

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 patch 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

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. Gilson.

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

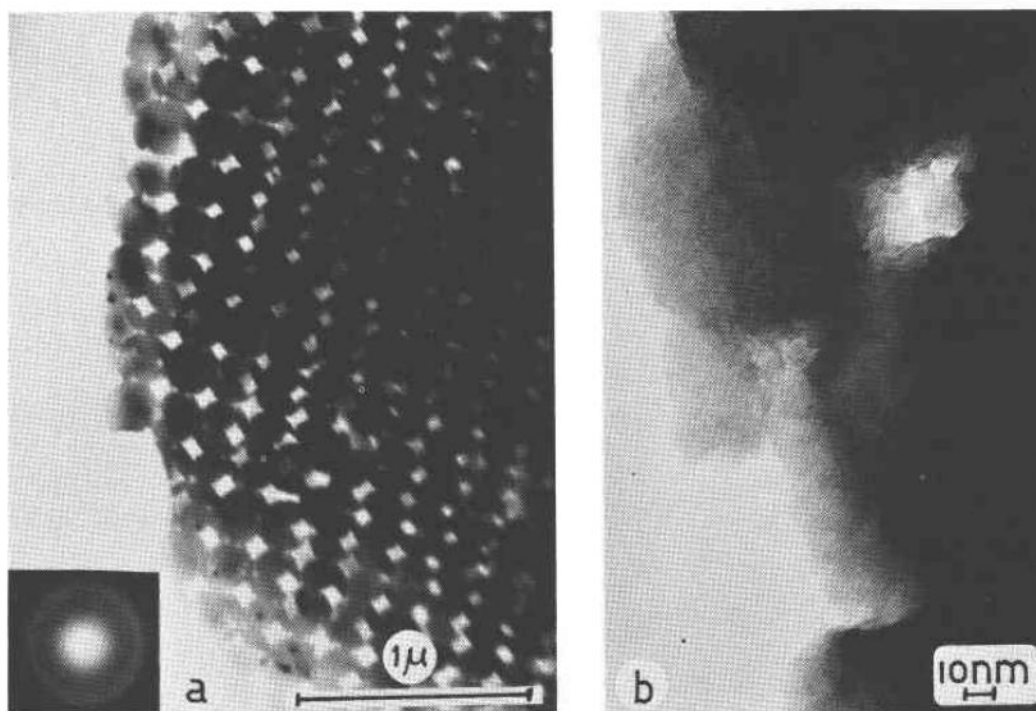


FIG. 1. Transmission electron micrographs of fragments of gem opals from sedimentary hosts: (a) Andamooka, 35,000 \times ; insert, diffraction pattern consisting of a strong halo at about 4 Å; (b) detail of the thin edge of a fragment from Lightning Ridge, 400,000 \times .

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 (VI, Rocky Bridge Creek, and V2, Tooraweenah) and one sample from Czerwenitza (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	Cooper 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
VI	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

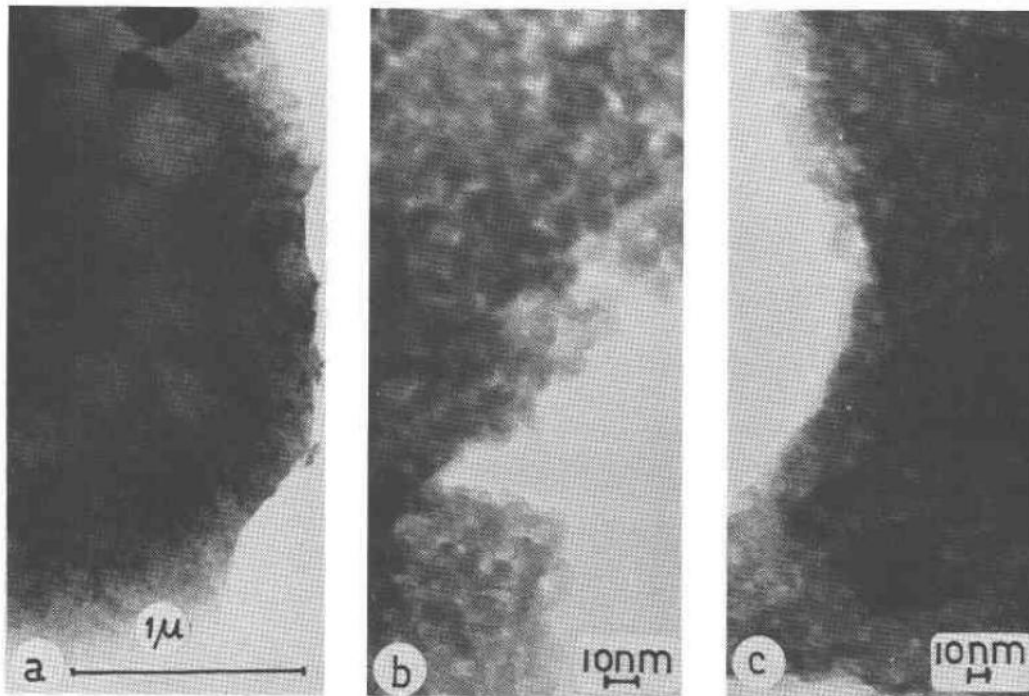


FIG. 2. Microstructure of volcanic gem opals composed of 10 nm primary particles: (a) Melanie, Queensland (V4), 35,000 X; (b) Melanie, Queensland (V4), 450,000 X; (c) Mexico (V10), 300,000 X.

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 microscope to give essentially single crystal patterns which were simple reciprocal lattice nets. From these it was established that the six patterns analyzed were consis-

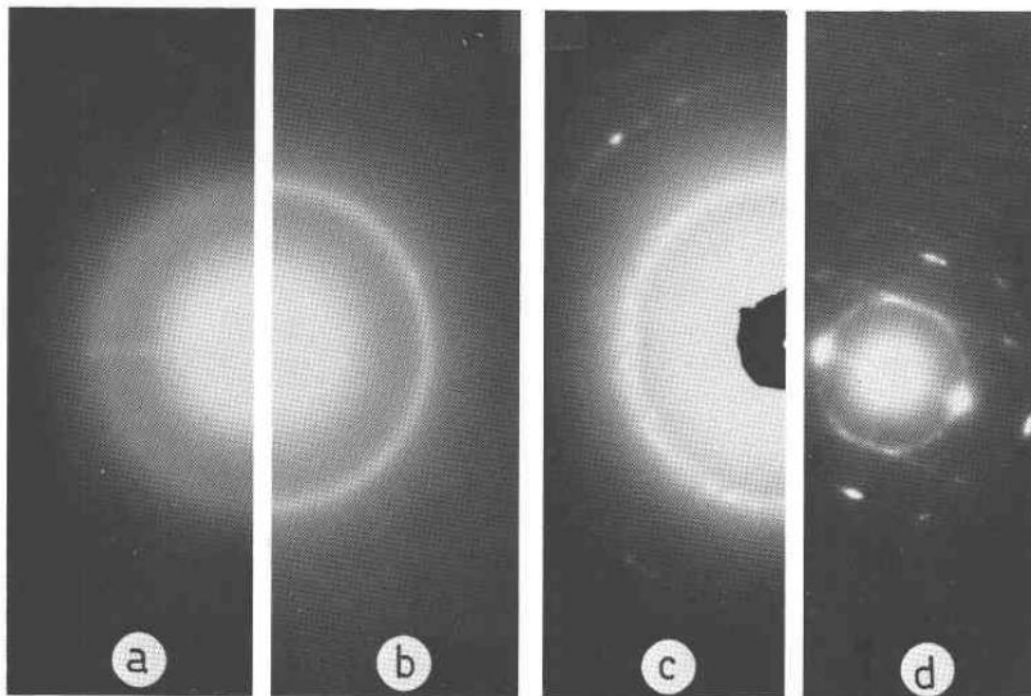


FIG. 3. Examples of the types of diffraction patterns given by gem opal from volcanic host rocks. Specimen localities are: (a) Rocky Bridge Creek, N.S.W. (V1); (b) Mt. Bougrom, Queensland (V5); (c) Tevern, Queensland (V9); (d) California (V12); the diffraction pattern in (d) is reproduced at a lower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

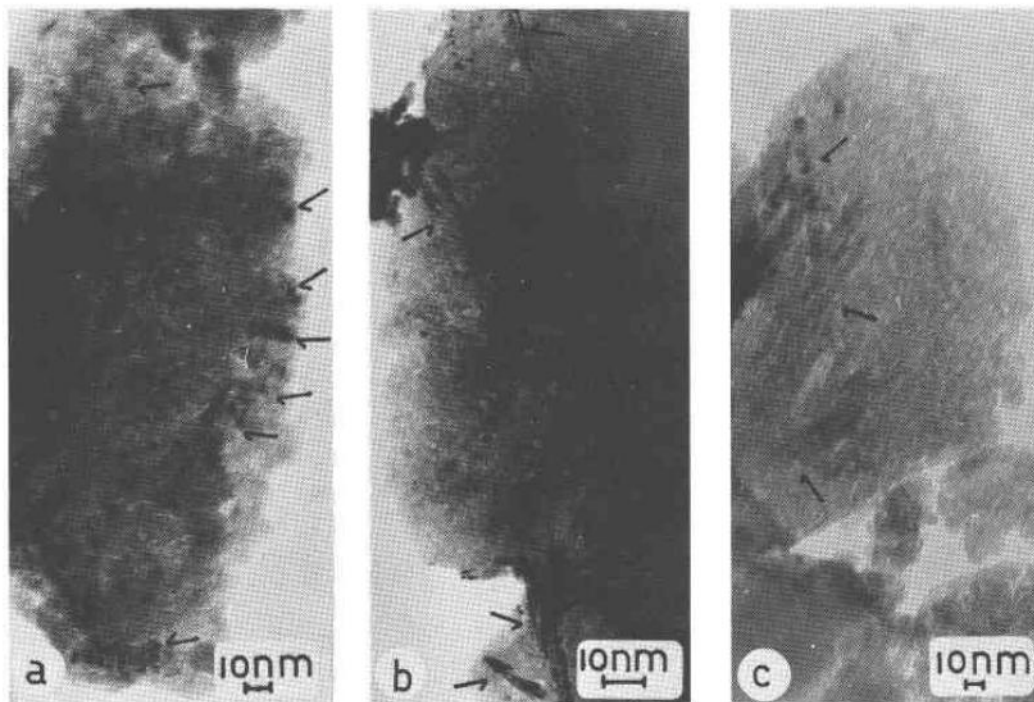


FIG. 5. Examples of crystals within a matrix of otherwise amorphous silica in fragments of volcanic gem opal. (a) "slightly" crystalline, Mt. Bougrom, 350,000 X; (b) "moderately" crystalline, Honduras, 600,000 X; (c) "extensively" crystalline, Honduras, 250,000 X.

