

## An Alternative Hypothesis for the Natural Formation of Opal

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### Introduction

The structure of opal was first elucidated by P. J. Darragh and A. J. Gaskin in 1966, (1), working in two laboratories of the Commonwealth Scientific and Industrial Research Organization, in Perth and Melbourne, Australia. In their first paper they also suggested a natural origin of the structure. A recent paper, (2), summarized the findings of continuing work from those laboratories to 1976.

These authors determined, largely by electron microscopy, that opal possesses a structure which resembles a system of packed spheres. In some opal the size of the spheres is very uniform and the packing is that of a regular lattice, either hexagonal close packed or face centered cubic. In others the size, shape and packing are very irregular. No compositional distinction has been reported between the two.

“Precious opal” is so called because it possesses a “play of color” which was clearly recognized as an optical diffraction phenomenon and was shown by Darragh and Gaskin to originate from the regular lattice structure. “Common opal” has no regular lattice structure and possesses no “play of color”. Precious opal, whether formed in sedimentary or volcanic rocks was found to have the regular lattice structure, though many features of the two such as amount of crystallinity and the appearance of electron micrographs of cleaved surfaces were quite different.

These authors proposed an hypothesis for the natural formation of opal (1, 2) which may be referred to as the “sedimentation hypothesis”. Their hypothesis postulates the formation and sedimentation of spheres of silica in a pool of a very dilute but saturated solution of silica. The solubility of silica at pH below 9.0 is approximately 0.015%, (3). Such pools were said to be in a steady state in which supply by entry of new silica solution is in balance with evaporation of water from the pool, precipitation of silica spheres from the saturated solution, and aggregation and settling of aggregated spheres into a regular lattice of uniform spheres as revealed in their electron micrographs of precious opal.

After this process of settling of silica spheres into a close packed lattice is complete, calculated by those authors to take from one to several millions of years, dehydration of the mass is postulated to convert it to the opal state.

Those authors were able to form silica spheres by hydrolysis of silica esters and to sediment them into a regular array which was said to display play of color. They were not able to consolidate the mass into an opal-like solid. A U.S. patent was obtained by the authors, (4).

To date no other hypothesis has been put forward for the natural formation of opal, to explain the well documented lattice structure of precious opal. A secret process has been found and used by Pierre Gilson of Paris, France by which a stone is produced having optical effects closely resembling natural opal and said to have the same lattice structure seen in natural opal, (5). This secret process can have little relationship to the process of natural formation as postulated by Darragh and Gaskin, (1), which requires one to several million years.

### An Alternative Hypothesis

In sharp contrast to the sedimentation hypothesis it is here proposed that a process is involved which begins with the entry of a magmatic alkaline solution of silica into a cavity in a host rock or alternatively into porous masses such as dried wood or porous earth. Precious as well as common opal can form in either situation. At pH 11.0 the solubility of silica is 0.45% and would approximate 4.0% at pH 12.0.

An alkaline solution of silica intruding upward should remain fluid until it reaches levels close enough to earth surface to come under the influence of carbon dioxide and oxygen from the atmosphere. If a pool of alkaline silica solution is formed close to earth surface it should come under the acidifying effects of carbon dioxide and of acids formed by oxidative processes. The pool should then become acidified. If the solution contains 4.0% or more of silica it should gel upon acidification, as is readily observed in the laboratory. Even lower concentrations may gel upon acidification and long standing. Also evaporation from a more dilute alkaline fluid solution may concentrate it to a degree allowing it to gel upon acidification. Note that in the sedimentation hypothesis the formation of a gel is not postulated to occur.

Intrusion of alkaline (high concentration) silica solution into the host cavity may occur in successive surges, causing the appearance of layers—sometimes thick, sometimes very thin—in most opal found in sedimentary host rocks.

The successive layers are formed of silica solution differing in such characteristics as concentration of silica, pH, presence of other dissolved constituents, notably carbonate and di- or multi-valent metal ions, etc. Also between the surges of intruding silica solution some evaporation and some acidification and gelling of earlier layers may occur. This may account for absence of mixing of new layers with older layers and the generally sharp and flat layering of sedimentary opal. In opal formed in cavities in volcanic rocks such layering is minimal or absent.

After intrusion of alkaline silica solution into host cavities and after acidification and gelling of the pool, the gel may remain relatively stable for many years before it begins to be dehydrated, or it may begin to dehydrate soon after gelling. It is generally believed that most opal forms under arid surface conditions. It is here proposed that during ageing and dehydration of the gel a structural rearrangement of the hydrated silica occurs in the gel mass. The rearrangement may be supposed to increase the number of Si-O-Si bonds at the expense of Si-O-H bonds.

When silica gel is dried it shrinks very little—unlike many other gels. The implication is that a structure remains in the dry gel which is ninety percent void space, (from a five percent gel retaining an equal weight of water). The present hypothesis suggests that under appropriate conditions, some of which will be suggested, the retraction of silica from its fully hydrated sponge structure in the gel may form a regular honeycomb or closed cell foam structure. These cells must be filled with gas as water is lost. The gas is predominantly carbon dioxide with some oxygen and water vapor. Throughout this process surface tension must play an important role, the more so that the dimensions of the cells are so small.

A mechanism is suggested in the following by which the cellular foam may become established during the course of drying of a silica gel. When soluble silica is acidified and gelled it was observed by conductivity measurements to undergo little conductivity change, indicating that the gel has a sponge structure rather than a closed cell structure. Upon dehydration of the gel energetic considerations would require some kind of further polymerization of silicic acid.

If gas cells are nucleated in the gel as it begins to dehydrate perhaps by carbon dioxide such gas bubbles could not move in the gel medium. As the water leaves, however, the bubbles could grow until they become close packed with the hydrated silicic acid forming the septa between and occupying only some ten percent of the gross volume of the original—and also of the dried gel. Such mechanism of retraction from the sponge—to a well polymerized form of hydrous silica would appear energetically plausible.

At this stage also the now dry silica structure is stable until a later intrusion of silica bearing solution occurs. The closed cell foam may be a regular lattice of uniform sized cells or it may be irregular with respect to cell size, shape, and arrangement. The obvious suggestion then is that this is a precursor of the later development of the opal structure.

To become opal this foam must be silicified. In increasing degrees and perhaps in successive stages it may become silicified by deposition of chalcedony, opal-cristobalite, or hydrous silica. The process is supposed to be similar to or identical to that by which other porous bodies are silicified.

The widely observed banding of the spheres in precious opal, visible in the electron micrographs in reference (2) may be due to successive phases of silicification rather than to the mechanism suggested in the sedimentation hypothesis. The present hypothesis supposes that silicification builds upon the inner surfaces of the cells of the silica foam. The structure remains permeable to a true solution of silicate, and undergoes a series of filling—gelling and drying with retraction onto the previous surfaces. This would result in concentric rings of silica within the cells of the foam. Some opal shows some degree of crystallinity (opal-cristobalite) while some is purely amorphous.

While opal formed in cavities in sedimentary rock typically shows layering, that formed in cavities in volcanic rocks generally does not. Also, while layering of the spheres in sedimentary opal suggests successive surges of silica solution during filling of the foam no layering in the spheres of volcanic opal has been reported. This suggests that fewer surges of silica solution are involved in formation of volcanic opal.

The well known variation in friability of opal and resistance to the stress of drying or heating on its stability is believed to be largely attributable to the varying completeness of the silicification stage in the natural development of opal.

An important aspect of this foam hypothesis is the proposed role of carbon dioxide in the formation of the foam on ageing/drying of the gel. It is proposed that the alkaline silica solution from which the pool is formed contains dissolved carbonate in an amount at least about 0.4 gram (calculated as sodium bicarbonate) per 100 ml solution. This is an amount which upon acidification produces enough carbon dioxide to saturate the solution at 25°C, and also the amount of carbon dioxide necessary to fill the voids left by evaporation of water from the gel. Accordingly carbonate content of the alkaline silica solution may be an important variable in opal formation.

### **The Nature of Evidence for the Foam Hypothesis**

(1) A precedent appears to exist in the structure of novaculite, which is said to appear under microscopic examination to resemble a silica-filled foam, (6).

(2) The author has made extensive observations on hyalite opal from Mexico which displays play-of-color when sliced thin and observed by transmitted light and minimal play-of-color by ordinary observation. Evidence is seen that gas (presumably carbon dioxide) was being evolved in and around the gel mass up to the time the gel set. The gas was trapped at varying stages of its movement in and around the gelling mass.

This is incompatible with the sedimentation hypothesis. It supports the proposition that the lattice structure was established *after* the mass gelled.

(3) The sedimentation hypothesis appears to be untenable for other reasons. A steady state process is invoked requiring more than a million years of balance between several critical factors. One of these is the sedimentation of only one size of silica particles—in the case of precious opal—particles of other sizes being rejected and not accumulating to disrupt the process further. Alternating repeatedly with this process is one in which many sizes and shapes of particle sediment together, also forming a close-packed mass, (2) the septa between looking much like the septa between the gas cells in a foam.

(4) Natural products related to gelled silica and to progressively silicified silica gel have been reported, (7). These include silica gel and opalites or opaloids. The degree of silicification of the gel is indicated by the varying ability of the product to take up water and the initial and final properties such as density and refractive index.

(5) An as yet secret process exists by which an artificial opal is made (8) resembling natural precious opal in many properties including play-of-color and a lattice structure similar to natural opal (5). The process is obviously achieved in a "short" time, contra-indicating the involvement of any process analogous to the sedimentation hypothesis. A "short" process is not necessarily incompatible with the operation of the foam hypothesis.

**Literature Cited**

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