

Water in sphere-type opal

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SUMMARY. Surface areas of 'amorphous'-type opals measured by nitrogen-absorption techniques were not consistent either with the surface area of the spheres of about 2000 Å diameter observable by electron microscopy or with the thermal dehydration data. This apparent inconsistency can be explained in terms of a smaller particulate structure of the order of 100–200 Å shown by higher resolution electron micrographs. This structure also accounts for a marked shrinkage shown in dilatometer curves of this type of opal.

IN an earlier paper (Segnit, Stevens, and Jones, 1965) the part played by water in opaline silica was discussed. In 'amorphous'-type opals it was found that there were anomalies in the relationship between water and hydroxyl content and certain physical properties. Although the surface area of these opals as measured by nitrogen absorption was small (less than 0.5 m²/g) an anomalously high proportion of the water appeared to be bound as surface hydroxyls. Further electron-microscopic examination and supplementary infra-red and dilatometric measurements have led to an explanation for these phenomena.

Electron-microscopic examination. With the exception of hyalite, geyserite, and diatomaceous earth, all 'amorphous'-type opals we have examined have a basic physical structure of more or less close-packed spheres of silica of diameter of the order of 1500–3500 Å (Jones, Sanders, and Segnit, 1964). Although regular packing of these spheres is responsible for the play of colours in precious opal (Pense, 1963; Sanders, 1964), in most cases the packing is not sufficiently regular to cause light diffraction. Higher resolution electron micrographs showed that the internal structure of these spheres is not homogenous, showing evidence of surfaces within the spheres. Commonly a concentric arrangement is conspicuous (Darragh *et al.*, 1966) and closer examination reveals in many cases a smaller particulate structure of the order of a few hundred angstroms or less (fig. 1).

Infra-red data. In our previous publication (1965) only one 'amorphous'-type opal was studied in detail. We have now examined the infra-red spectra of a further four 'amorphous' and five 'crystalline' opal samples using a Fluorlube mull in a Unicam SP200 spectrometer. We find nothing in these results to conflict with our earlier conclusions. Fig. 2 shows typical infra-red absorption curves of some of these opals in the OH region of the spectrum with corresponding curves for a 'crystalline' opal. In all cases of 'amorphous' opals a major absorption peak at 3700 cm⁻¹ and a weaker at

3550 cm^{-1} were recorded, indicating the presence of single and double surface hydroxyl groups. This therefore appears to be typical of 'amorphous'-type opals.

Dilatometry. Dilatometric curves of natural opals obtained using a Chevenard dilatometer show a wide variety of effects. Crystalline opals (disordered cristobalite-tridymite) examined showed an initial expansion of the order of 1% up to 400–500 °C followed by a shrinkage, commonly negligible, but which in some cases is sufficient

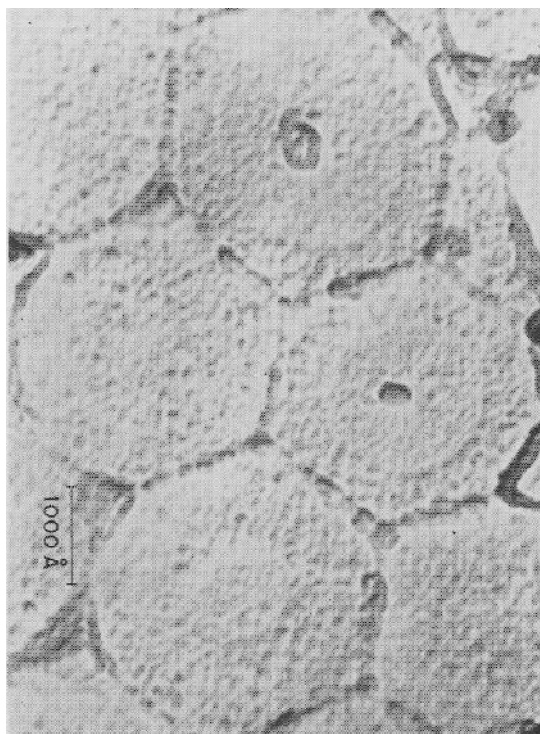
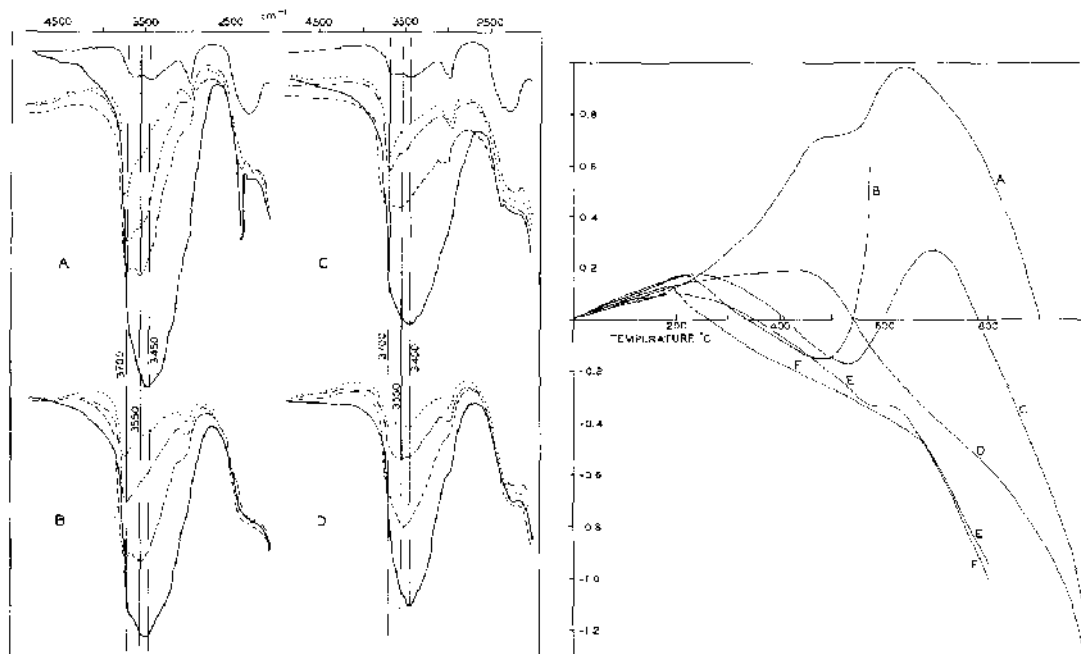


FIG. 1. Electron micrograph (carbon replica, platinum shadowed) of an 'amorphous'-type opal showing 2700 Å spheres composed of small particles.

at 1000 °C to compensate the original expansion. Comparable results have been obtained by Jourdain and Dulery (1950). Our results on these materials will be discussed in more detail in a paper on the structure of opal.

The 'amorphous' opals showed much less regularity in their expansion curves (fig. 3). Certain features, however, are common to most curves. An initial expansion up to 200–50 °C is terminated by an inflection (except for D). The behaviour up to about 450–500 °C is varied, but at about 450–650 °C another inflection occurs. Unless affected by severe macroscopic cracking all samples undergo strong shrinkage at higher temperatures. The same bar of opal used to produce curve F (fig. 3) was also heated a second time in the dilatometer (A, fig. 4). The expansion is little greater than that of silica glass (B, fig. 4) and no inflections are encountered, thus confirming that the inflections are connected with loss of water from the original opal.

The infra-red spectra shown in fig. 2 indicate that twin hydroxyls are lost preferentially to single hydroxyls with increasing temperature; twin hydroxyls are largely removed between 200 and 600 °C, which corresponds to the interval between the two major inflections in the dilatometer curves. Above 600 °C, most of the remaining hydroxyls are stripped off. The 200 °C dilatometer curve inflection may therefore be



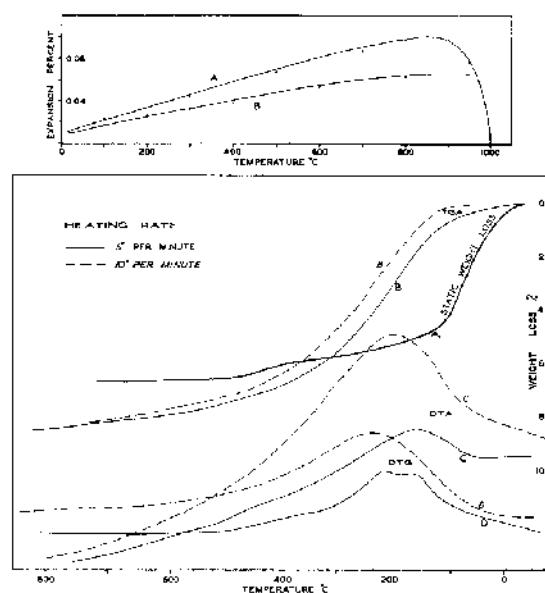
FIGS. 2 and 3: FIG. 2 (left). Infra-red absorption curves of 'amorphous'-type (A-C) and crystalline (D) opals before and after heating. Top curve in each case gives absorption of Fluorlube mount. — original opal; ---- after heating to 200 °C; -.-.- after heating to 400 °C; after heating to 600 °C. A, Rocky Bridge, New South Wales; B, Tasmania; C, Andamooka, South Australia; D, Williamstown, South Australia. FIG. 3 (right). Dilatometer curves of 'amorphous'-type opals. A, Transparent patch opal, Andamooka, South Australia. B, Grey patch opal, Coober Pedy, South Australia. C, Grey patch opal, Coober Pedy, South Australia. D, Transparent patch opal, Mintabie, South Australia. E, Wood opal, White Cliffs, New South Wales. F, Grey patch opal, Coober Pedy, South Australia.

tentatively correlated with the onset of loss of twin hydroxyl groups, and the 600 °C inflection with final loss of most of the single hydroxyls. Between these temperatures both groups are lost, but the ratio of single to double groups condensing increases with temperature. The variable expansion and contraction behaviour of the opals between 200 and about 600 °C may be related to the nature of the fine pore structure within the silica spheres; a closed pore structure will tend to delay loss of water, which could cause the high expansion seen in the sample of curve A (fig. 3). The cracking of some natural opals on exposure to the atmosphere after mining may well be related to a feature of this type. If the major pore structure is such as not to allow the physically absorbed water to escape freely, sudden exposure to a temperature higher than that underground will increase the pressure within the pores, and develop stresses

that could lead to delayed cracking. Slow movement of the opal to the surface, as was done in the old Bohemian mines (Leechman, 1961) would allow diffusion of water from the opal without undue stresses being developed.

It is interesting to note here a crystalline wood opal from Lake Eyre, South Australia (Segnit, Stevens, and Jones, 1965, no. 1445C and M), which consists of a clear section with a closed pore structure and a milky part with an open pore structure; the clear portion contains abundant cracks, whereas the milky material is free from cracks.

Discussion. Nitrogen-absorption surface area measurements on an 'amorphous'-type opal from Coober Pedy (Segnit, Stevens, and Jones, 1965) gave a figure of



FIGS. 4 and 5: FIG. 4 (top). Dilatometer curves of opal previously heated to 900 °C (A) and silica glass (B). FIG. 5 (bottom). Thermal curves of an 'amorphous'-type opal.

0.41 m²/g, while calculation of surface area based on a structure of close-packed 2000 Å spheres gives about 8 m²/g. These figures are not only inconsistent with each other, but neither is adequate to account for the amount of water, which several independent lines of investigation suggest is chemically bonded. However, the presence of a smaller particulate structure of diameter of the order of 100–200 Å within spheres leads to a calculated surface area of the order of 200–100 m²/g. A complete monolayer of hydroxyls on this surface is equivalent to approximately 2.4–1.2 % water content. This percentage is, however, minimal, as it makes no allowance for the presence of twin hydroxyl groups or multilayers.

Lakhanpal, Sud, and Puri (1955) showed that water can be physically held in capillaries up to about 150 °C. Thus, in the static weight loss curve (A, fig. 5) it may be assumed that water lost above the inflection at about 150 °C is chemically bonded. This amounts to about 2.0 %, which is readily accounted for by the internal surface

area available in a sample such as is illustrated in fig. 1. Hockey and Pethica (1961) have shown that the minimum temperature under vacuum for the condensation of twin groups on pure silica is about 200 °C, and that loss of these groups is complete by 400 °C. The static weight loss curve (A, fig. 5) shows that at 200 °C 1.6% water remains, and at 400 °C, 1%. This residual water must represent silanol (single) groups and would be consistent with a figure of 1.2% for a complete surface cover of these groups on spheres of 200 Å diameter or an incomplete cover on smaller spheres. Furthermore, a comparison of the DTG (D, fig. 5) and dilatometer (E, fig. 3) curves of the Coober Pedy opal reveals that the reversal of the dilatometer curve at about 200 °C is matched by a maximum rate of loss near the same temperature.

We can now visualize the sequence of dimensional changes on heating as follows. Up to approximately 200 °C a normal thermal expansion of the 100–200 Å silica spheres and the water and hydroxyl layers occurs, with concomitant loss of physically absorbed water from the larger pores of the structure. Above this temperature loss of surface hydroxyl groups begins, producing the observed shrinkage. A single layer of hydroxyls represents only 0.3% of the diameter of 2000 Å spheres, but is approximately 3% of the diameter of 200 Å spheres. Complete stripping of the surface hydroxyls from the small spheres with accompanying close packing of the 'anhydrous' spheres can therefore result in a theoretical linear shrinkage of 3%. The dilatometer results show a shrinkage of as much as 1.2% at 900 °C but it is evident from the curve that this is not the final shrinkage figure.

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