; the high-cristobalite is the same material as that described in the preceding section.

A careful comparison of the three patterns reproduced in plate V is highly instructive. Particularly noteworthy is the fact that the principal ring of common opal is of considerable width, this being approximately the same as the total width covered by the triplet of lines appearing in the pattern of low-tridymite, while on the other hand, the principal ring of high-cristobalite is single, sharp and well defined. But in other respects, the patterns of common opal and of high-cristobalite exhibit a close similarity. But even so, there are recognisable differences. While the rings of high-cristobalite are all sharp and fairly intense, those of common opal are definitely weaker and also rather diffuse though to varying extents. The pattern of the opal also exhibits a much more intense small-angle scattering than that of high-cristobalite. A continuum of varying intensity is also present in the pattern of the opal which is absent in the case of high-cristobalite. On careful scrutiny, a close correspondence is revealed between the intensity of the continuum in the pattern of common opal and the integrated intensity of the groups of lines appearing in the corresponding parts of the low-tridymite pattern.

All the facts set forth above indicate that common opal is a material in which high-cristobalite and low-tridymite co-exist in intimate juxtaposition.

4. The structure of hyalite

In our earlier paper which appeared in these *Proceedings* for August 1953, the X-ray diffraction patterns of four specimens of hyalite were reproduced. The pattern

of specimen no. I which was recorded with a 3 cm radius camera is reproduced again as figure 14(b) in plate VI. For comparison with it, the patterns of high-cristobalite and low-tridymite recorded under identical conditions are once again reproduced in plate VI as figures 14(a) and 14(c) respectively. Apart from the circumstance that only one side of the pattern of the hyalite has been recorded, it will be seen that it closely resembles the pattern of common opal appearing in figure 13(b) in plate V, except that the outer rings are generally rather sharper and more intense in the case of the hyalite. Hence, the remarks made above regarding common opal apply *mutatis mutandis* to the case of hyalite.

To make the position clearer, the pattern of hyalite no. IV which had a very sharp edge has been recorded once again with X-ray cameras of higher resolving power. A picture taken with a camera of 5.73 cm radius and an exposure of seven hours is reproduced as figure 9 in plate III. Three prints of a pattern of the same specimen recorded with a camera of 19 cm diameter and an exposure of twelve hours are reproduced as figure 10 in the same plate. It is very clearly seen in both pictures that the principal ring in the pattern is a triplet, with a strong central component. Both the positions and relative intensities of the components of the triplet are explicable if the pattern is recognised to be a superposition of those of high-cristobalite and low-tridymite. This will be evident from table 1 where the respective d -values of the more prominent lines have been tabulated. The table also makes it clear that the suggestion made in our earlier paper that the X-ray pattern of hyalite is a superposition of the patterns of high- and low-cristobalite is untenable.

5. The structure of gem-opal

The density of gem-opal ranges between 2.1 and 2.2, and its refractive index between 1.45 and 1.46. The density and the refractive index of hyalite are respectively 2.0 and 1.44 respectively, these lower values being related to those for gem-opal at least approximately in the manner demanded by the Gladstone-Dale formula. The principal difference between gem-opal and hyalite is that while the latter, as we have seen, gives a well-defined X-ray diffraction pattern, the pattern of the former is diffuse and resembles that of vitreous silica, though there are recognisable differences. Figures 11(a), (b), (c), (d) and (e) in plate IV are X-ray diffraction-patterns recorded with a camera of 5.73 cm diameter and the filtered radiation from a molybdenum target of the materials indicated respectively against each figure. Figures 11(a) and (e) are of two different specimens of gem-opal, while the other figures refer respectively to silica gel, vitreous silica and the natural silica glass from the Sand Sea in the Libyan Desert collected by Dr L. J. Spencer. At a first glance, all the patterns seem to be similar, but a more careful scrutiny reveals significant differences. Remarkably enough, the difference is greatest as between gem-opal and vitreous silica. In the patterns of opal the two

outer rings are seen clearly separated from each other and from the next inner ring, whereas with the vitreous silica, the two outer rings have nearly coalesced, and the next inner ring has joined up with the bright central area. The differences between the opal and the silica gel on the one hand, and between opal and the Libyan glass on the other, are of a less striking character. It should be remarked that in the case of all four materials, there are two outer bands of low intensity which can be scarcely glimpsed in the reproductions. The d -values calculated for the principal ring and for the five outer bands for the case of gem-opal are respectively 4.1 Å, 2.05 Å, 1.45 Å, 1.20 Å, 0.97 Å and 0.80 Å.

Table 1. d -values in Angstroms with intensities

Low-cristobalite	High-cristobalite	Hyalite	Low-tridymite
—	—	4.32 (moderate)	4.32 (intense)
—	4.13 (intense)	4.12 (intense)	4.10 (strong)
4.04 (intense)	—	—	—
—	—	3.9 (weak)	3.82 (strong)
3.12 (moderate)	—	—	—
—	—	—	2.97 (moderate)
2.85 (moderate)	—	—	—
2.48 (strong)	2.52 (strong)	2.51 (strong)	2.49 (moderate)

The use of the short-wave molybdenum radiation and a camera of small radius results in obscuring much of the visible detail in the inner parts of the pattern. The latter are much clearer when recorded with the filtered radiation from a copper target. Two pictures, namely those of gem-opal and of silica glass, taken with CuK_α radiation and a flat camera with a film to specimen distance of 4 cm are reproduced as figures 8(a) and 8(b) respectively in plate III. The density of gem-opal being rather less than that of vitreous silica which is 2.22, one might have thought that the principal ring of opal should have a smaller angular diameter and give a larger d -value than that of silica glass. The actual position is the reverse, as can be seen on a careful comparison of the two figures. It will also be noticed that the first diffraction ring of gem-opal is definitely sharper and of greater intensity relatively to the region inside it than for silica glass.

Using the CuK_α radiation and an X-ray camera of 3 cm radius with adequate exposures, the complete pattern of gem-opal can be satisfactorily recorded and shows features of great interest. Unfortunately, however, owing to the weakness of the outer bands relatively to the principal halo, it is difficult to copy it in a satisfactory manner for reproduction. Hence we have to content ourselves here with a description of the observed features. One can clearly see in the

photographs besides the principal ring and a strong continuum stretching out from it, a distinct concentration of intensity along a ring with a d -value of 2.50 \AA , besides the other bands with smaller d -values which are the same as those recorded with molybdenum radiation. The pattern in fact is essentially similar to that of hyalite reproduced as figure 14(b) in plate VI, provided that one supposes that the rings appearing in the latter had broadened out sufficiently to become a set of diffuse bands. The continuum seen in the hyalite pattern between its first and second rings is a conspicuous feature also in the pattern of the gem-opal as recorded with the CuK_α radiation.

Thus, the X-ray data point clearly to the conclusion that the structure of gem-opal is essentially the same as that of hyalite; except that the crystallites are now much smaller, thereby tending to make the material simulate a vitreous solid.

The essential similarity between hyalite and gem-opal indicated by the X-ray data is supported by other facts of observation. One of the most striking features observed with gem-opal is the appearance of visible stratifications in it. These are very conveniently observed with the aid of an 'Ultropak' microscope. In this arrangement, a conical beam of light is directed from above the stage on to the surface of the specimen and the latter is viewed by the light reflected from its interior and returned to the objective of the microscope. A great variety of geometric patterns are observed, a few particularly striking examples of which are reproduced as figures 1, 2, 3 and 4 in plate I. Figures 1 and 4 refers to exactly the same portion of a particular specimen but under slightly different conditions of illumination. Figure 2 refers to another area on the same opal. Figure 3 is a particular area on the finest gem-opal in the collection of this Institute. It will be seen from these pictures that the stratifications run in several directions simultaneously and in fact the entire material is honeycombed by them. The material is divided up into layers parallel to one, two or even three sets of parallel planes crossing each other. It is to be noted that hyalite also shows visible evidence of internal stratifications. One may refer for example, to the picture of our specimen II under transverse illumination reproduced as figure 5 in plate IV of the earlier paper in which triangular patches shining by reflected light are clearly to be seen. The essential similarity of the structures of opal and hyalite is thus made clear.

6. Observations with monochromatic light

In examining the optical behaviour of regularly stratified media, the use of monochromatic light is very helpful. We shall proceed to recount some observations made with opals, respectively in the light of a sodium vapour lamp and of a mercury arc.

The finest opal in the collection of this Institute is a square tablet which in

diffuse daylight exhibits bright green, blue or violet flashes of internal reflection. In the light of a sodium vapour lamp, however, this brilliance disappears and the gem is seen transformed to an insignificant and unsatisfactory object exhibiting numerous defects, including especially a cloudiness over part of its area on one face in which no iridescence is visible even in diffuse daylight. Every one of the opals in the collection of the Institute which exhibits a green or blue iridescence resembles in the light of a sodium lamp a piece of common but rather turbid glass. Such disappearance of the iridescence is intelligible in the light of optical theory, for a regularly stratified medium ceases to reflect at any incidence if the wavelength λ of the light is greater than $2\mu t$, where μ is the mean index and t is the spacing of the stratifications.

The opals which show up so badly in the light of the sodium lamp present a very different appearance in the light of a mercury arc. The difference between the mercury arc and diffuse daylight is however conspicuous in the colour exhibited by the internal reflections, as also in the colour of the transmitted light. The former shows less variety than in daylight, while, on the other hand, the transmitted colours are more lively, being less diluted by the light of longer wavelengths present in daylight.

In our earlier paper,¹ we described and illustrated the optical effects exhibited by hyalite which were individually different in our three specimens I, II and III. The first showed a diffusion halo around the direction of the transmitted light, the second a set of radially directed diffraction spectra, while our specimen III behaved much like an opal and showed a great number of individual monochromatic reflections backwards towards the source of light, many of which are of a red colour. Examined in the light of a sodium lamp, hyalite no. III showed many sparkling reflections from its interior which disappeared and reappeared in other positions as the specimen was turned round.

It is clear from the facts that the optical effects exhibited by transparent hyalite and by iridescent opal form a continuous sequence in which there are three stages. In the first stage, the stratifications are too widely spaced to result in internal reflections, but give rise to diffraction haloes or diffraction spectra in forward directions. In the second stage, the stratifications are too closely spaced to give diffraction effects in forward directions, but result in reflections backwards towards the source. Finally, we have a third stage when the stratifications are too closely spaced to give any effects at all, unless the wavelength of the light is sufficiently small. In the crypto-crystalline hyalites, we would naturally expect the first stage to be commonest, and the second stage less common. In the gem-opals, on the other hand, where the material is approaching the vitreous condition, the stratifications may be expected to be much finer and the third stage therefore attained, unless the wavelength of the light is chosen sufficiently small. We do indeed have opals which exhibit a bright yellow or red iridescence. But those with a green, blue or violet iridescence are commoner, indicating that the more closely-spaced stratifications are favoured.

7. The reflection patterns of opal

In studying the optical behaviour of opal rather more closely, we may adopt one of two different methods. In the first method, we view the opal directly or through a microscope, illuminating it from one direction and viewing it in another, and vary these directions. The second method is the same as that described in our earlier paper. We illuminate the opal by a intense narrow pencil and the light reflected backwards is received on a white screen held not too far away from the specimen, a small aperture in the screen permitting the illuminating pencil to pass through and fall on the opal. The complete pattern of reflected, diffracted or scattered light returned by the opal is then visible on the screen.

Observations made in the manner described disclose a great variety of effects in different cases. With some specimens, we observe a bright spot or a group of bright spots constituting a reflection-pattern properly so-called. There are also cases in which no pattern appears but only a diffuse area of light on the observing screen, its colour being the same as that of the observed opalescence of the specimen. Opals giving brilliant localised reflections give, in general, complex patterns composed of bright spots, bright coloured streaks of light and brilliant diffraction spectra crossing each other in different directions, the whole pattern altering rapidly as the opal is moved with respect to the illuminating pencil of light. Even those opals which are not of much value as gems, exhibiting colour only in tiny specks or spots on a non-iridescent background, give interesting patterns of various kinds.

It would take us too far from the main purpose of the paper to describe or discuss the reflection patterns of opal in greater detail. We may, however, make a brief reference to the behaviour of a particularly interesting specimen in our collection. This is a so-called "black-opal" in other words, a layer of opal on a background of opaque ferruginous material. When it is illuminated by a narrow pencil of sunlight, the pattern seen on the viewing screen is a single bright streak of light covering a wide range of angles and exhibiting the usual sequence of colours seen in a diffraction spectrum. The distribution of intensity in the spectrum is however anomalous, a concentration of intensity appearing at one place and a dark gap elsewhere, the position of the former altering with the inclination of the reflecting surface to the incident pencil of light. Examination of the specimen under the microscope reveals the presence of parallel striations over its area. These presumably represent the stratifications of the opal meeting the surface of the specimen obliquely. That in these circumstances a diffraction spectrum appears and not a simple reflection is scarcely surprising.

8. The spectroscopic facts and their significance

Figures 5 and 6 in plate II reproduce some spectroscopic records of the reflection of light by some specimens of gem-opal, a beam of white light being

allowed to fall at nearly normal incidence on a restricted area of the specimen and after reflection being received on the slit of the instrument. Particularly remarkable is the spectrum reproduced in figure 5(d). It shows a single monochromatic reflection in the red, the spectral width of which is only about 20 Å. Figures 6(a), (b), (c), (d), (e) and (f) are a series of reflection spectra recorded with a single specimen of opal immersed in a cell containing liquid paraffin, the angle of incidence of the light being varied by steps from nearly normal incidence to about 50°. The exposures with which the spectra were recorded were not the same in all cases, and hence it is not possible to attach any quantitative significance to the spectral width as seen in the reproductions. In a general way, however, it is evident that there has been no noteworthy increase in the spectral width of the reflection in spite of the wavelength at which it appears having been shifted from 5820 Å to 4930 Å with the increasing angle of incidence.

Figures 7(a), (b) and (c) in plate II are the extinction spectra of three different gem-opals in the collection of the Institute. They were recorded by the simple device of holding the specimen against the slit of the recording spectrograph and allowing the light from a filament lamp 50 cm away to enter the slit after passing through the specimen. The photographs exhibit the extinctions produced by the entire thickness of the opal which was about 3 millimeters in each case. They represent the joint effect of the sets of stratifications present at different depths and possibly also differently inclined to the path of the light-rays through the opal. The spectrograms exhibit a great variation in the effects recorded at different points along the slit of the instrument. Well-defined extinctions usually about 100 Å wide appear in the blue-green region, accompanying which are seen streaks of transmitted light extending towards the violet end of the spectrum. In other regions, there appears a general cut-off of the shorter wavelengths and a free transmission of the longer wavelengths. These facts will be readily understood in the light of the remarks made earlier in this paper.

The theory of the reflection of light by a regularly stratified medium has been elaborately discussed in these *Proceedings* by G N Ramachandran.³ As has been shown by him, the degree of monochromatism of the reflections by such a medium cannot be indefinitely increased by increasing the number of its stratifications, their spectral width having a minimum limiting value which depends only on the reflecting power of an individual stratification. If such reflecting power be large, the monochromatism would necessarily be very imperfect; *per contra*, if high monochromatism is actually observed, it indicates that the reflecting power of an individual lamination is small. These conclusions have an important application to the case of opal. They indicate that the difference in refractive indices of the alternate layers of the stratifications in opal is quite small. Further, such variation is strictly periodic and of the same magnitude throughout an individual set of stratifications.

9. The nature of the stratifications

The considerations set forth above suffice by themselves to exclude the explanations of the iridescence of opal which appear in the earlier literature of the subject. It is likewise not possible to entertain the idea that the presence of adsorbed water in opals is responsible for their iridescence, as it would then be necessary to assume that the adsorbed water is so distributed as to give rise to a regular periodic variation in refractive index of small magnitude, an assumption for which there is no *prima facie* justification. We have made some observations on the effect of heating opals to temperatures sufficiently high to drive out all adsorbed water. This drastic treatment usually results in a disintegration of the opal, but the iridescence as such remains unaffected. We are thus forced to recognise that the iridescence of opal is a consequence of the inherent structure of the silica in the material.

The densities of low-tridymite and of high-cristobalite are not very different and their refractive indices would therefore differ just sufficiently little to account for the observed behaviour of opal if they exist as separate layers side by side. The same difference could equally account for the observed cloudiness of opal in many cases if the distribution of the two materials were irregular in such cases.

As is well known, high-cristobalite is a form of silica which is stable over a wide range of temperatures, but which reverts to low-cristobalite below 300° C. The presence of high-cristobalite admixed with low-tridymite in opal may be reasonably accounted for by assuming that its association with low-tridymite, which is itself a stable form at ordinary temperature, confers on it the requisite stability. Since the two materials have the same chemical composition and nearly the same density, and since their structures have the silicon-oxygen tetrahedra as a common factor, there is no inherent difficulty in making such an assumption. Since the two structures are not identical, the materials would naturally tend to segregate and form layers so disposed with respect to each other as to present the maximum possible degree of continuity in the chains of valence bonds between the silicon and oxygen atoms extending through the material. Since the structure of low-tridymite is pseudo-hexagonal while that of high-cristobalite is cubic, geometric patterns in which the two structures alternate may be expected to arise, as is indeed actually observed in opal.

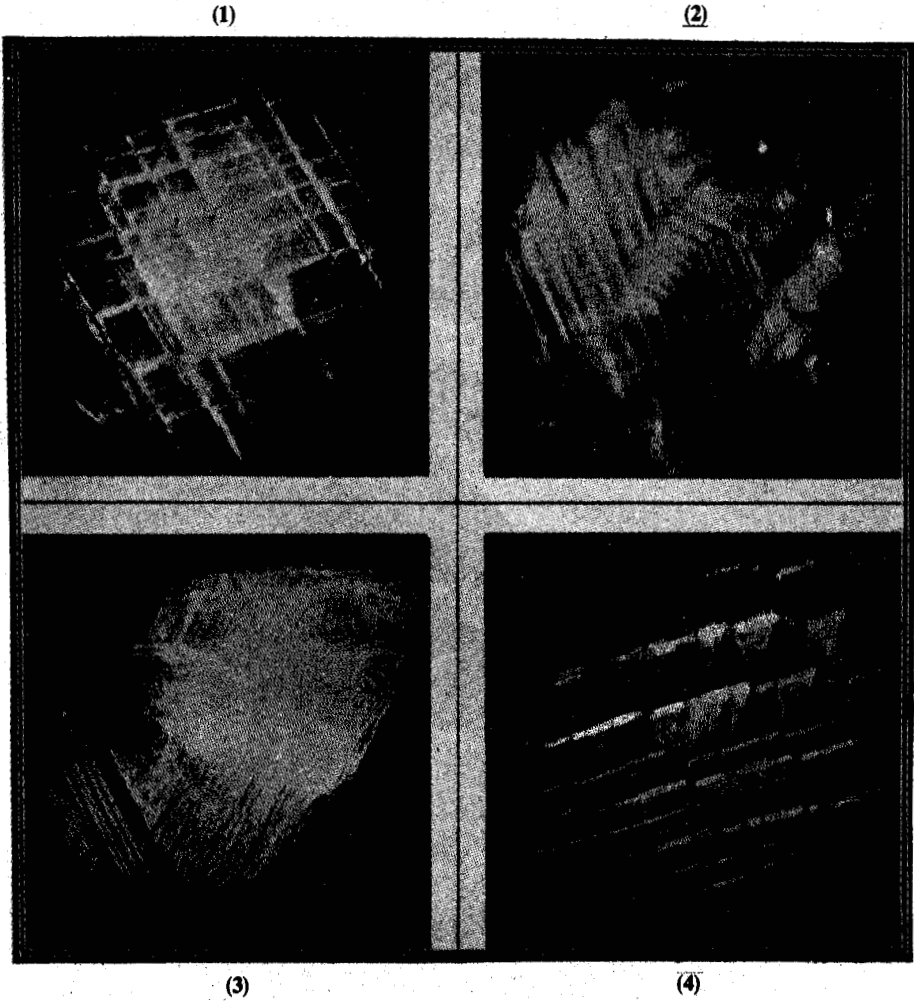
Summary

The X-ray investigation of the structure of the cryptocrystalline hyalites reported in an earlier paper has now been revised using cameras of higher resolving power. Precise measurements of the resulting photographs reveal that low-tridymite and high-cristobalite are present associated with each other in this material. Investigation of the structure of common opal exhibiting a waxy lustre leads to

similar results. From a detailed examination of the diffuse X-ray patterns given by gem-opals as well as a comparative study of the iridescent hyalites and opals, it is concluded that in both of these materials, the presence of alternating layers of high-cristobalite and low-tridymite is responsible for the iridescence.

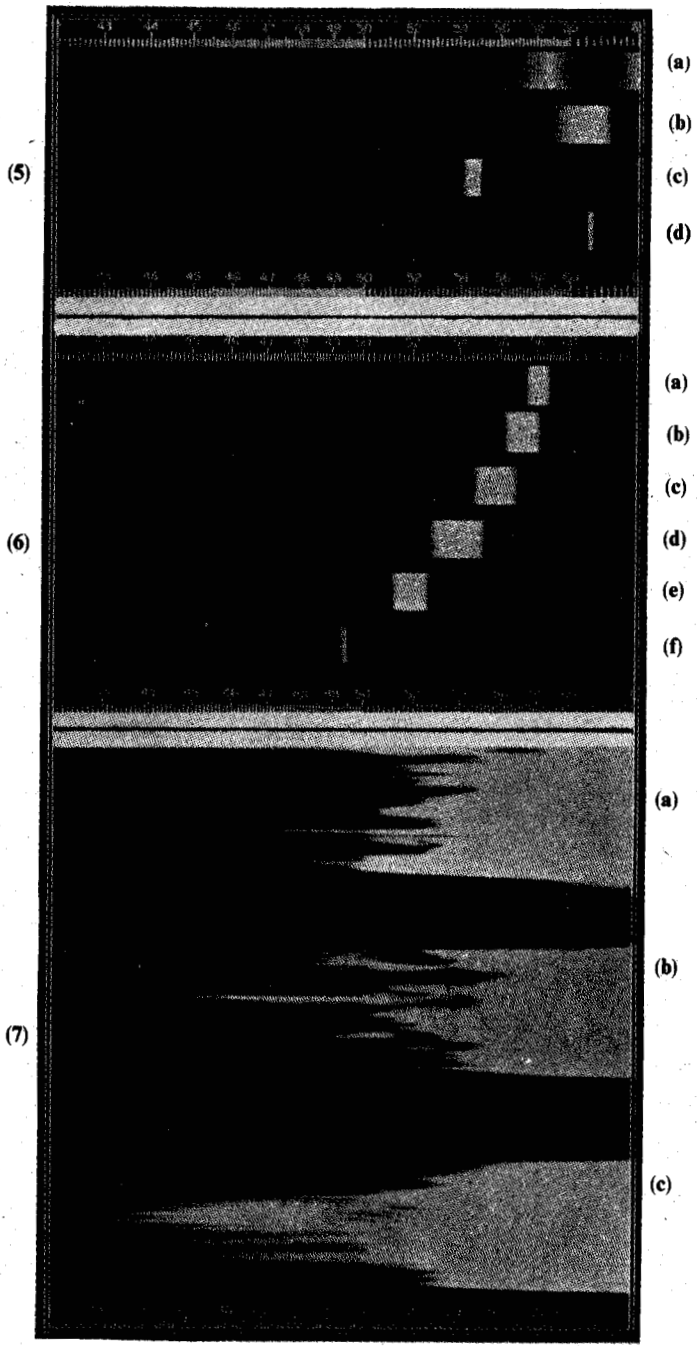
References

1. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1953, **38A**, 101.
2. C V Raman and A Jayaraman, *Ibid.*, 1953, **38A**, 199.
3. G N Ramachandran, *Ibid.*, 1942, **16A**, 336.



Figures 1-4. Lamellar structures in precious opal.

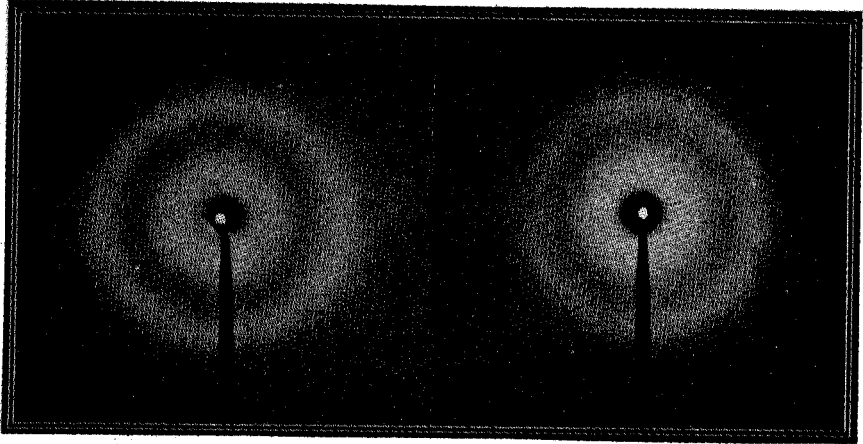
Plate I



Figures 5-7. Reflection and extinction spectra of precious opal.

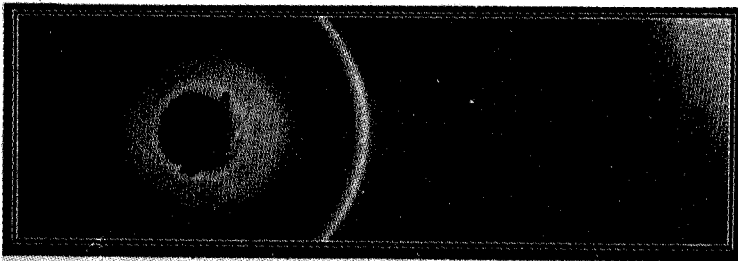
(a) Precious opal

(b) Silica glass



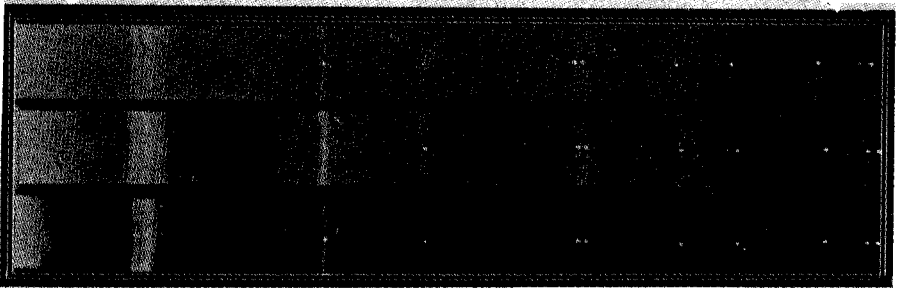
(8)

Hyalite IV



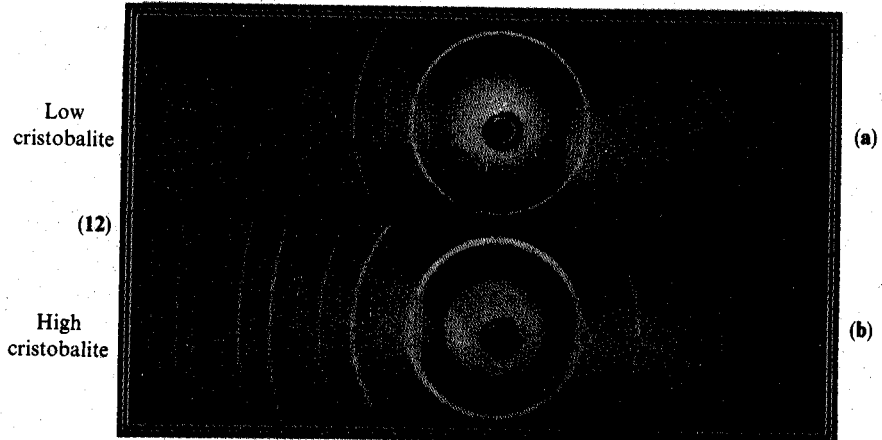
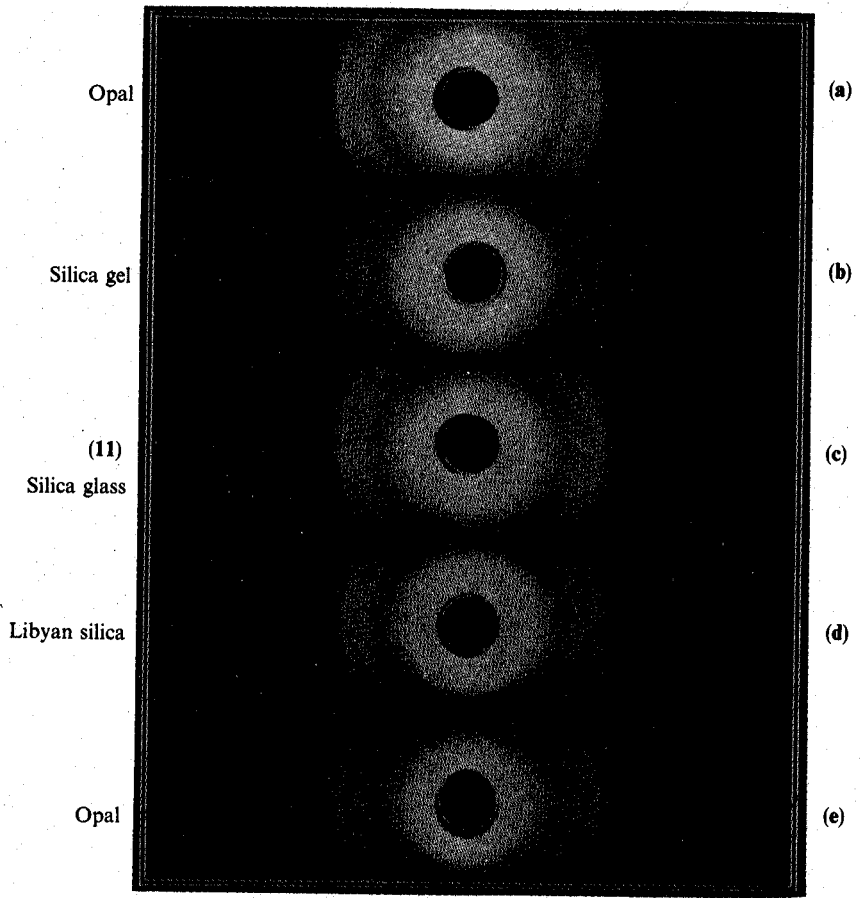
(9)

Do



(10)

Figures 8-10. X-ray diffraction patterns.



Figures 11 and 12. X-ray diffraction patterns.

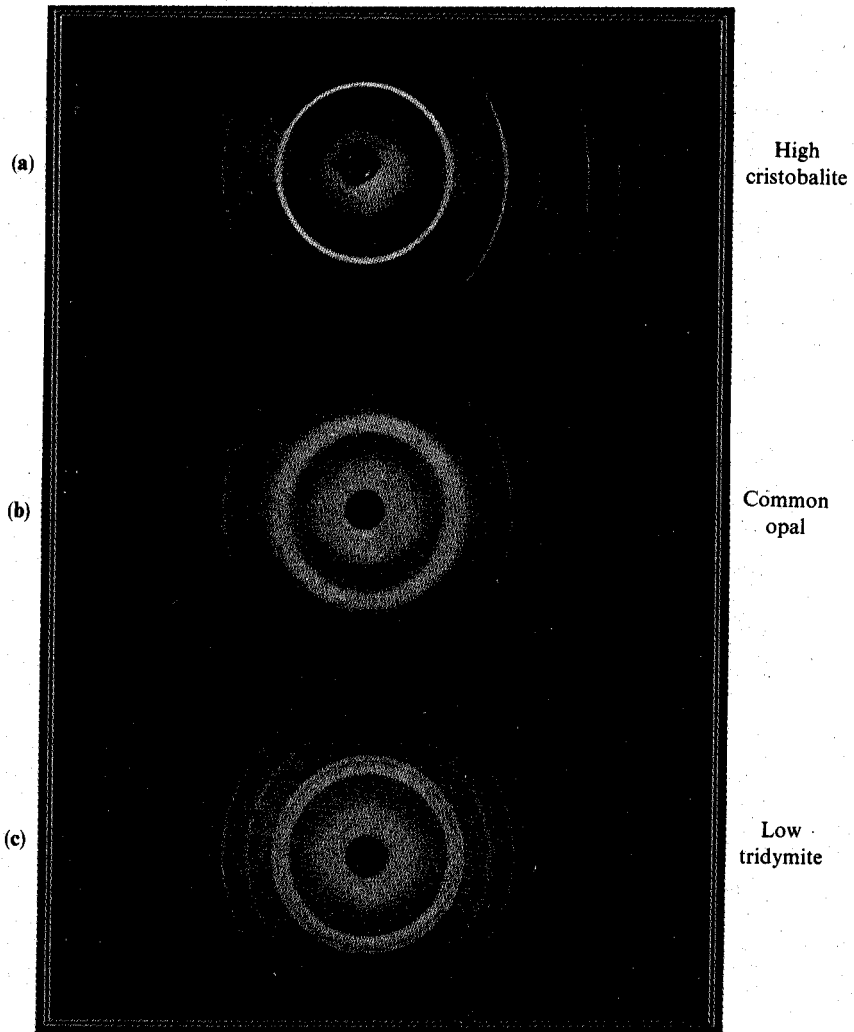


Figure 13. X-ray diffraction patterns.

Plate V

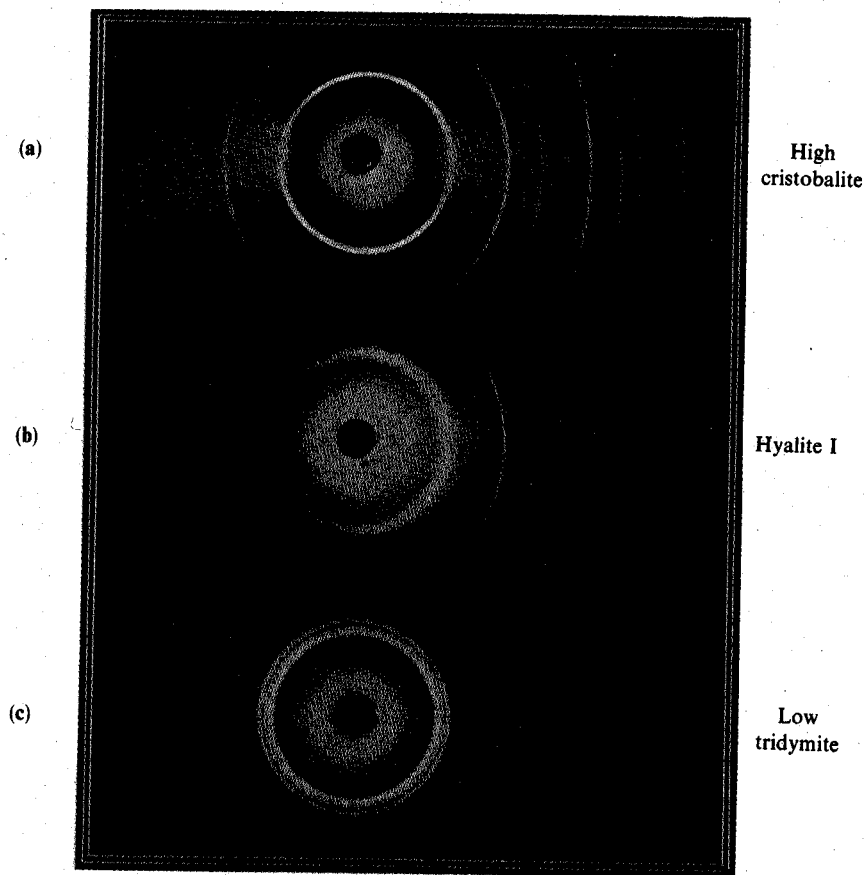


Figure 14. X-ray diffraction patterns.

Plate VI