

Formation of Precious Opal

by

Dr. R. K. Iler

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*Industrial and Biochemicals Department, E. I. du Pont de Nemours and Co.,
Wilmington, Delaware.*

Precious opal is distinguishable from other opaline silicas by being essentially amorphous, as shown by J. B. Jones, J. V. Sanders and E. R. Segnit¹. The relation between the remarkable particulate structure and the reflected colors of precious opal has been described by J. V. Sanders², who found that this mineral consists of regularly packed uniform spheres of amorphous silica a few tenths of a micron in diameter. From electron micrographs, Sanders concluded that the spheres must have grown in suspension by deposition of silica on to precipitated nuclei and then the spheres must have been later packed together, possibly during a filtration process.

The purpose of this article is to describe the spontaneous formation of brilliantly colored, opallike masses of 0.1μ spheres of colloidal amorphous silica by aggregation from a sol, and to point out the physical similarity between this and other types of similarly colored, regular aggregates formed from inorganic and organic colloidal particles in this range of particle size.

The preparation of sols of uniform spherical particles of amorphous silica by depositing soluble silica on pre-formed nuclei has been described by M. F. Bechtold and O. E. Snyder³, and the characterization of such silica has been summarized by me⁴.

In a 30 percent silica sol of particles about $100\text{ m}\mu$ in diameter, prepared by George W. Sears of this laboratory, he and I observed that after two years in quiescent storage in a 1-gallon bottle an intermediate layer showing brilliant colors in reflected light had been formed at the boundary between a dense, white, concentrated layer of colloid at the bottom and a more dilute opalescent sol remaining above.

To investigate the effect of pH , a number of 4-oz. samples of colloidal silica were withdrawn from the intermediate colored layer, diluted with equal volumes of distilled water, adjusted with the hydrochloric acid and dilute ammonia to pH values ranging from 3 to 10, and then allowed to stand in sealed glass or polyethylene bottles for another two years. In samples at pH

5 and 7, colored layers formed within a period of 3 months; in all cases, colored layers appeared after two years. Above pH 7, the colored region consisted of a thin, dense intermediate layer of uniform thickness. Between pH 4 and 7 at the boundary between the concentrated and dilute regions, brilliant platelets were formed, growing upward into the supernatant liquid. These have the appearance of leaflike or bladelike crystals, and will be referred to as *pseudocrystals*. These objects have been found repeatedly in silica sols of relatively uniform particle size averaging about 100 m μ in diameter; in most cases, the initial silica concentration was 5 to 10 percent by weight of silica and the pH between 5 and 7. In these circumstances, the blade-shaped, colored pseudocrystals grew to a length of 2 mm., with relatively straight sides but with the upper edges less well defined.

The color of the pseudocrystals depends on the angle from which the light is reflected. As the bottle containing the specimen is carefully turned, new pseudocrystals of different colors come into view. It should be noted that a given pseudocrystal can be seen only by one eye at a time, since the other eye is usually not at the correct angle to see the reflected light. The colors range from brilliant yellow through yellow-green, orange, deep red, blue and violet. These pseudocrystals are extremely fragile and disappear if the container is jarred or slightly shaken, and are formed again only after the mixture has stood again for several months.

Unsuccessful attempts were made to produce pseudocrystals more rapidly by

centrifuging sols to bring about settling in several hours, but the silica particles were packed into white, opaque layers, leaving a translucent, almost transparent supernatant liquid. It is apparent that time is necessary for the particles to attain the required perfection of packing.

The colored material has been isolated in dry form as chalky-white masses of silica gel, still showing weak interference colors, by permitting the sol containing the colored layer to evaporate very slowly over a period of two more years, so that the silica in the supernatant liquid is drawn down slowly on the colored masses without disturbing them. More rapid evaporation, which obviously must involve movement of water from the bottom to the top of the mass, disturbs the structure. The slowly dried, fragile, opaque material was heated to 900° C. over a period of 12 hours and then slowly cooled. When the mass was impregnated with water or preferably with benzene or alcohol, the interference colors were again observable. The refractive index of the impregnating liquid had a marked effect on the reflected colors. Water with a refractive index of 1.33, as compared with 1.46 for the amorphous silica, gave a white opaque mass in which green flecks of color could be seen. Normal butyl alcohol, refractive index 1.39, gave an almost transparent mass, showing green-blue flecks of color in reflected light. Carbon tetrachloride, refractive index 1.46, gave a perfectly transparent mass that, however, showed slight green reflexions. An oil with a refrac-

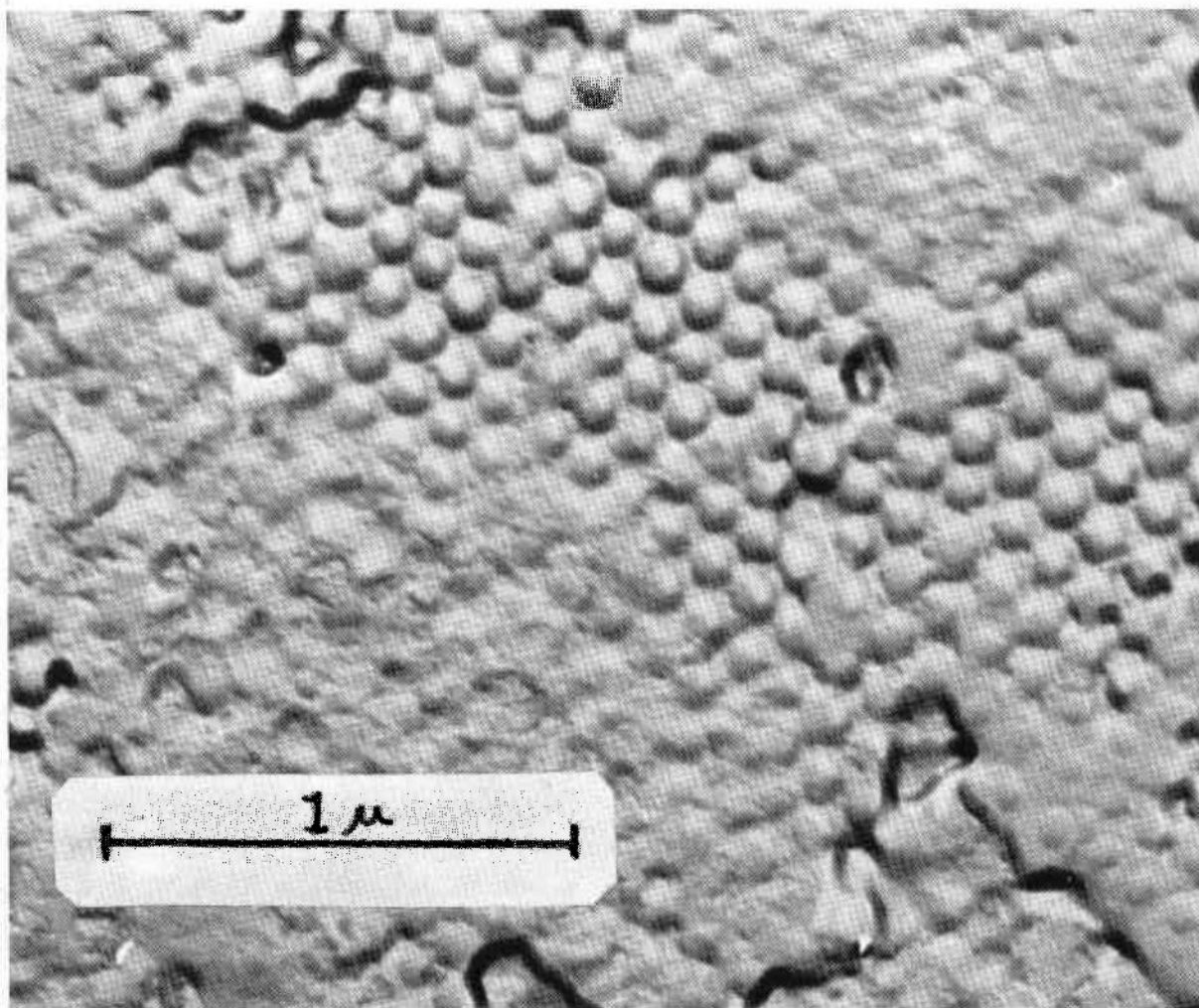


Figure 1

Electron micrograph of replica of polished section of close-packed spheres of colloidal silica showing reflected interference colors (x c. 25,000)

tive index of 1.6 gave deep-red reflexions, while liquids of still higher refractive index resulted in a white opaque mass with a brownish tinge.

The bulk density of solid pieces of the slowly dried silica, still showing interference colors, dried and fired to 1,000° C., was 1.53 g/c.c., corresponding to 69.6 percent by volume of amorphous silica. This approaches the value of 72 percent by volume, corresponding to close-packed, uniform spheres. An electron micrograph of a replica of a polished section is shown in *Figure 1*.

Formation of natural opal. The brilliantly colored but very fragile layers

containing the pseudocrystals, viewed through the glass walls of the container, look exactly like natural precious opal. There is little doubt that the colors originate from uniform arrays of silica spheres, as Sanders² has described in the case of natural opal. However, in natural precious opal the spheres are larger, and the space between them is at least partially filled with hydrated amorphous silica, which serves to harden the mass. Such a cementing process probably occurred after the spheres were packed in regular array, by long-continued impregnation with soluble silica. Cementing or reinforcing of

suspended aggregates of silica particles has been carried out in the laboratory to produce mechanically strong silica gels⁵. Impregnation of dense-packed masses of opal may have occurred by a similar but far slower process in Nature, since the solution would have to pass through the mass in order to achieve such a uniform deposition of silica.

It is probable that a critical step in the formation of natural precious opal was the creation of spheres of amorphous silica in dilute suspension and subsequent slow settling in quiescent underground pools. Since geyser waters are often supersaturated with silica, it is conceivable that in some circumstances the rate of cooling might be such that relatively large uniform particles of colloidal silica were formed. In undisturbed subterranean pools such particles might have become concentrated, and uniformly packed aggregates may have been formed just as observed in the laboratory. Once such uniform aggregates had been formed, further hardening of the structure by deposition of silica within the interstices over thousands of years could result in the type of structures described by Sanders *et al.*

There remains the question as to why uniform spherical particles of amorphous silica should become packed together in regular arrays as pseudocrystals. In the silica-water system, the changes that occur spontaneously are those that lower the area of the silica-water interface, since there is an interfacial surface energy of about 80 ergs/cm² (ref. 6). Minimum interfacial area is achieved when the surfaces

of such particles are brought together, excluding the water from the areas of contact. The formation of these points of contact represents the first stages in reducing the overall silica-water interfacial surface area. Greatest reduction in interfacial area is obtained with the closest packing of spheres in which each sphere makes the greatest number of contacts with surrounding spheres. In a sol containing charged particles of different sizes, particles that are either smaller or much larger than the average will not fit as perfectly into the growing uniform array of the pseudocrystals, and their inclusion is thus thermodynamically less favored. Unless the particle colliding with the surface is held with several points of attachment, it will be repelled by the surface of the pseudocrystal that is of like charge. This is analogous to the fact that a potassium ion does not fit into the lattice of a growing crystal of sodium chloride, and is thus excluded. Thus, spheres of like size tend to fit into a given growing pseudocrystal.

Analogous systems. Analogous aggregation of spherical particles of colloidal size to form highly colored masses has been observed with organic materials. N. Xeros⁷ reported that a virus in an insect caused the formation of iridescent nodules that showed brilliant colors in reflected light; when the virus is purified it is obtained as a mass showing iridescent colors. The properties of this lattice, consisting of very uniform spherical particles, 130 m μ in diameter, is further described by Williams and Smith⁸.

The close packing of uniform poly-

vinyl toluene latex particles in the size range of 100-1,000 $m\mu$ has been described by Alfrey, Bradford, Vanderhoff and Oster⁹. The spontaneously formed, close-packed, crystalline array acted as a diffraction grating and particle sizes in the range of 302-481 $m\mu$ were determined by the diffraction method.

Another instance of uniformly arrayed colloidal particles showing brilliant interference colors is the formation of the so-called "schiller layers" from colloidal hydrated iron oxide. The structure and arrangement of regularly packed masses of uniform colloidal particles of this type have been described by Watson, Cardell and Heller¹⁰.

In instances in which the spontaneous regular and uniform aggregation of charged colloidal particles occurs, it appears that at least one of the dimensions, whether the diameter of a sphere, or the width of a rodlike particle, is of the order of 100 $m\mu$ or more. Possibly this is because uniform arrays of colloidal particles are most easily recognized when the particles are in this size

range and thus reflect monochromatic light of visible wavelength. However, this is also the size range in which slow sedimentation occurs. Particles larger than about 100 $m\mu$ in diameter or thickness tend to settle so that there is a gradual increase in concentration at the bottom of the container; conditions are thus favorable for the slow segregation of particles into regular aggregates or pseudocrystals, each consisting of particles of a particular uniform size.

On the other hand, in the case of smaller particles, the Brownian motion is so strong that the rate of sedimentation is negligible and the particles do not become concentrated by settling. If the concentration is increased rapidly by centrifugation, the particles become packed randomly, since there is no time for segregation and for ordered arrangements to be developed. However, if the size is extremely uniform, as with virus or certain latex particles, a relatively rapid increase in concentration can still result in the formation of a highly ordered array.

1 Jones, J. B., Sanders, J. V., and Segnit, E. R., *Nature*, 204, 990 (1964).

2 Sanders, J. V., *Nature*, 204, 1151 (1964).

3 Bechtold, M. F., and Snyder, O. E., U. S. Patent 2, 574, 902 (E. I. du Pont de Nemours and Co., 1951).

4 Iler, R. K., *The Colloid Chemistry of Silica and Silicates*, 90 (Cornell Univ. Press, Ithaca, N.Y., 1955).

5 Iler, R. K., *The Colloid Chemistry of Silica and Silicates*, 133 (Cornell Univ. Press, Ithaca, N.Y., 1955).

6 Iler, R. K., *The Colloid Chemistry of Silica and Silicates*, 10 (Cornell Univ. Press, Ithaca, N.Y., 1955).

7 Xeros, N., *Nature*, 174, 562 (1952).

8 Williams, Robley C., and Smith, Kenneth M., *Nature*, 179, 119 (1957).

9 Alfrey, jun., Turner, Bradford, E. B., Vanderhoff, J. W., and Oster, Gerald, *J. Opt. Soc. Amer.*, 44, 603 (1954).

10 Watson, John H. L., Cardell, jun., R. R., and Heller, Wilfried, *J. Phys. Chem.*, 66, 1757 (1962).