The Origin of Color in Opal

Based on Electron Microscopy

by

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Although many attempts have been made to understand the origin of play of color in precious opal, scientists have not been able to explain this phenomenon satisfactorily or to relate it to the possible structure in opals. A recent study by scientists of CSIRO, using electron microscopy, has solved this problem and revealed the remarkable way that Nature has made this gemstone.

All precious opals have been formed from spherical particles of amorphous silica. In a gem opal, the spheres are of a uniform size and are packed together in a very regular manner. Spaces, or voids, have been left between the spheres, and these are also regularly arranged. This structure is too small to be seen with any optical microscope, but is easily visible when replicas of fracture surfaces are viewed in an electron microscope *(Figure 1)*.

Since electron microscopes are not generally available to gemologists, it is necessary that the method of preparing specimens should be explained. Electrons have a very low penetration through matter compared with X-rays and light, and it is possible, therefore, to view only very thin specimens (generally 2000 Å). In this investigation, a freshly fractured surface was prepared, and an exact replica of this surface was taken with a thin film of carbon. This film was stripped from the surface with hydrofluoric acid and supported on a fine-mesh grid, which goes into the microscope.

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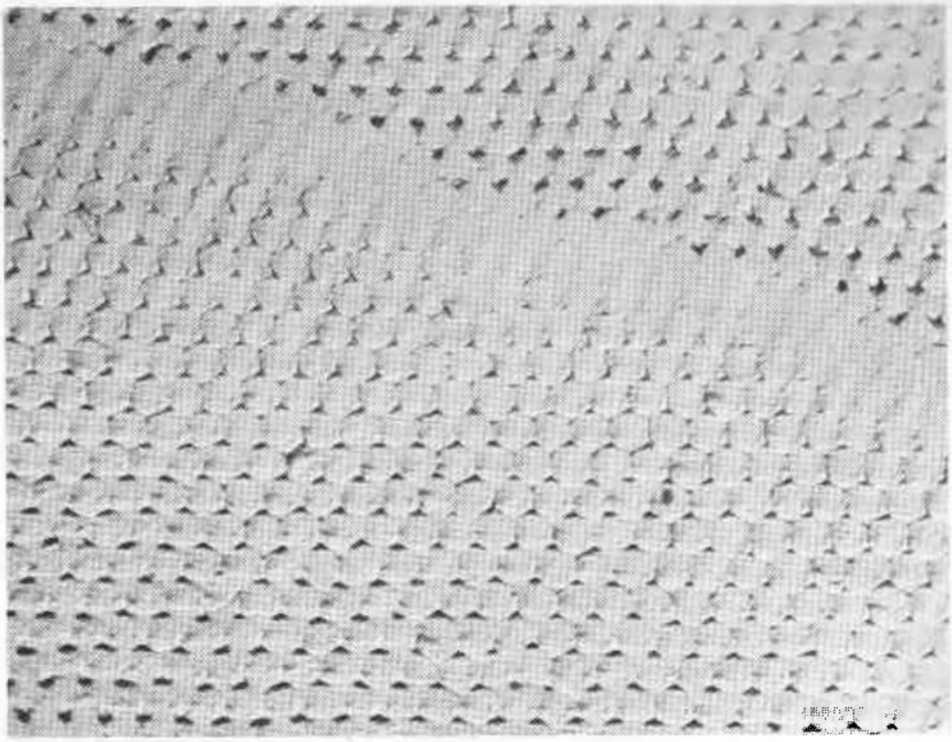

Figure 1. Regularly arranged holes in a fracture surface of gem opal *(20,000x)*

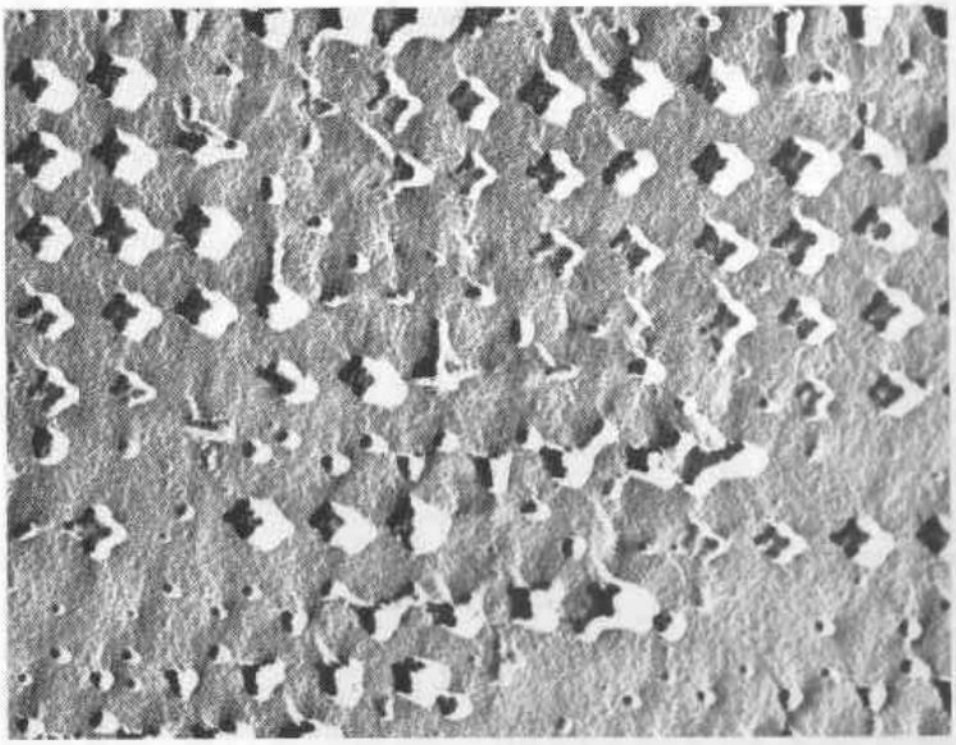

Figure 2. Varying shapes of holes in opal *(25,000x)*

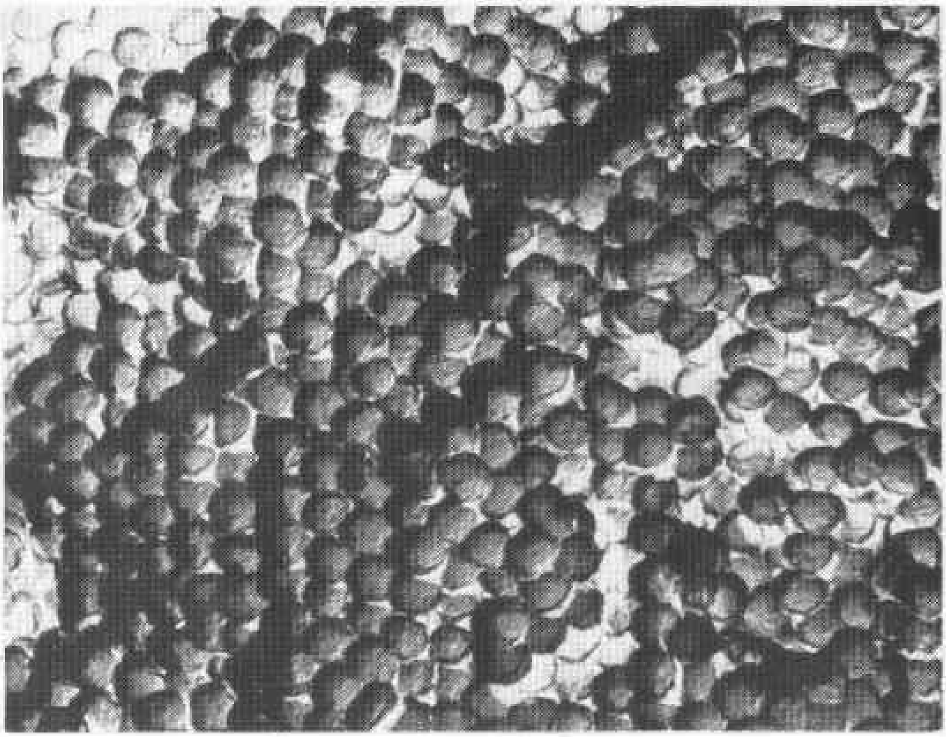

Figure 3a. Spheres revealed by etching opal. Sample 1, Table 1 *(24,000x)*

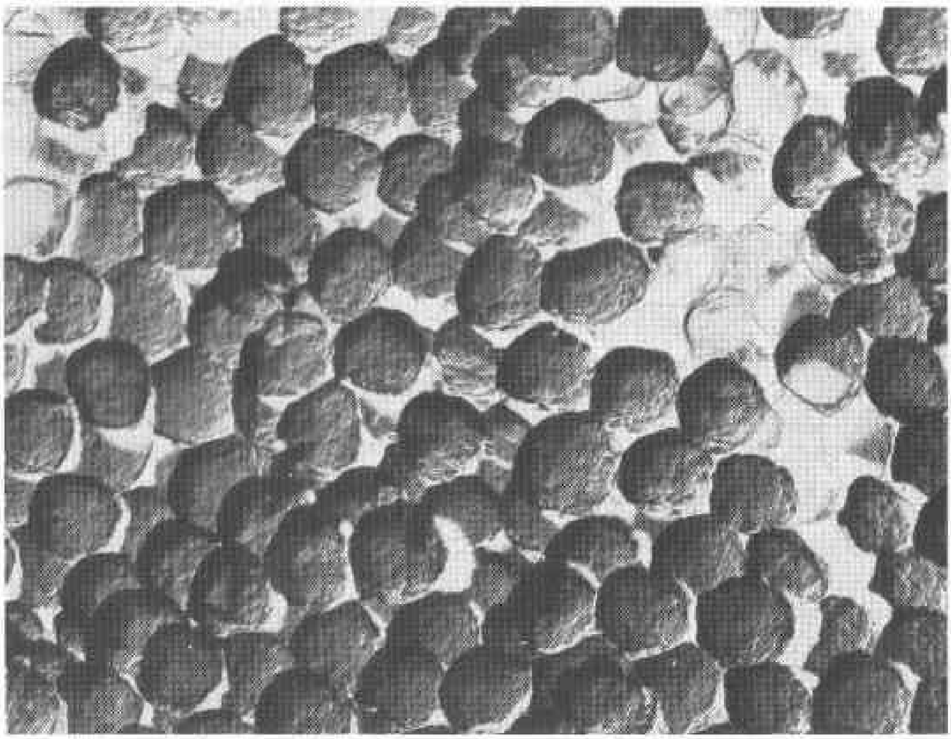

Figure 3b. **Sample 111, Table 1 *(24,000x)***

The replicas from the opals always show that the surface contains holes, whose shape and arrangement appear to vary because the fracture surface intersects the voids at various depths and angles, hence giving differing cross sections. Some of the curious sections can be seen in *Figure 2*. Nevertheless, the arrangement is always regular. By etching a fracture surface, it is possible to reveal the spheres themselves and their remarkable uniformity *(Figure 3)*.

Once the basic feature of the opals (i.e., the regular stacking of uniform spheres), is known, it is possible to predict their optical properties and check these by experiment. The silica spheres themselves are optically transparent, but some light is scattered at the surface of the voids, because there is a change in refractive index at the interface. The holes may be empty or filled, the only requirement being that there should be a change in refractive index. The spheres, and hence the voids, are arranged regularly in three dimensions (face-centered cubic), so that the whole arrangement makes a three-dimensional diffraction grating. The important feature is that the spacing of the holes is the same as that of the spheres, and when this is about that of the wavelength of visible light, Bragg diffraction of light occurs. This process is the same as that in which X-rays are diffracted by regularly packed molecules in crystals. The angle through which the light is diffracted varies continuously with wavelength, so that different colors appear at different angles, thus producing the play of colors. It also follows that only pure spectral colors can arise from this process.

In gem-quality opal, the sizes of the spheres are just right for the visible wavelengths to be diffracted back through angles up to 180°. Therefore, opals are best viewed on a black background, where any light that is not diffracted will be transmitted through the stone and absorbed by the background. If it were reflected or scattered back through the opal the colors would appear weaker, because of dilution by the reflected white light. This explains the effectiveness of doublets and dyed opal.

The visible spectrum that covers wavelengths from 4000 to 8000 Å is commonly divided into the following colors in order of increasing wavelength: violet, indigo, blue, green, yellow, orange, red. The theory of three dimensional diffraction tells us that the maximum wavelength (λ_{max}) that can be diffracted by an array of spheres (diam. d) close packed in a cubic manner is given by

$$\lambda_{max} = 2.37d$$

This color of maximum wavelength is diffracted back directly into the incident direction and colors of shorter wavelengths are spread on either side in spectral order. This is shown in a simplified sketch in *Figure 4*. If the particle size is such that λ_{max} corresponds to blue light, no color but blue, indigo or violet can be seen, since only shorter wavelengths can be diffracted back. Similarly, if λ_{max} corresponds to

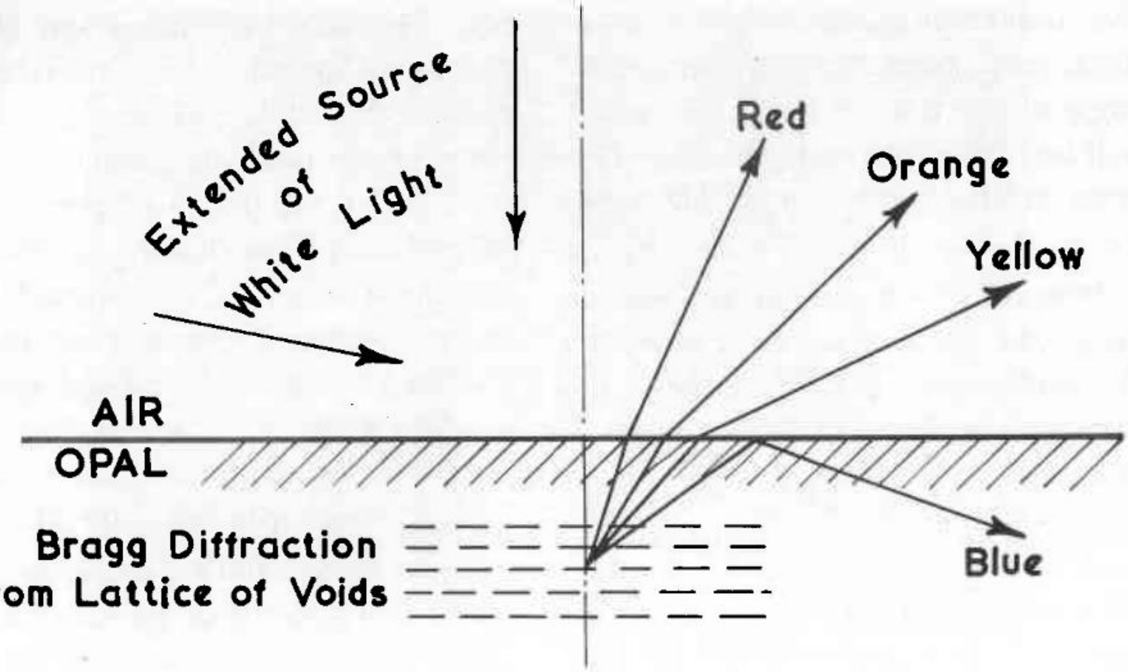

Figure 4. Diagram of the angular displacement of diffracted colors

orange, all colors but red can appear; this is supported by visual observation of opal. A specimen that shows red by normal back diffraction may show a range of colors, but one that shows blue is restricted to that end of the spectrum. Any gemologist can check these conclusions by observing opals with this law in mind.

By assessing the maximum wavelength that can be seen, the size of the spheres may be predicted. This effect was checked by experiment. Three samples, selected by color, were etched and replicas examined in the electron microscope. The results, given in Table 1, show clearly that there is a difference of size, as predicted.

This diffraction theory relates the color to the size of the spheres. However, as mentioned previously, refraction is important, too, because it limits the range of colors that can emerge from a flat surface. Because the refrac-

Table 1

		diam. measured Å	λ_{max} calculated Å	λ_{max} observed Å
1	violet	1750	4150	4000
11	green	1900 - 2100	4500 - 5000	5000
111	red	2500 - 3500	5900 - 8300	7000

tive index of opaline silica is about 1.45, any diffracted ray making an angle of less than 44° with the surface will be totally internally reflected. This effect is illustrated for the blue ray in *Figure 4.*

It can be shown that this restricts the range of colors that can be seen from a flat surface such that the ratio of the maximum wavelength (λ_{max}) to minimum wavelength (λ_{min}) is given by

$$\lambda_{min} \qquad \lambda_{max} \qquad = 0.72$$

This means that the flat surface of an opal made of large spheres of uniform diameter can give, for instance, only red to green or, for smaller spheres, from blue to violet. Exceptions to this rule may occur but only under very special conditions. The limit set by refraction no longer occurs if the surface of the opal is not flat, if it is covered with a dome of transparent material of the same refractive index, or if it is immersed in a liquid of refractive index close to 1.45; e.g., glycerol. Under these conditions, more of the spectrum may be seen but, of course, the geometry of the system is altered. This explains why the cabochon displays an opal to its best advantage.

The color will be homogeneous in a patch of opal where the regularity of packing of the spheres is maintained in the same orientation. Such a patch is like a grain in a polycrystalline material. Grains orientated in different ways will produce different colors in a given direction, even though the spheres may be of uniform size throughout the sample. The electron microscope shows that opals contain many mistakes in packing and faults in stacking, such as occur in the molecular packing of crystals. The most obvious of these faults in opal is multiple twinning, which is commonly observed by reflected light in an ordinary optical microscope. Patches of irregularly packed spheres produce generally scattered light and give a background milkiness to opal; many Coober Pedy opals are like this.

Potch is very similar to precious opal and is also made from spheres of amorphous silica, but the spheres are not regular in size or spacing. Voids still exist between them *(Figure 5)* and light is scattered by them. The lack of regularity in their arrangement prevents the regular interference that gives the colors, and so the scattered light produces just a milky, opaque appearance. The dark-body-colored potch from Andamooka must contain impurities to cause the color, since basically it is still made from silica spheres *(Figure 6)*. In the almost transparent jelly opals, the voids have nearly disappeared and only a small amount of light is scattered. If the stacking is correct, this may still produce a flash of color. Mexican fire opals have a distinctive body color produced by selective absorption but are still composed of regularly packed spheres.

It is felt that this theory satisfactorily accounts for all the optical properties peculiar to opal, but it is still not clear how this regular structure was produced. When the opal is lightly etched,

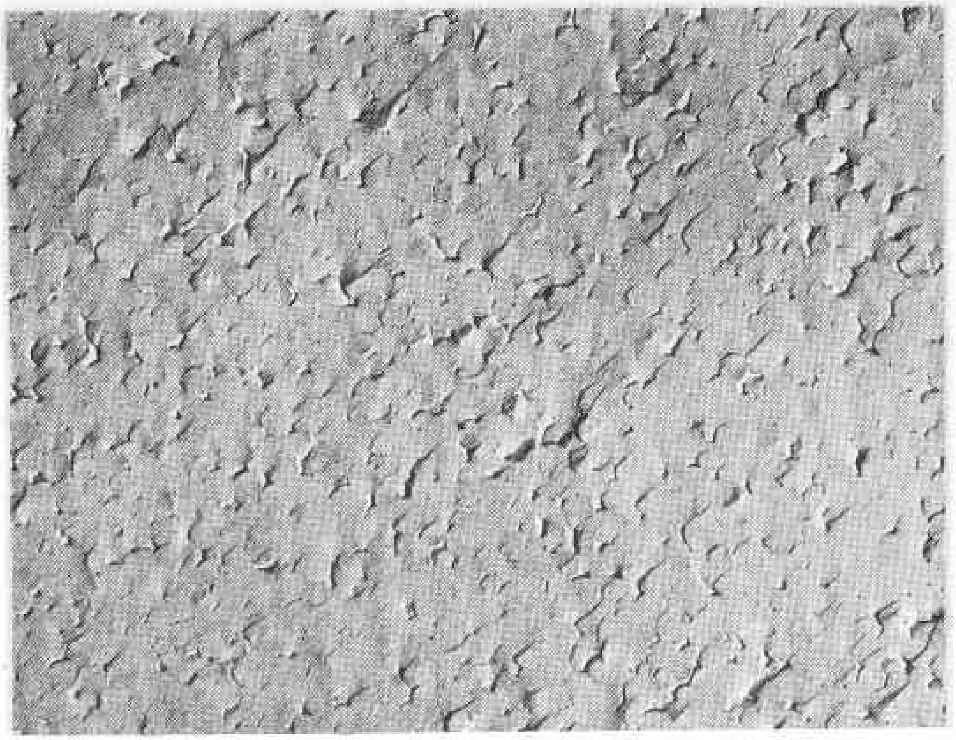

Figure 5. Fracture surface of potch opal *(6,400x)*

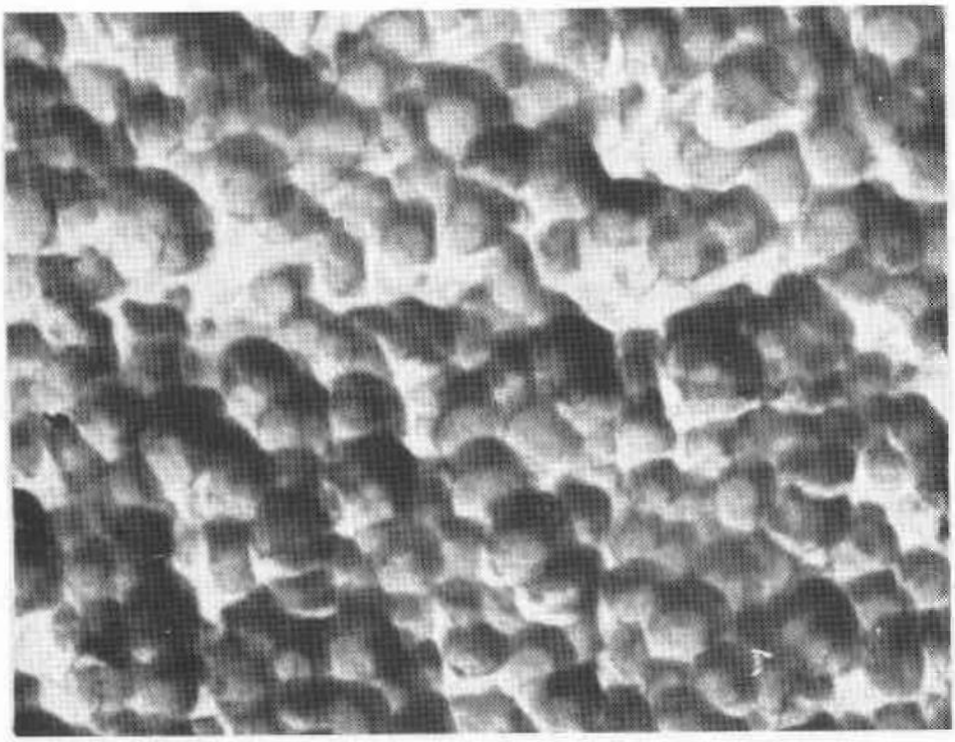

Figure 6. Etched surface of Andamooka potch reveals the irregular spheres *(42,000x)*

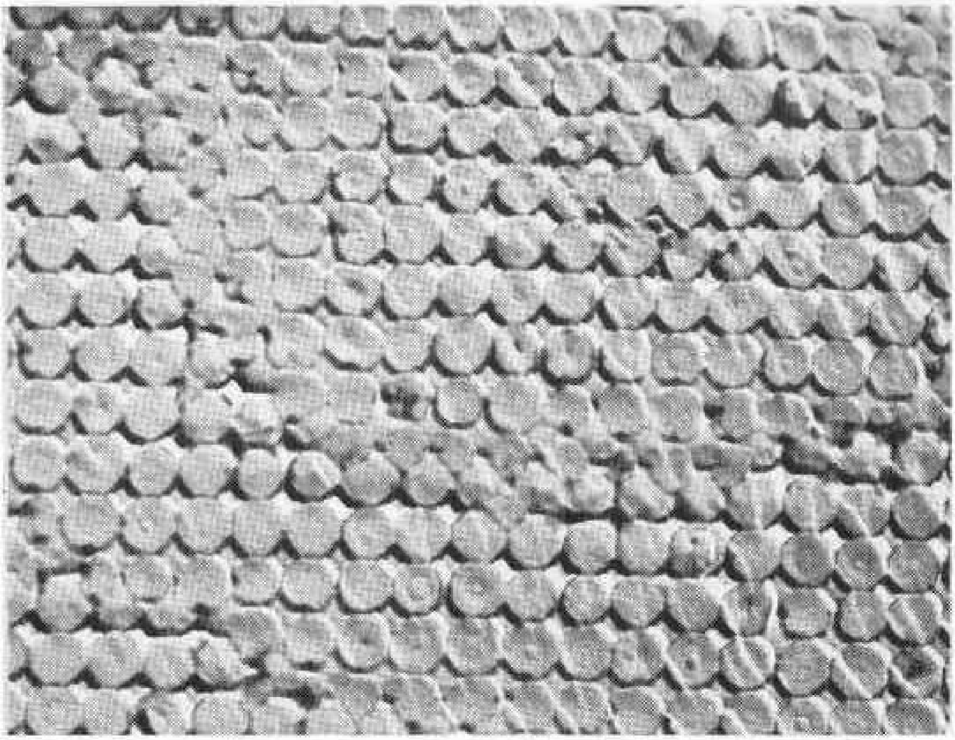

Figure 7. Growth structure in spheres shown by light etching *(18,000x)*

it is possible to reveal structural details within the spheres. Within many of the spheres a central dot and a concentric ring are seen *(Figure 7)*. This may represent a nucleus and a growth ring and suggests that the spheres have grown at a constant rate in an undisturbed aqueous medium. Subsequently, they settled and packed in a regular manner and were cemented together, leaving voids between them.

The geochemical significance of these results is now receiving attention at CSIRO, Division of Applied Mineralogy, and may eventually lead to a synthetic opal.