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The 'fire' of opals

The mineral opal, chemically a form of hydrated silica, is found on practically all continents, but mostly as an "opalescent", milky–white, soft rock. However, in some parts of Australia small pieces of beautifully coloured gemstones, "precious opal", are to be found embedded in a matrix of ordinary opal.

What makes these quintessentially Australian gemstones sparkle with flecks of pure spectral colour (Fig.1)? Oddly enough, the answer to this question was a mystery to mineralogists for a long time until noted CSIRO electron microscopist John Sanders discovered the surprising answer as recently as the 1970s [1],[2].

Because of the spectral colours exhibited, the phenomenon of diffraction from periodic features was suspected to be the cause, but nobody could guess at the nature of such periodic structures until they were revealed by electron microscopy.

It was surmised that the optical properties of precious opal, as distinct from the milky-white appearance of common opal that shows no 'fire', depends on the existence of orderly, regular arrays of optical discontinuities, spaced at repeat distances of the order of 150 to 350 nanometers, *i.e.*, distances that correspond to half the wavelength of visible light.

Chemically, opals are made of pure, transparent, hydrated silica, *i.e.*, hydrated Silicon Dioxide. But what the electron microscope revealed was that the silica is in the form of tiny spheres, of the appropriate range of sizes, stacked in close-packed regular arrays, as may be seen in Fig. 2, just like atoms or molecules in crystalline substances.

How are these little spherical objects formed is answered by noting that the solubility of silica in water increases markedly with temperature so that, upon cooling, silica is usually deposited as quartz crystals that are said to grow in what is called a hydrothermal process.

Alternatively, in the presence of centres of nucleation, the silica can precipitate from saturated solutions in the form of amorphous clusters. These continue to grow as concentric spheres, which then fall through the solution and end up in interstitial cavities. In most cases, a poly-disperse range of sizes results, which when dried out results in a milky-white solid of ordinary, or so-called 'potch' opal.

However, in rare cases, where the little spheres have a greater distance through which to fall, a gravitational separation can take place, where the larger spheres fall more quickly than the smaller ones and arrange themselves in layers upon layers of uniformly sized regions of hexagonal close-packed groups, like oranges in a crate. Hence the quasi-crystalline arrangement of precious opal, usually in small pieces consisting of separate small regions, is analogous to crystal grains. The opal 'grains' can vary in size, from a few millimeters, known as pin-fire opals, up to quite large ones in what is known as boulder opals.

Because the individual silica spheres are completely transparent, pieces of opal show practically no colour when viewed in transmission. However, when viewed in reflection, strong diffraction colours are seen. These diffraction phenomena are not like those from a two-dimensional grating, such as is seen from the surface of a CD or DVD, and erroneously shown in illustrations in some popular articles. On the contrary, 3-dimensional diffraction

▲ **FIG. 1:** Precious opal

is involved, just like in the diffraction of x-rays by crystalline solids, discovered by Laurence Bragg.

The only difference is one of scale: whereas x-rays (and thermal neutrons) have wavelengths comparable with the unit cells of ordinary crystals, Bragg diffraction of visible light by opals is governed by the spacing between the layers of the silica spheres which corresponds to their sizes.

To prove the case and to further investigate the different types of opals (containing different types of so-called stacking faults), back around 1970, John Sanders built an apparatus consisting of a spherical glass flask with frosted walls, with a transparent entrance hole through which a collimated beam of white light was admitted.

When a sample of gem-quality opal was suspended in the centre of the flask, the resulting visible diffraction pattern, consisting of coloured spots and streaks on the frosted walls, was exactly in accord with Bragg's well-known formula: $n\lambda = 2d\sin\theta$ (see Fig. 3). Changing the angle of incidence θ is, of course what gives rise to the play of colours or the 'fire' of the opals.

Another immediate, visible consequence of this is the background colour of the precious opal when viewed in direct reflection, *i.e.*, when $\theta = 90°$ which determines the longest wavelength that can be diffracted - the so-called Bragg cutoff, which is simply $\lambda = 2d$. This, in turn, determines the rarity, hence market value, of a piece of opal. The so-called 'black opals', which show a deep red reflection because they contain the largest silica spheres, are the most valuable, all other things being equal.

One rather interesting fact is the very high efficiency of the Bragg diffraction process: Quite a thin layer of material is sufficient to produce complete reflection by virtue of the constructive interference of the light reflected from a relatively small number of layers. Thus, relatively thin layers of opal, sliced from a single piece can be mounted between layers of glass and still exhibit the full, beautiful coloured appearance of the much more expensive solid opals. These so-called doublets and triplets are the basis of the items of jewelry that are widely available at much cheaper prices but are just as interesting from the point of view of optics !

Once the structure of opals was elucidated, it was only natural that making synthetic opals was attempted in various laboratories by producing little spheres of colloidal or polymeric materials and letting them settle into close-packed arrays. Opal-like materials, with similar optical properties were actually successfully produced, but their mechanical and chemical properties precluded widespread practical uses.

More recently, however, it was recognized that periodic structures of dielectric objects of appropriate sizes, of which opals are the prime examples, can be generalized, giving rise to the whole new field of photonic crystals.

First proposed as late as 1987 by Eli Yablonovitch [3] and Sajeev John, a multi-faceted field of research has arisen, concerning methods of fabrication as well as new applications, in a variety of fields – well beyond the purely decorative.

Photonic crystals are still a hot research topic in laboratories all over the world. But, as usual, nature got there first: Opals are only the simplest, 3-dimensional examples; the colours of butterfly wings and bird feathers are also the products of more complex types of photonic crystals. ■

About the author

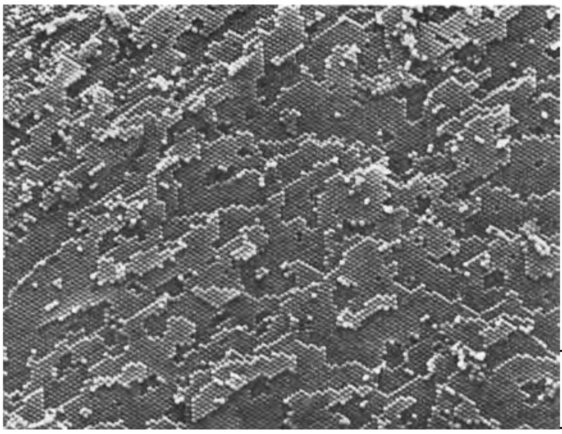
Emeritus Professor **Tony Klein**, held a Personal Chair at the University of Melbourne (1983 – 1998) and is a Fellow of the Australian Academy of Science and a Foundation Member and a Past President of the Australian Optical Society.

References

[1] P.J. Darragh, A.J. Gaskin and J.V. Sanders: *Scientific American*, April 1976.

[2] My friend John Sanders (1924 -1987) died at a tragically early age. His co-authors were both mineralogists.

[3] See E. Yablonovitch: "Photonic Crystals: Semiconductors of Light" *Scientific American*, December 2001



◂ **FIG. 2:** Electron Micrograph of precious opal

▾ **FIG. 3:** The geometry of Bragg Diffraction