Microstructure and Crystallinity of Gem Opals

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Abstract

Gem opals, from volcanic host rocks from a variety of sources, have been examined by electron microscopy and diffraction. They are generally a mixture of amorphous and crystalline silica, the extent of crystallinity varying between samples from different localities. The crystalline phase in some samples has been identified as tridymite. Their microstructures are compared with those of gem opals from deposits in sedimentary rocks, and with specimens heated in the laboratory. Changes in morphology produced by sintering occur at about 400°C, and crystallization at about 1100°C. Both tridymite and cristobalite were identified in material recrystallized by heating.

Introduction

The major sources of the world's gem opals are the Australian fields of Andamooka, Coober Pedy, and Lightning Ridge. Here, the opal occurs in sedimentary host rocks, where it was deposited in cavities by concentration of an aqueous solution of silica, forming first a gel and finally particles of silica generally 0.1-0.5 μm in diameter (Darragh *et al*, 1966). In this type of gem-quality opal the particles are uniform in size and form a three-dimensional optical diffraction grating which produces the play of color (Sanders, 1968). The much more common potch opal accompanying the gem quality material is similar in structure, but the particles are not uniform in size or shape (Sanders, 1964). Because the particles consist of several (generally <5) concentric shells, Darragh *et al* (1966) suggested that they were formed by aggregation in a gel of smaller, primary particles several hundred Ångstroms in diameter.

Precious opal also occurs in smaller quantities in many other places in the world, but mostly in conjunction with rocks of volcanic origin rather than in sedimentary host rocks. The most extensive and best known deposits occur in Mexico, where opal is mined commercially. Typically it is found in vesicles in solidified lavas, and because it exhibits a weaker play of color than that of opal from the sedimentary fields in Australia, it can generally be distinguished by eye. Opal of like origin and similar in appearance to Mexican opal is also found in Australia near the east coast, but in smaller quantities than on the sedimentary fields. Electron microscopy showed that the diffracting structure of some of these opals is less distinct than that of opals from sedimentary host rocks, but the diffracting arrangement of particles can often be revealed only by etching the fracture surfaces and examining replicas (Darragh and Sanders, 1969; Sanders and Darragh, 1971).

This paper compares the structure and crystallinity of precious opal from these less common volcanic deposits with that of gem opal from the Australian sedimentary fields. The two types will be distinguished as "volcanic" or "sedimentary" opal. For completeness comparison is also made with some synthetic samples.

An extensive examination by X-ray diffraction of opaline silicas has established that gem opals are in the least crystalline group and give a diffuse diffraction pattern of broad rings corresponding to lattice spacings of 4.1, 2.0, 1.5, and 1.2 Å (Jones and Segnit, 1971). Electron microscopy has many advantages over X rays for examining materials of poor crystallinity, such as opal. First, images can be obtained from thin fragments, showing the shape and distribution of any crystalline components. Second, diffraction patterns can be obtained and used to identify phases, and because of the shorter wavelength of the electrons, line broadening from small crystals is much less than for X rays. Third, single crystal patterns can be obtained from individual crystals less than 1 μm in size.

It seems possible that when crystallinity occurs in gem opal, it may have been caused by a temperature rise produced by a subsequent flow of lava over the opal deposit. Samples of specimens of each type of

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opal were therefore examined by transmission electron microscopy after they had been heated in a controlled manner to temperatures up to 1200°C.

Experimental

As far as possible, specimens were from identified localities, and frequently with the host rock attached. The kindness of many people in providing overseas specimens is gratefully acknowledged.

Three different synthetic samples were examined. Two were made by the C.S.I.R.O. Division of Applied Mineralogy (L1, L2 in Table 3); L1 was made by the concentration of pure silicic acid in aqueous solution at about 80°C, and the subsequent separation to produce mono-dispersed spheres of silica; for L2, spheres of silica were made from tetraethylorthosilicate dissolved in alcohol and reacted with water (Stöber, Fink, and Bohn, 1968). In both cases the spheres were allowed to settle, dehydrate, and consolidate. The third sample, L3, was a commercial sample, kindly provided by P. Gilsen.

A small (~10 mg) typical piece was broken off each specimen and ground to a powder in a mortar, first dry and then in acetone. Fragments were collected on carbon-coated grids. In annealing experiments a specimen was broken into pieces (~1 gm) which were heated in an open ceramic boat in a tube furnace at a set of controlled temperatures. Small pieces were subsequently broken off and ground to fragments which were mounted for examination in the electron microscope.

Specimens were examined in a Philips EM 200 electron microscope at 100 kV. Diffraction patterns were obtained from individual fragments about 1 μm in size, isolated by a selector aperture.

Results

Sedimentary Fields

Microstructure. When opals fracture, the break generally occurs through rather than between the silica particles, so that thin fragments formed by grinding consist of sections of the particles and the naturally formed cavities between them. Figure 1a shows how the appearance of fragments in an electron microscope at lower magnifications is dominated by a regular array of cusp-shaped cavities; sections of the spherical particles can also be distinguished. No internal structure is visible in thin edges of these fragments at higher magnifications (Fig. 1b); the small variation in contrast or graininess is about the same as that from the supporting carbon
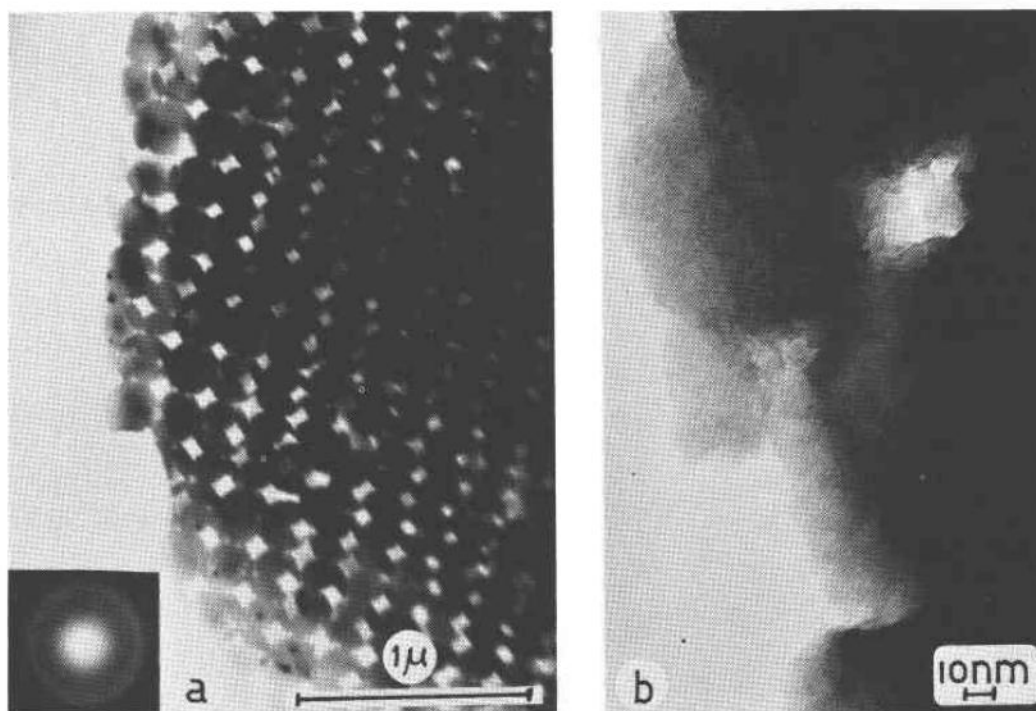

FIG. 1. Transmission electron micrographs of fragments of gem opals from sedimentary hosts: (a) Andamooka, 35,000 ×: insert, diffraction pattern consisting of a strong halo at about 4 Å; (b) detail of the thin edge of a fragment from Lightning Ridge, 400,000 ×.

film which always shows some random variation of electron density in slightly underfocussed images.

Crystallinity. Although it had been established previously that opal from sedimentary fields is amorphous to electrons (Jones, Sanders and Segnit, 1964), samples from a number of these fields were re-examined, and samples from a few additional fields included. The diffraction patterns from all samples (Table 1) consisted mainly of a diffuse halo centered on a spacing of about 4.1 Å (Fig. 1a insert), any other haloes being concealed by the diffuse rings of the carbon supporting film (Jones, Milne, and Sanders, 1966); these opals are therefore confirmed to be amorphous.

Deposits in Volcanic Rocks

Microstructure. The appearance in the electron microscope of opal from volcanic hosts (Table 2) depended upon its origin. Two samples from Australian deposits (V1, Rocky Bridge Creek, and V2, Tooraweenah) and one sample from Czerwer-nitza (V3) appeared similar to those from sedimentary deposits. In all other samples no cusp-shaped holes were detected, and there was no evidence at comparable magnifications (Fig. 2a) of the diffracting array of particles seen in sedimentary opals (Fig. 1a). At higher magnifications a microstructure of small particles could be resolved to varying extents. These particles, about 100 Å in size, linked together, are shown in Figure 2b. In other samples, although the individual particles could not be resolved, the fragments nevertheless appeared porous (Fig. 2c) and are so described in Table 2.

Crystallinity. The diffraction patterns (Fig. 3) varied from a single halo ($d = 4.1$ Å) as for "sedimentary" opal, through sharper continuous rings, to spotty rings in which single crystal nets of spots could be distinguished. Diffraction patterns like these, taken from single fragments of about the same size, were used to assess the extent of crystallinity in samples from various sources (Table 2).

The most significant feature of these patterns is the innermost ring, corresponding to the halo in Figure 3a. It consisted sometimes of a single ring whose sharpness depended upon the sample (Fig. 3b), or in the most crystalline samples it consisted of at least two resolved rings, whose positions were usually defined by spots (Fig. 3c). In the latter case the presence of tridymite is immediately suggested, and measurement confirmed the identification.

Figure 4 shows the positions of the most intense reflections expected from cristobalite and tridymite

TABLE 1. Opal Associated with Sedimentary Host Rock

	Locality	Country	Degree of Crystallization
S1	Andamooka	South Australia	None
S2	Coober Pedy	South Australia	None
S3	White Cliffs	N.S.W., Australia	None
S4	Kalgoorlie	W.A., Australia	None
S5	Lightning Ridge	N.S.W., Australia	None
S6	Grawin	N.S.W., Australia	None
S7	Quilpie	Queensland, Australia	None
S8	?	Brazil	None

(Dollase, 1965; Frondel, 1962), and indicates the difficulty of distinguishing a mixture of cristobalite and tridymite from pure tridymite in the patterns of diffuse rings. Careful measurement of patterns like that in Figure 4, in which the innermost ring was not resolved into components, gave $D = 4.12 \pm 0.03$ and $d = 2.50 \pm 0.01$ Å for the two clearest rings. This does not distinguish the material as cristobalite rather than tridymite, but the width of the innermost ring suggests that the crystalline phase is tridymite. Annealing experiments, to be described later, support this interpretation.

The diffraction patterns from the most highly

TABLE 2. Opal Associated with Volcanic Host Rocks

|	Locality	Country	Internal Structure	Degree of Crystallinity
V1	Rocky Bridge Creek	N.S.W., Australia	None	None
V2	Tooraweenah	N.S.W., Australia	None	None
V3	Czerwenitza I	Hungary	None	None
V4	Spencer	Idaho, U.S.A.	None	None
V5	Melanie	Queensland, Australia	Porous	Slight
V6	Mt. Bougrom	Queensland, Australia	100-150 Å primaries	Slight
V7	?	Indonesia	100 Å primaries	Slight
V8	Virgin Valley	Nevada, U.S.A.	Porous	Slight
V9	near Redlands	California, U.S.A.	50-100 Å primaries	Slight
V10	Tevern	N.S.W., Australia	100 Å primaries	Moderate
V11	?	Mexico	Porous	Moderate
V12	?	Honduras	100 Å primaries	Extensive
V13	Lead Pipe Springs	California, U.S.A.	70-150 Å primaries	Extensive
V14	Czerwenitza II	Hungary	50-100 Å primaries	Extensive
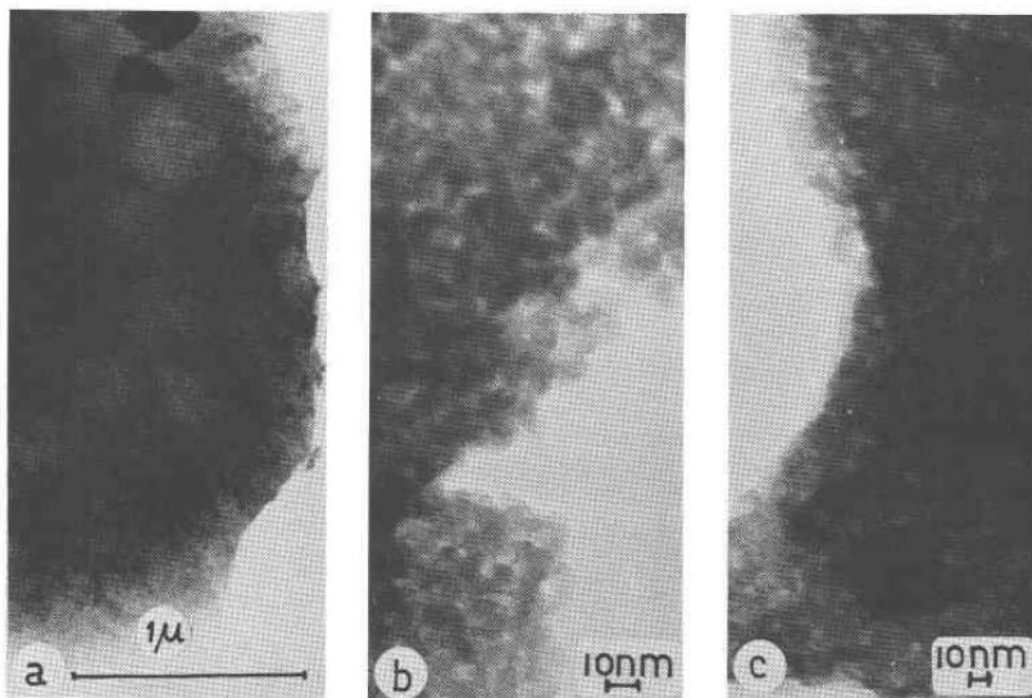
FIG. 2. Microstructure of volcanic gem opals composed of 10 nm primary particles: (a) Melanie, Queensland (V4), 35,000 ×: (b) Melanie, Queensland (V4), 450,000 ×; (c) Mexico (V10), 300,000 ×.

crystalline samples (*e.g.*, V12, Lead Pipe Springs, California, U.S.A.) contained streaks passing through the first ring of the group of three innermost tridymite rings (Fig. 3d). Some suitable fragments were selected and tilted in the electron mciroscope to give essentially single crystal patterns which were simple reciprocal lattice nets. From these it was established that the six patterns analyzed were consis-
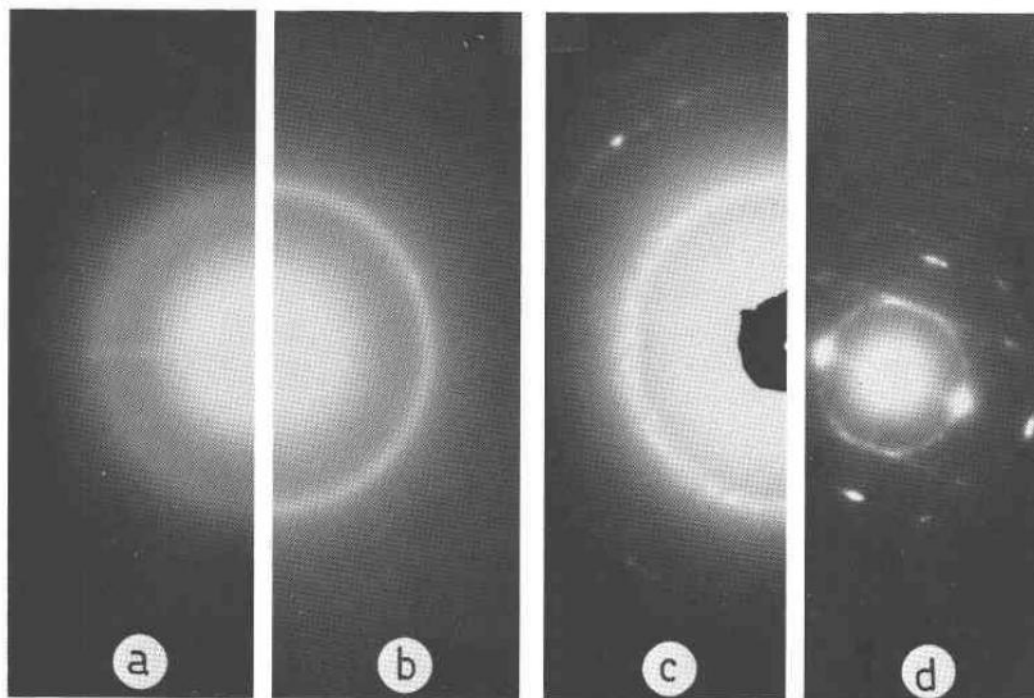

FIG. 3. Examples of the types of diffraction patterns given by gem opal from volcanic host rocks. Specimen localities are: (a) Rocky Bridge Creek, N.S.W. (V1); (b) Mt. Bougrom, Queensland (V5); (c) Tevern, Queensland (V9); (d) California (V12); the diffraction pattern in (d) is reproduced at a lower magnification to show the diffraction streaks.

tent with tridymite and not with cristobalite. The streaks passed through $h0l$ ($h = 2n$) tridymite reflections in the $c*$ direction.

Morphology of the Crystalline Component. By means of the dark field technique in which an image is formed by transmitting diffracted electrons through the objective aperture, it is possible to distinguish those parts of a fragment contributing to the crystalline component of the diffraction patterns. In this way it was established that in general only small parts of fragments were contributing to the sharp rings. Having identified such areas at first by the dark-field technique, one can subsequently recognize them in normal bright-field images where they appear as dark patches in a more homogeneous background. They are marked by arrows in Figure 5.

In samples judged to be "slightly" to "moderately" crystalline, and giving diffraction patterns as in Figure 3b, most fragments contained irregularly-shaped crystals with maximum dimensions about 50-200 Å. Figures 5a and b show examples of such crystalline patches in a matrix of the primary particles. Generally only a small proportion of each fragment was crystalline. Where crystallinity was more extensive, some crystals took the form of needles about 100 Å wide and about 1000 Å long, sometimes in bundles (Fig. 5c). The most extensive crystallization yet observed was found in a sample of gem opal

FIG. 4. Diffraction pattern of a sample from Mt. Bougrom, Queensland (V5) together with *111* and *200* rings from aluminium. The most intense lines from cristobalite ($C\beta$) and tridymite ($T\alpha$) are marked.

known to be from Mexico, but otherwise unidentified. It appeared to have been almost completely converted to crystalline needles, of more or less uniform size in random directions and so forming a criss-cross network throughout the sample. Micrographs (Fig. 6) of a surface extraction replica show its structure, at low magnification (Fig. 6a), at intermediate magnification (Fig. 6b) showing the network of needle-shaped crystals, and at high magnification (Fig. 6c) showing the shape and internal structure of individual needles. These crystals are good examples of the structure and shape of well-developed crystallinity in opal generally.

Intense irradiation with electrons in the electron microscope destroyed the crystallinity, although the shape of the crystalline area was retained. For this reason, care is necessary in studying these materials
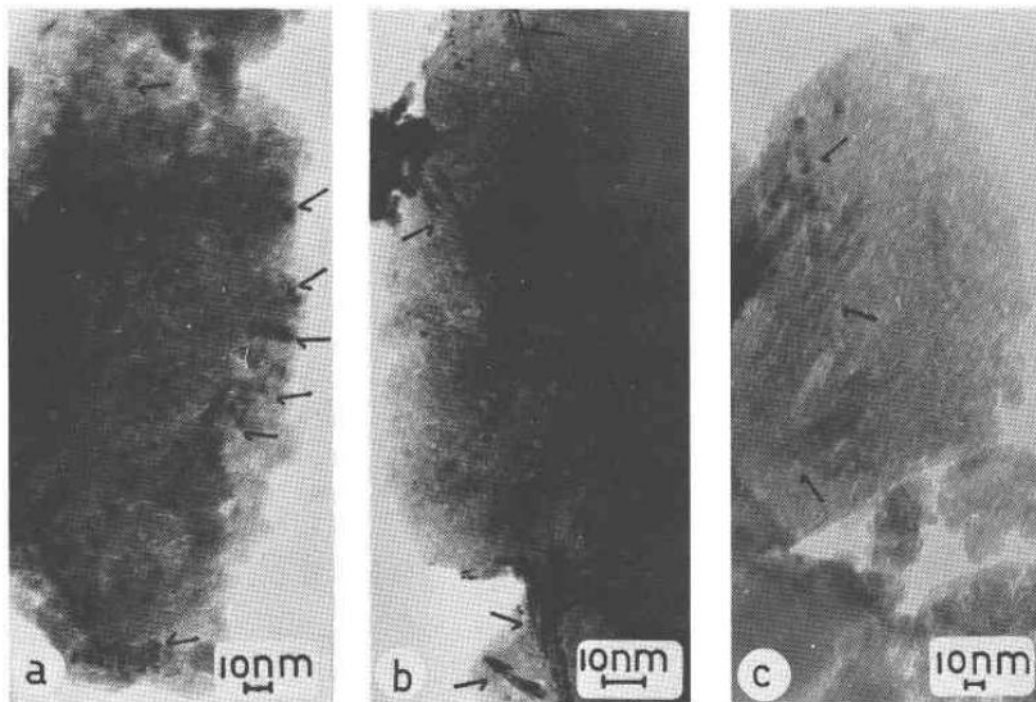

FIG. 5. Examples of crystals within a matrix of otherwise amorphous silica in fragments of volcanic gem opal. (a) "slightly" crystalline, Mt. Bougrom, 350,000 ×; (b) "moderately" crystalline, Honduras, 600,000 ×; (c) "extensively" crystalline, Honduras, 250,000 ×.
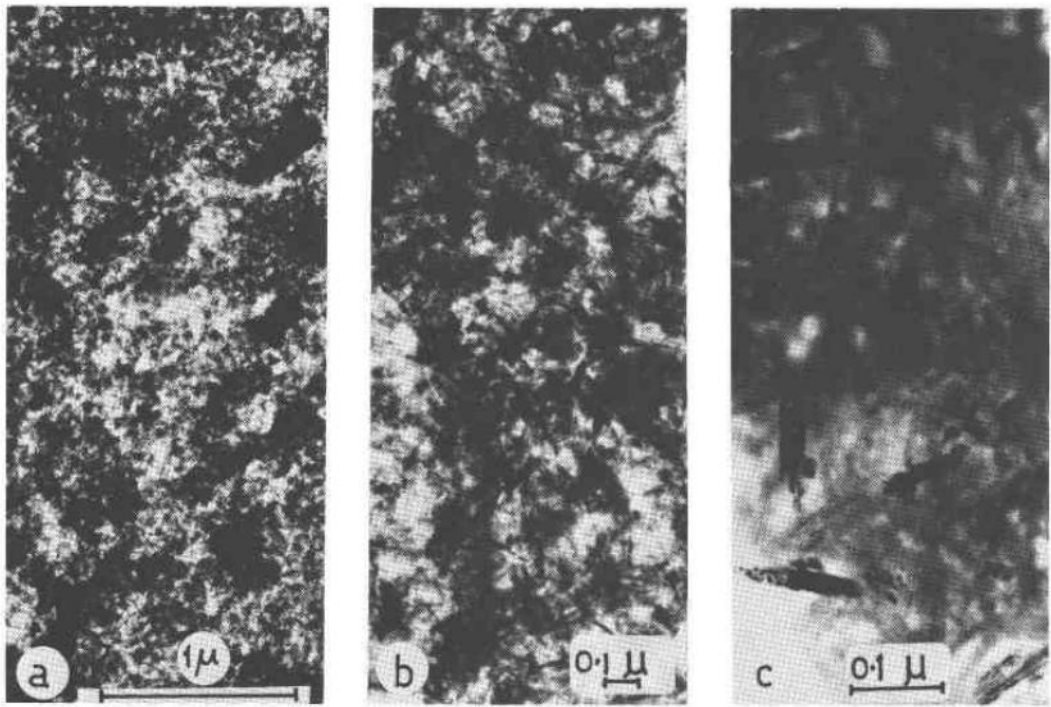
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FIG. 6. An extensively crystalline gem opal from Mexico: (a) surface extraction replica; the darker patches, about 1 mm in size, are the regularly arranged particles which make up the diffracting array; 30,000 ×. (b) part of area shown in (a); 50,000 ×. (c) Fragment showing almost complete conversion to needles, and faults within the crystals, 140,000 ×.

at high magnification to ensure that no changes are produced by the electron beam.

Synthetic Material

In three different synthetic samples no crystallinity was detected, and no microstructure could be seen by transmission electron microscopy of thin edges of fragments (Table 3). In these respects the microstructure of the synthetic material is similar to that of opal from sedimentary deposits.

Annealing

Heating caused crystallization and internal morphological changes due to sintering in both volcanic and sedimentary opals. In all cases sintering preceded the onset of crystallization by about 700°C. *Sintering.* Opal from both sedimentary and volcanic deposits contains natural voids. In the former they are the regularly arranged cavities left

TABLE 3. Synthetic Opal

	Locality	Country	Degree of Crystallization
L1	CSIRO I	Australia	None
L2	CSIRO II	Australia	None
L3	Gilsen	Switzerland	None

between the spherical particles and are therefore cusp-shaped holes with a maximum dimension of about 0.1 μm (Fig. 1a). In the "volcanic" opals they are the much smaller, irregular spaces between the primary particles (Fig. 2). Sintering by heat changes the shapes of the cavities into spherical voids, so that one then sees circular pores in an otherwise featureless matrix. In both types of opal, sintering is simply detected by a close examination of the shapes of the cavities, which change from cusps to rounded holes. A set of specimens from each of the three different Australian sedimentary fields of Lightning Ridge, Andamooka, and White Cliffs, was heated for 10 minutes at a variety of temperatures up to 1100°C. For each set sintering became appreciable in the temperature range 350°C < T < 480°C. Although the majority of fragments which were viewed contained round holes in sintered samples, some fragments showed no signs of sintering; this indicates either an inhomogeneity in the sample, or that the time was insufficient for temperature equilibrium to have been attained. In gem quality sedimentary specimens that exhibit diffraction colors, heating to 600°C or 700°C changed the shapes of the holes but did not alter their spatial arrangement, so that they still formed a regular array (Fig. 7c; *cf* Fig. 1a). This is in keeping with the observation that heating up to about 1000°C
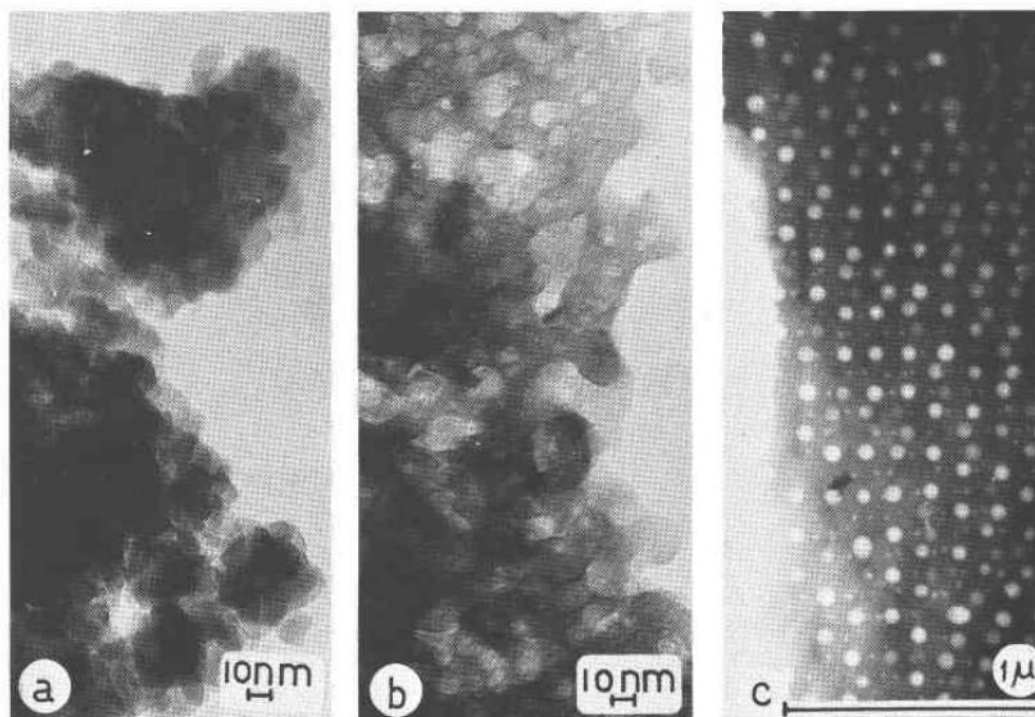
FIG. 7. Morphological changes produced by heating amorphous gem opals: (a) before heating sample from Mt. Bougrom, Queensland (V5), 300,000 ×; (b) same sample after being heated for 4 hours at 800°C, 300,000 ×; (c) opal from White Cliffs, N.S.W. (S3) after being heated for 10 min at 700°C, 40,000 ×.

generally does not destroy the color in opal, showing that the diffracting array is retained.

The onset of sintering is less easily detected in samples from volcanic sources, but it was found to be in the range $400°C < T < 600°C$. The change to round cavities of irregular size is shown in Figures 7a, b. *Crystallization.* Crystallization is detected by diffraction, just as for natural material. In opal from sedimentary fields, the initially amorphous material was completely crystallized after 3 hours at 1200°C to give irregularly shaped grains, about 1 μm diam., of either cristobalite or tridymite. Partial crystallization (*e.g.*, ½ hour, 1200°C) produced similar grains quite unlike the needle-shaped crystals in naturally occurring ring opal, in an otherwise amorphous matrix. Diffraction patterns from a completely recrystallized sample (Fig. 8), with many fragments in the diffraction field, look very similar to the patterns from well crystallized natural specimens (Fig. 3c). In particular, the ring from spacings near 4 Å is well resolved into components. With this sample it was possible to select fragments which were single crystals and by orienting them in the electron microscope to obtain simple reciprocal lattice sections. Positive identification of the phase is then possible; it was found that the low temperature form of cristobalite (Dollase, 1965)

predominated but some patterns from high tridymite were also identified, (of fourteen patterns analyzed, twelve were from cristobalite and two from tridymite.) With this knowledge it is possible to see that the ring patterns of Figures 8 and 3c represent patterns from these two phases, super-imposed; consequently, the group of rings near 4 Å spacings consists of a central component containing many spots corresponding to a high concentration of cristobalite, and less densely populated outer components from smaller concentrations of tridymite.

The crystals of cristobalite were twinned and contained faults on planes parallel to (101). However, there was no evidence of an intergrowth of

FIG. 8. Diffraction pattern from initially amorphous opal from Andamooka (S1) after being heated to 1200°C for 3 hours. This diffraction pattern comes from an area containing many fragments.

cristobalite and tridymite. The patterns from single fragments of tridymite contained no reflections consistent with intergrown cristobalite, and vice-versa.

Discussion

Within the limited number of localities examined here, "sedimentary" gem opals consistently exhibit no microstructure in transmission electron microscope (TEM) images at high magnification, to the limit of the present resolution (~4 Å). Their electron diffraction patterns were all diffuse, suggesting that such opals are amorphous. The synthetic samples were also structureless at this scale, and amorphous.

Some opal from volcanic rocks has a similar structure, but more often it is partly crystalline and the extent of crystallinity varies with its origin. Furthermore, a microstructure of primary non-crystalline particles, about 100 Å in diameter, can frequently be detected in these specimens. This structure is consistent with the appearance of replicas of fracture surfaces of these types of opal (Darragh and Sanders, 1969) in which a rough texture on a 100 Å scale is visible. Similar structures have been recognized in phytoliths (silica particles within plants), tabashir (silica deposited inside bamboo), and in silica gel (Jones et al, 1966). In these cases the silica is certainly deposited at ambient temperatures from an aqueous solution. It therefore seems likely that the primary particles in opal in volcanic rocks were formed under similar ambient conditions.

It is surprising that the structure of concentric shells in spheres in opal from sedimentary deposits (Daragh et al, 1966) is not apparent in thin fragments examined by direct TEM. This implies that between the primary particles there is infilling by silica which is indistinguishable by TEM but which has sufficiently different solubility in HF for the primary particles to be made visible by etching. If the shell width represents the diameter of the primary particles, this is about 500 Å, and is therefore much larger than the size of primary particles in volcanic opals.

Many of the samples from volcanic deposits contained crystals imbedded in the otherwise unchanged amorphous matrix. The appearance of these crystals—and the way they have grown within the matrix of primary particles to sizes greater than that of the particles—is similar to that of crystals formed by heating compacts of amorphous materials produced by precipitation from aqueous solutions, such as $AlOOH$, ZrO_2, MoO_3. These materials are also composed of primary particles a few hundred Ångstroms in diameter, and when heated, they

recrystallize before they sinter; crystallization proceeds from particle to particle to produce crystals larger than the primary particles (Garrett and Sanders, unpublished).

The relative stabilities of the phases of silica have been considered recently by Jones and Segnit (1972). Quartz is the phase of silica thermodynamically stable at ambient temperatures; the transition to tridymite occurs at 876°C and the tridymite to cristobalite at 1470°C. The absence of reflections with a lattice spacing of 3.4 Å, a diagnostic for quartz, shows that quartz is not present in the specimens examined. The next most likely phase is tridymite, and its presence in volcanic opals has been established here. However, Wahl, Grim, and Graf (1961) using X rays, found that amorphous opal crystallized to cristobalite above 1000°C, and they detected no tridymite in their experiments on heated quartz and opal. Also Mizutani (1966) detected no tridymite when amorphous silica was heated at 300°C in aqueous KOH under pressure, finding cristobalite first and then quartz. It seems likely that the tridymite crystals are too small to be distinguished by X rays, particularly in the presence of small cristobalite crystals, but that they can be recognized in electron diffraction patterns.

The essential difference between cristobalite and tridymite is the stacking sequence of hexagonally linked tetrahedra of SiO_4, the sequence being cubic in cristobalite and hexagonal in tridymite (Frondel, 1962). There was no evidence for an intergrowth of cristobalite and tridymite as might be expected if the stacking sequence changed from cubic to hexagonal within the one grain.

The co-existence of separate crystals of cristobalite and tridymite in samples heated in the laboratory suggests that crystallization was nucleated in the random network of linked SiO_4 tetrahedra at places where linkages naturally occurred in the planar arrangement which would be appropriate for the formation of cristobalite or tridymite. Along with faulting and microtwinning, once a stacking sequence had been established, it was retained in further growth and determined whether the crystal became tridymite or cristobalite.

Bossi et al (1973) found that pure amorphous silica did not sinter below 1100°C, and that the onset of sintering was lowered to about 600°C by the addition of 1-3 percent NaOH. Australian opals have been found to contain generally up to 0.5 percent Na (Bayliss and Males, 1965). This suggests that impurities control the sintering kinetics in natural opals.

The lower temperatures observed here for the onset of sintering may be due in part to the nature of the impurities, and in part to the high sensitivity of TEM for detecting the morphological changes produced by sintering.

Several conclusions can be drawn from the observation that opals heated in the laboratory sinter at a much lower temperature than that required for crystallization, whereas there is no sign of sintering in opals containing naturally-formed crystals. First, this seems to preclude the possibility that crystallization in natural volcanic opals was produced thermally by a flow of lava on top of the opal deposit after its formation. Second, it suggests that the mechanism of natural crystallization was quite different from that of laboratory heated samples.

The process of sintering is one of molecular rearrangement. By contrast, to form crystals of tridymite or cristobalite, which contain planar hexagonal Si–O networks, bonds must be broken in the random chains in the amorphous network. This is why in annealing experiments much higher temperatures are required for crystallization than for sintering. But when crystals are observed in natural volcanic opals, the matrix is not sintered, showing that the crystallization has taken place by a low temperature process. In natural crystallization, impurities may aid the rupturing of bonds, in a catalytic manner. The temperature being low, the impurity cannot diffuse away from the site of nucleation and so crystallization can continue there. On this basis the concentration of crystals should depend on the concentration of the impurity and, because the size of the crystals is perhaps indicative of the time the process has been operating, size should be a measure of the age of the material. If this is so, then the opal from the sedimentary fields contains no crystals either because it is younger than that from volcanic rocks, or because it does not contain the type of impurity necessary to catalyze crystallization.

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