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Origin of precious opal revisited: Possible quick formation of precious opal

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Silica minerals are commonly found in nature, sometimes as a filler of pores and cracks in rocks. Even when they do not show their euhedral shapes, most of those are crystalline or microcrystalline. In reality, truly amorphous phases are rarely found as a filler of such void. Opal-AG (aka “sedimentary” precious opal^{1,2}) is one of those truly amorphous phases and have distinct feature, play-of-colour. It has been well known that a precious opal is composed of closely packed uni-size silica spheres with voids filled by an air or water, and that an interference among reflections from the boundaries of those spheres and filler yields play-of-colour (iridescence)³. So, occurrence of a play-of-colour means occurrence of natural selection in size of spheres, or suppression of further nucleation after initial outburst of spheres, during its formation process. Here comes a question: How did nature avoid variation in size of spheres in precious opal filling small cavities and cracks?

We had been exploring the possibility if we can regard a Stöber process⁴ as an analogue of the formation process of precious opal. The key is the reason why variation in size is rarely found on both precious opal and Stöber colloid. To give a clue, we examined the internal structure of Stöber particles and how those particles were formed at very initial stage of the process. The answers for evenness in shape and size are a quick supersaturation of reactive silica species, consecutive formation of large and loose polymers by fast dehydration, and their quick aggregation as the initial burst of silica spheres in highly diffusive medium. These can be achieved in nature by quick but continuous decrease in temperature on “basic” (high pH) geothermal hot water moving upward through cracks in rocks. Sedimentary precious opal can thus be formed when such naturally occurring colloid is filtered by a permeable bed. Accumulation of

remnant silicic acid in the flow will fill the pathway of the flow in the stack of spheres and make the stack hard.

Sedimentary precious opal and a Stöber colloid

Amorphous silica spheres of desired size can easily be prepared, and play-of-colour can also be reproduced (Fig. 1a) in labs with a Stöber process, which utilizes hydrolysis of Si-alkoxide and condensation of thus yielded silicic acid by dehydration in one reaction medium. This process has clear similarities with that of precious opal; both are segregation of solid from a liquid, both utilize coagulation and thus dehydration of silicic acid, and final products are monodispersed amorphous silica spheres. Their products also have similarities. Particulate structure for each sphere has been reported on sedimentary precious opals by several authors⁵⁻⁷. Silica spheres produced with the Stöber process were porous⁸, and aggregation of solid primary particles (aggregation-growth model) has been proposed as their formation process⁹.

Structure of Stöber particle

Monodisperse silica spheres of virtually the same size were prepared with the method reported previously¹⁰. In the present experiments we had set concentration of Si-alkoxide (tetraethyl orthosilicate: TEOS) at 0.22 M to obtain larger spheres in shorter time.

Mixed chemicals had been gently stirred over sampling period ($t < 960$ min). However, continuous stirring was ample to attain mono-disperse colloid. We could attain such colloid even with 0.5 min of initial stirring to accomplish homogeneity of the reaction medium (Fig. 1a). The reaction medium started to be translucent blue at 3 min and became turbid at 8 min after mixing of chemicals. By settling down the medium for some weeks, or utilizing centrifugal separation, we could get a precipitate of silica spheres. Wet precipitates showed typically green and orange play-of-colour, and the colour rarely retained when dried. Dried white pellets of precipitates (inset of Fig. 1a) were easily broken by hand, indicating that the pellets were composed of loosely bound silica spheres stacked in close-packing manner with no solid filler. This was later confirmed under field emission-type scanning electron microscope (FE-SEM) (Fig. 1a). Sizes and morphologies of these spherical particles, some

were attempted to crack in an alumina mortar, were directly determined under FE-SEM (Fig. 2). No metal plating was applied to preserve their sizes and fine structures on their surfaces, except as noted. Particles sampled at $t \leq 5$ min showed unevenness on their shapes as if those were assemblage of finer particles, and their sphericity was improved with reaction time. Surfaces of spheres sampled after completing their growths ($t \approx 120$ min: Fig. 3) were smooth even under high resolution, while they showed sandy texture under higher acceleration voltage (e.g., $t = 240$ min, Fig. 2d). This reflected remnant of inhomogeneity inside the spherical particles. As one of the authors (H.O.) had reported previously on simultaneously formed thin film, this accretion was well dehydrated and thus hard even before the drying process¹⁰. Nonetheless, as-prepared particles sampled at early stage ($t \leq 5$ min) had kept faint translucency for electron beam (Fig. 2c) and those after their growth ($t = 480$ min) had not been hard, inner part in particular, enough to be fractured (Fig. 2e). We could find a fracture surface through the centre of the sphere on a well-dried (kept for four months in desiccator) one (Fig. 2f). Interesting feature was found on this fracture surface; central part of the spherical particle was an agglomeration of finer particles, approximately 20 nm in diameter, instead of a uniform one expected for monomer-addition growth¹¹ based on a classic “nucleation-and-growth” model¹². This “core” part was around 200 nm in diameter, while boundary of the core and mantle was ambiguous. Indeed, the texture looked as if the size of accretion got finer with reaction time after aggregation of “primary particles” which made the core part. Similar but multi-step aggregations had been proposed for a Stöber colloid¹³. However, we could not find any sign of multi-step aggregation and our silica spheres were simple “secondary particles” composed of primary ones. This growth process, namely growth by accumulation of primary particles which reduce their sizes with time, had already been proposed for the growth of the silica thin film¹⁰. Present observation disclosed at the first time that silica sphere in the Stöber process was initially formed as an aggregation of unsized primary particles and grown by accumulation of later-formed, and smaller, primary particles.

Growth kinetics of silica spheres in Stöber process

Prior to an exploration of the identity of the “primary particles”, we explore the growth process of these spheres with a little kinetics. Change in size of silica spheres in our Stöber

colloid was linear in logarithmic time until 20 min, then gradually reduces its rate, and finally stopped at no later than 120 min (Fig. 3). Steady growth of the spheres at the early stage, from 2 to 20 min, can be explained by a simple diffusion-limited model^{10,14} no matter what reactive silica species, monomers, polymers or nanosized primary particles, is accumulating on the surface. When a growth is diffusion-limited, in other words limited by a collision frequency between a reactive silica species and a particle, its growth rate depends on an amount of reactive silica species in the medium. In the present case hydrolysis of TEOS itself is a slow-rate step¹⁵ and the rate of dehydration of reactive species is faster, too fast to allow the reactive species keep dissolving in the medium, than the rate of hydrolysis of TEOS¹⁶. Linear fashion in particle growth therefore means continuous supply of reactive silica species by hydrolysis of TEOS with a fixed rate (this case amount of unhydrolyzed TEOS is inverse proportional to a duration time). The cause which slowed the growth down over 20 ~ 120 min is unclear but back reaction on hydrolysis is likely. Depression of TEOS in the medium finally ended the growth at no later than 120 min.

Identity of primary particles, and formation and growth of secondary particles

Particles sampled at 1 and 2 mins showed notable difference in their morphologies. In general, appearance of bright fringe on an outline of objects under SEM means presence of an edge or vertical face (the so-called edge effect). From this viewpoint, the particle sampled at 2 min (Fig. 2b) had certain vertical dimension, while those at 1 min (Fig. 2a) did not. The particles sampled at 1 min looked as nearly translucent white spots on the substrate, like a dried jellyfish. This shape indicated that density of the particles sampled at 1 min was quite low as a blob, namely loosely bound homogeneous spherical large polymers, and they shrunk anisotropically when dried.

The horizontal sizes of these dried polymers (≈ 35 nm) were comparable to the diameter of the particles sampled at 2 min ($d \approx 40$ nm), and both of these were far larger than the “primary particles” ($d \approx 20$ nm) found at the core part of the later-sampled one (Fig. 2f). Their sizes indicated that each of the particles sampled at 2 min was not a further grown and dehydrated form of each large polymer sampled at 1 min but an aggregation of those, that is to say “secondary particles”. This means that these silica spheres were initially formed as an

assemblage of blobs which correspond to primary particles referred to above, and dehydrated simultaneously with their growth. This explains the reason why the core part was softer, namely less dehydrated, than the mantle on the as-prepared spherical particle (Fig. 2e). Furthermore, this can explain also the reason why particle sizes had not been determined with a dynamic light scattering during the induction period (3 ~ 8 min in our experiments) and the smallest sizes detected by the light scattering had been already within 50-70% of their final values¹⁵. They had simply not been condensed enough to be detected by a light scattering in the reaction medium. We have no way to estimate actual size and number of the large polymers when they started to aggregate. However, their population should be very high otherwise no aggregation had occurred and they had grown individually.

Since the size of the core part ($d \approx 200$ nm) is larger than the size of particles sampled at 5 min, these spherical particles were grown basically by adhesion of large polymers for some more minutes. However, homogeneity in size of the secondary particles was already attained at 5 min: Averaged particle diameter was 168(7) nm at $t = 5$ min ($n = 31$, experiment #13). It should be stressed here that brutal stirring had negative effect for uniformity of Stöber particles⁴ and in reality uniformity of the particles had been attained even without stirring when homogeneity of the reaction medium had been accomplished. This implies that the reaction medium was fractionated for each of secondary particles. If this is the case, one fraction corresponds to the volume in which initially formed large polymers participate into formation of one aggregate. Thus formed secondary particles would have enough separations to each other to avoid their collision and they could retain their sizes even. Fractionation model had been proposed also in ref. ⁵ for formation of opal-AG, in which they had to assume high viscosity (sol state) of reaction medium to suspend silica spheres in millions of years. In fact, sol state can be attained by hydrolysis of TEOS under acidic condition¹⁷. However, dehydration is quite slow under acidic condition and, more importantly, no segregation of silica from the medium occurs under such condition (this chemistry has been utilized as a sol-gel method in industries). On our experiments low viscosity of ethanol did not hinder formation of uni-sized spherical particles. Conversely, viscosity should be low enough to realize aggregation of primary particles prior to their own solidification. Silica spheres should grow quickly to cope with low viscosity of a reaction medium.

For high diffusivity of the reaction medium, later-formed polymers only collided onto secondary particles nearby and they seldom formed a new aggregation by themselves. While later-formed polymers could grow in size comparable to the initially formed ones for some more minutes, their sizes became smaller with time with reducing production of reactive silica species. Lack of distinct boundary between core and mantle, and improvement on evenness of their outer shapes too, are due to this gradual change in size of polymers.

Keys

Particulate structure of our Stöber particles suggests that the formation process of our artificial precious opal is virtually identical with, or at least similar to, that of a natural precious opal. So, what were the keys to attain monodispersed spherical particles with a particulate structure?

Formation process of our silica spheres based on observations is as follows. Within a minute or less the system was quickly supersaturated with a reactive silica species by hydrolysis of TEOS. For fast dehydration under basic condition, those reactive species formed loosely bound large polymers (primary particles). Most, if not all, of initially formed primary particles participated into formation of secondary particles as their agglomeration. Population of later-formed polymers did not achieve high enough to form secondary particles by themselves and they accumulated onto already formed secondary particles. From above, the reaction system should obey requirements as follows. Firstly, fast dehydration of reactive species in a basic medium is essential for formation of large polymers (primary particles). Population density of these large polymers should be raised quickly to make yielded polymers unavoidable to collide to each other and form an aggregation (secondary particles). Their agglomeration, and accumulation of later formed ones, also should occur quickly prior to their solidification. To attain these, large amount of reactive species should be supplied in the system in a short period and the medium should have low viscosity to attain high diffusivity. Entire process should be finished in rather short period prior to precipitation of thus formed secondary particles in low viscosity medium. A reaction field should have certain dimensions for fractionation to accomplish uniformity in sizes of secondary particles. Balances among speeds of dehydration (pH), aggregation (viscosity) and supersaturation

(here this corresponds to a rate of hydrolysis of TEOS but in general this corresponds to change in solubility of silica species in a medium) determines whether precipitate is a particles of a few tens of nanometers, spherical particles with a particulate structure, or a bulk body.

Structure of sedimentary precious opal

Natural precious opal (Fig. 1b,c) gave us some insights on its formation process. While a particulate structure of each sphere was not visible in our observation since no chemical etching was applied, packing of spheres and inter-particle voids were apparent under FE-SEM (Fig. 1b). The bulk body was fractured along a two-dimensional array of six-coordinate voids (centre of regular octahedron with spheres on its apices). Observed aspect ratio ($\div 1$) of the square array of spheres indicated cubic closest packing of those as had been analyzed in ref.¹⁸ in detail. This also guarantees that the centres of these spheres were located virtually on the fracture surface. Yet another kind of voids, smaller four-coordinated ones, had not be seen under FE-SEM. Indeed, an amount of overlaps among connected spheres, namely difference among distances from the centre of a sphere to its surface and a half of that between centres of connected spheres was enough to fill tetrahedral voids around the spheres. Large curvature radius of the surface of each particle indicated occurrence of post-stack growth rather than shrinkage of void by compression.

Untextured slabs (veins) were found as insertions in the stack. The walls of such cracks were composed of non-spherical (deformed) particles with no sequence from the body of the stack (Fig. 1c). Presence of these slabs indicates occurrence of post-stack shrinkage of spherical particles and presence of continuous “flow” of a water which was supersaturated a little with a reactive silica species. This flow caused a post-stack growth of spheres until all tetrahedral voids were filled and the body lost its permeability. Once this was accomplished each of octahedral voids was isolated from the outside of the stack and left unfilled. This flow carried also soft spherical particles from the upstream side, which were adhered onto the wall of cracks.

A model

Here we avoid to get deeply involved into forms of dissolved silica species and their chemistry at actual geological sites, instead we give a simple and qualitative model which can yield a sedimentary precious opal.

It is needless to say that a solubility of silica in water is fairly low at ambient temperature, but the solubility increases with increasing temperature particularly under basic condition¹⁹. It is interesting to note that this enhancement in solubility is maximized at 225°C; at this temperature the solubility at pH = 10.2 is ten times greater than that at pH = 8.0 (ref. ¹⁹). This means that a steep increase in an amount of reactive silica species and their fast polymerization can happen in basic geothermal hot water moving in a low temperature environment. When hot water in aquifer is covered by an impermeable strata, and once the strata is fractured by a diastrophic event, this hot water will be released for high pressure and moves upward through the cracks having certain dimensions. This motion will associate decrease in temperature of the flowing liquid and induces supersaturation of silicic acid. When change in temperature is steep enough, a lot of large polymers will quickly be generated and spherical secondary particles grow in the flow. This naturally occurring colloid will be filtered by a permeable host rock and will fill the very end of the path by a stack of particles. Flowing water soak through the stack and the stack grows on the upstream side. Simultaneously, remnant reactive silica species in the soak water fill tetrahedral voids in the stack and make the body hard. Filtered water soak into the permeable host rock too and may make the host rock harder.

The remaining issue is a possibility where nature attain an appropriate balances among speeds of dehydration, aggregation and supersaturation in subterranean water. It is intuitively understood that this seldom occurs in nature, and this makes precious opal precious.

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Figure legends are given beneath each figure at the end of this manuscript

Methods

Spherical silica particles were fabricated by modifying Stöber's method⁴, that is, by the hydrolysis, dehydration and condensation of TEOS ($\text{Si}[\text{C}_2\text{H}_5]\text{O}_4$) in an aqueous solution of ethanol with ammonia as a catalyst. TEOS (FUJIFILM Wako Pure Chemical Co., Japan), 99.5% ethanol (FUJIFILM Wako) and 25% aqueous solution of NH_3 (FUJIFILM Wako) were selected as the Si-source, solvent and catalyst, respectively. Ethanol was dehydrated with a molecular sieve and filtered through a 0.45 μm pore-size filter. TEOS and ammonia water were used as received. The concentrations of TEOS, NH_3 and H_2O (distilled and filtered) were 0.22, 2.0 and 6.0 M, respectively. The flow chart has been published previously¹⁰. The reaction temperature was set at 20°C.

The reaction vessel was placed in an incubator and covered with a polyethylene film, and mixture of chemicals was gently stirred by a magnetic stirrer for 1 min. Then this mixture was divided in 10 sealed vials and stirred by rotation (200 rpm) on an incubator-shaker (experiment #13). Under the condition the solution became translucent blue at approximately 3 min and changed to turbid white at no later than 8 min. Silica particles were sampled at 5,

10, 20, 30, 45, 60, 120, 240, 480 and 960 min from dedicated one of these vials. An aliquot of the suspension was spread directly over bare Si(1 0 0) substrate for industrial use and dried at room temperature in desiccator for several days before FE-SEM observations. Particle diameters were measured on particles with no contact to its neighbours ($n = 31, 19, 26, 20, 18, 14, 29, 19, 22$ and 18 for 5, 10, 20, 30, 45, 60, 120, 240, 480 and 960 min samples, respectively). Silica spheres in a portion of suspension (480 min) was directly transferred in an alumina mortar and manually ground for SEM observation.

The suspensions sampled at early stage ($t \leq 5$ min) contain unignorable amount of reactive silica species and unhydrolized TEOS. These remnants covered the dried surface of the samples like a glue with objects beneath. To deal with this, these samples were rinsed immediately after spreading by dropping dehydrated ethanol on a tilted surface. Surface of the Si-substrate was roughen with a polishing paper (4000 grid; 3M) and then diamond paste ($1 \mu\text{m}\phi$) for these samples so that uneven surface hold soft and tiny particles even on rinsing process. These substrates were used on experiments #11 and #12. In these experiments, the reaction vessel was placed in an incubator but its top was left open for sampling purpose and stirred by a magnetic stirrer over sampling period (3 and 5 min on experiment #11, 1, 2, 3 and 5 min on experiment #12). Particle diameters were measured on particles with no contact to its neighbours (experiment #11: $n = 3$ and 26 for 3 and 5 min, experiment #12: $n = 6, 4, 4, 4$ for 1, 2, 3 and 5 min).

In experiment #14 120 ml of the mixture of chemicals was stirred for 0.5 min and poured into a cylinder of $35 \text{ mm}\phi$ and 200 mm in hight. Top of the cylinder was covered with a polyethylene film and the cylinder was kept 1 month at 20°C to precipitate the particles. The precipitate was dedicated to examine variations in sizes of the spheres from the bottom to the top.

Mechanical grinding was applied also on well-dried silica spheres from preliminary experiment. An aliquot of suspension was taken after 240 min stirring and its precipitate was dried as-prepared for 4 months in desiccator. This precipitate was manually ground in an alumina mortar with dehydrated ethanol as a dispersion medium.

All of SEM images were taken with JEOL JSM-7100F installed at a Venture Business Laboratory of Kanazawa University operated under accelerating voltage of 10-20 kV. No

metal plating was applied except the stack of silica spheres on which serious charge-up was unavoidable without plating (Fig. 1a). Au sputtering was applied on the stack with current of 50 mA for 1min. Thickness of Au plating was determined as 15 nm based on a difference in averaged diameters of silica spheres from same colloid with and without this plating.

Specimen of natural precious opal was taken from a semi-antique accessory of circa 1970's. Detail of locality is unknown. Fragments from this specimen were used for observations without any treatment.

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Author contributions

H.O. supervised the project. T.T. performed experiments and data analysis. Both of the authors contributed to the final manuscript.

Competing interests

The authors declare no competing interests.

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Fig. 1|FE-SEM images of opals with their play-of-colour (insets). a, Stöber particles (artificial opal) precipitated by leaving the reaction medium a month to stand still after 0.5 min of stirring (experiment #14). The stack for SEM observation was plated with Au of 15 nm thickness. **b,c,** Natural precious opal. Typical green phosphorescence after UV irradiation indicated this specimen as an Australian sedimentary precious opal²⁰. Stack of disarrayed and deformed silica spheres on the wall of crack is visible in **c**.

Fig. 2|Size, morphology and internal structure of Stöber particles. All images were taken with an acceleration voltage of 20 kV. **a**, Low-density large polymer sampled after 1 min of stirring. Si substrate has been scared to trap presumably soft objects in the reaction medium. Those scars could be seen through the white spots, namely anisotropically shrank low-density large polymers. **b**, Particle sampled at 2 min. **c**, Particle sampled at 5 min on tilted substrate. Edge of contacting face among the particle and the substrate is visible as a bright ring on the bottom of the particle, indicating semi-translucency of the particle under high-voltage electron beam. **d**, Particle sampled at 240 min with sandy texture on the surface. This texture, however, was vanished when an acceleration voltage was lowered to 10 kV. **e**, Particle squashed immediately after sampling at 480 min with no drying process. **f**, Fracture surface of a well-dried Stöber particle sampled at 240 min.

Fig. 3|Change in size of Stöber particles with reaction time and time segments on formation of Stöber colloid. Error bars represent 1σ on variation of particle diameter and in some cases they are hidden behind symbols. Solid lines are drawn for guide-for-eyes.