

## Solid opaline packings of colloidal silica spheres

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Precious opals are composed of amorphous silica spheres and their colours are caused by light diffraction from the regular packing of these uniform spheres [1, 2]. Since the silica spheres, 150 to 400 nm in diameter, are of colloidal size and since the synthesis of monodisperse silica spheres in a (non-aqueous) suspension is a well-established practice [3], the interesting question arises of whether it is possible to prepare an "imitation opal" out of such a suspension. The formation of ordered particle packings (i.e. colloidal crystals) in silica suspensions does not present a problem. This ordering phenomenon is well known [4]. However, a crystallized particle layer in suspension has a fluid-like consistency and the ordering is easily disturbed. Thus, the problem is rather how to stick the particles together in such a way that a solid, ordered packing can be taken out of the suspension.

Simply drying the suspension layer containing crystals results in a cracked, brittle and opaque material. This drying does not necessarily destroy the regular particle ordering. However, the dried silica displays diffusive Bragg colours produced by ordered layers at the surface. The brilliance of the crystals in suspension is lost because of the opacity of the dried compacts, due to the large difference between the refractive index of particles and pores.

Earlier attempts to fill these pores with a refractive index-matching organic or silicate monomer failed [5]. One difficulty was the shrinkage of the immersing material upon polymerization. Furthermore, repeated impregnation becomes more difficult as the permeability of the particle packing decreases.

A way to prepare a solid "opaline" silica packing was an unexpected result of an attempt to transfer silica spheres from ethanol to a viscous, transparent silicone oil with about the same refractive index ( $n \approx 1.45$ ) as that of the particles.

The starting suspension (laboratory code SA4(4)TPM) was a dispersion of charged, monodisperse silica spheres in absolute ethanol (particle radius 135 nm, silica weight concentration  $c = 40 \text{ g l}^{-1}$ ). The spheres were originally synthesized in ethanol-ammonia using the Stöber method [3] and during a surface modification with an organosilane ( $\gamma$ -methacryloxypropyltrimethoxy silane, TPM) were transferred to absolute ethanol. Extensive information about the purpose and details of the coating procedure can be found in [6]. A layer of (milky white) suspension was poured carefully on to the surface of

silicone oil (Hopkin and Williams, Silicon fluid MS 200, viscosity 200 P) in a Petri dish. The intention was to allow the TPM-coated silica spheres to settle into the silicone layer and to see whether the particles would form a stable suspension in this oil. However, after 1 day part of the suspension had sunk to the bottom of the dish in the form of opaque, white drops, some flattened or elongated, with diameters in the range 2 to 15 mm. The droplets shrank and, after about a further 2 days, displayed Bragg-like diffraction colours. The silica now appeared to be solid, and pieces were removed from the oil and cleaned with tissue. The pieces were nearly transparent when viewed in transmitted light but displayed intense colours (in particular green and to a lesser extent red) when viewed at other light-scattering angles. Fig. 1 shows an example of such a solid opaline silica and Fig. 2 shows the expected particle ordering in the silica. Silica pieces were stored in air for more than 2 years and did not crack or lose their colours or translucency.

The opaline silica fractured easily. Upon calcination for a few hours at 600°C the fracture strength increased. However, the silica was no longer translucent and only diffuse Bragg colours at the surface were observed. The silica retained its original appearance when immersed for a few days in silicone oil, indicating that the calcination process had not destroyed the regular particle ordering. Sintering of the silica for 2 h at 1200°C produced a white, opaque material in which the sphere structure (according to SEM micrographs) had disappeared. (The opacity of the sintered silica is due to light-scattering by cracks.)

The formation of opaline silica in silicone oil can be explained as follows. Suspension droplets sink into the oil because their mass density is larger. (The density difference increases as ethanol evaporates.) At the bottom of the vessel droplets flatten under their own weight and shrink because ethanol diffuses into the oil. Thus, the particle concentration in the droplets rises to the point where the nucleation and growth of ordered arrays can take place. During the "drying process" there is also migration of silicone oil into the particle packing. This follows from the translucency of the opaline silica, which must be due to refractive index matching. The oil probably also acts as a lubricant, giving some flexibility to the packing to withstand drying stresses (to avoid cracking) and facilitating the movement of particles into low-energy positions.

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*Figure 1* A solid piece of opaline silica (length 1 cm), showing diffraction colours, prepared by “drying” of silica suspension in silicone oil.

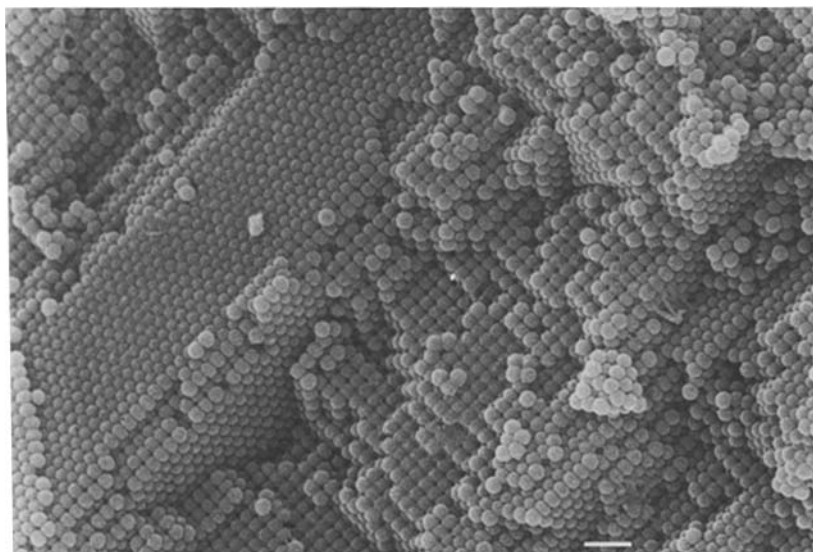
To check whether the oil indeed has any influence on the formation of opaline silica, other than serving as a drying medium, a comparison was made between the drying of silica suspension in oil and in air. The starting suspension consisted again of TPM-coated (but smaller) silica spheres in ethanol [6] (radius 80 nm,  $c = 45 \text{ g l}^{-1}$ , laboratory code SA6(2)TPM2). A layer of suspension (2 cm) was poured on to a layer of silicone oil (5 cm) in a reaction tube. After about 4 days a suspension layer of height 1 cm (with a concave meniscus) was present at the bottom, and after a further 2 days all of the suspension had sunk to the bottom. After a total time of about 12 days the silica had shrunk into a solid piece (in the form of a flattened drop), which was reddish-transparent when viewed in transmitted light. The red colour is due to light-scattering by the spheres in the packing, which again

consisted of ordered arrays (Fig. 3). (The particles were too small for the arrays to produce visible Bragg reflections.) The same volume of suspension was dried in a reaction tube in open air. A dry, white and opaque silica was obtained after about 2 weeks. A representative SEM micrograph is shown in Fig. 4, indicating a more irregular particle packing in which crystal domains can be observed, which are, however, clearly smaller than those in Fig. 3.

So the microstructures of the air- and oil-dried packings are different, even though they have been prepared on the same timescale. This indeed suggests that silicone oil facilitates the formation of opaline silica. A lubrication mechanism, as suggested above, seems likely, but one other factor should not be overlooked: the electrolyte concentration in the suspension. TPM-coated silica spheres are changed in ethanol [6] which prevents flocculation. Now if in silicone oil both ethanol and dissociable electrolyte diffuse away, the electrolyte concentration in a suspension droplet, and consequently the Debye screening length, will remain constant. However, when dried in air the electrolyte concentration in the suspension will rise and the Debye length will decrease, possibly to the point where the particles start to aggregate. Sticking of particles will certainly counteract the formation of a long-range order, required to obtain an “imitation opal”.

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*Figure 2* SEM micrograph showing the particle ordering in the silica of Fig. 1. The average sphere radius is 135 nm (marker is  $1 \mu\text{m}$ ).

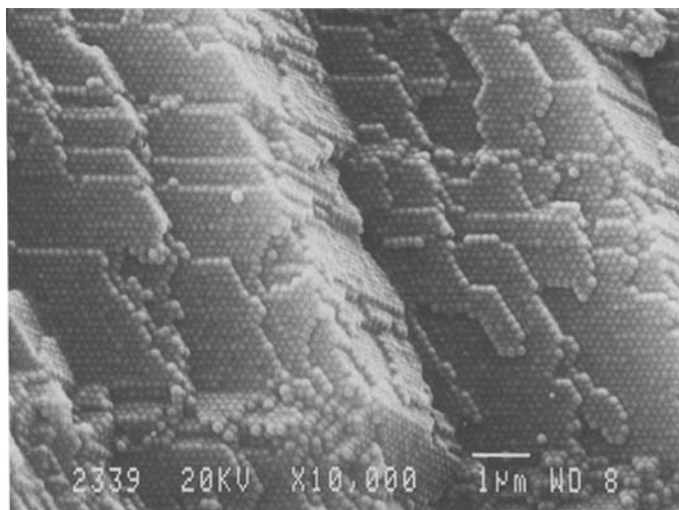


Figure 3 Ordered arrays of smaller silica particles (radius 80 nm) in a dried compact, again prepared in silicone oil.

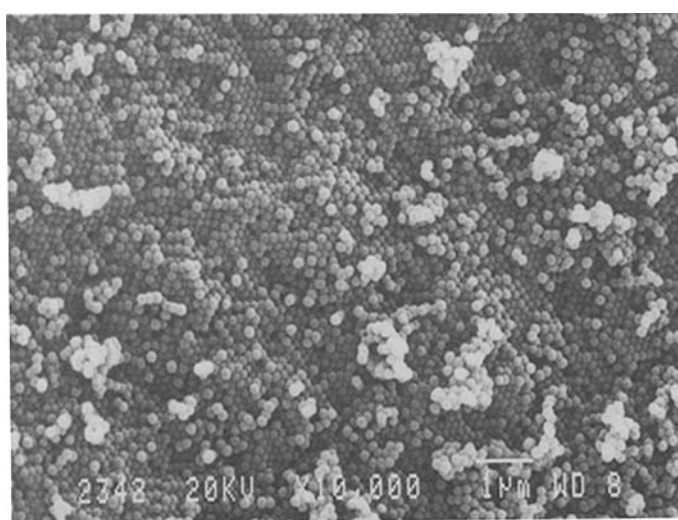


Figure 4 Particle packing produced by drying a suspension (same particles as in Fig. 3) in air.

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