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Hydrothermal Precious Opals of the Raduzhnoe Deposit, North Primorye: The Nature of the Opalescence

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Abstract—This paper reports the results of the study of hydrothermal precious opals. It was established that, in terms of their nanostructure and formation conditions, the hydrothermal opals differ from exogenic precious opals. They are made up of small globules and do not show any structuring of their nanoparticles on the basis of closest packing, which is typical of exogenic precious opals. During their formation, these opals were subjected to pneumatolytic annealing—they experienced the impact of a high-temperature vapor under elevated pressure. The influence of the thermal effect led to the formation of two-dimensional photonic band gaps in the chaotic opal matrix. These bands are composed of sheets whose cells were formed owing to the thermal effects according to the principle of "Benard cells." Precisely these structured blocks and thin films are responsible for the spectral dispersion of light and iridescence.

Key words: precious opals, nanostructures, photonic crystals, Primorye, Far East.

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INTRODUCTION

Precious opal occupies a particular role among the large family of amorphous and poorly crystallized minerals of hydrous silica. It is highly valued for its play of color (usually termed opalescence) in various ranges of the visible spectrum (Fig. 1). Recent studies showed that exogenic precious opal (for instance, Australian opal) represents classical 3-D photonic crystals with a band gap allocated in the visible range of electromagnetic radiation [1, 6, 9].[1] The nanosized three-dimensional structure of photonic crystals (called the photonic lattice) allows the propagation of coherent light in the optical wavelength range with minimal losses. The photonic lattice is a pile of thin two-dimensional diffraction lattices. It is considered that ten of these layers are sufficient to create an operating "photonic lattice." Such structures are of great significance for optical communications and computer technology.

Using exogenic precious opals as an example, it was established that the opalescence (the photonic band structure) arises from the diffraction of electromagnetic waves on the volumetric space lattice formed by spherical and icosahedral silica particles. These particles are homogenous in size, ordered according to the law of face-centered cubic or hexagonal packing, and arranged as peculiar well identified nanostructure of precious opal [4, 19, 20].

However, similar structures can be one- and two-dimensional. As was shown by our studies, this can be illustrated by hydrothermal precious opals showing excellent opalescence on two-dimensional photonic band gaps in the chaotic opal matrix [2, 3]. The photon band can also be formed by one diffraction lattice, not only by a combination of ten layers. In this respect, the natural examples of photonic crystals could significantly affect the creation of new nanomaterials.

In the 1980s, a deposit of precious opal was found in the Late Cretaceous altered andesites of the Severyanskaya Formation in northern Primorye (Fig. 2). Some researchers regarded it as an analog of the exogenic precious opals of Australia [10, 21]. However, our studies discarded this conclusion [2]. In this work, we report the results of studying the precious opals of

[1] From the general viewpoint, photonic crystals represent a crystal superlattice, i.e., material with an artificially created additional field, whose period is orders of magnitude higher than the period of the main lattice. For photons, this field can be obtained by periodic variations of the refraction index in one, two, or three dimensions (1D-, 2D-, and 3D-photonic structures, respectively). If the period of the optical superlattice is comparable with the electromagnetic wavelength, the behavior of photons cardinally differs from their behavior in the lattice of common crystals, whose sites are spaced from each other at a distance much less than the light wavelength. Therefore, these lattice were termed as photonic crystals (G. Zhuvikin, "Labyrinth of photonic crystals," Computerra, No. 30, 2001).

Fig. 1. Hydrothermal precious opal from the Raduzhnoe deposit in Primorye.

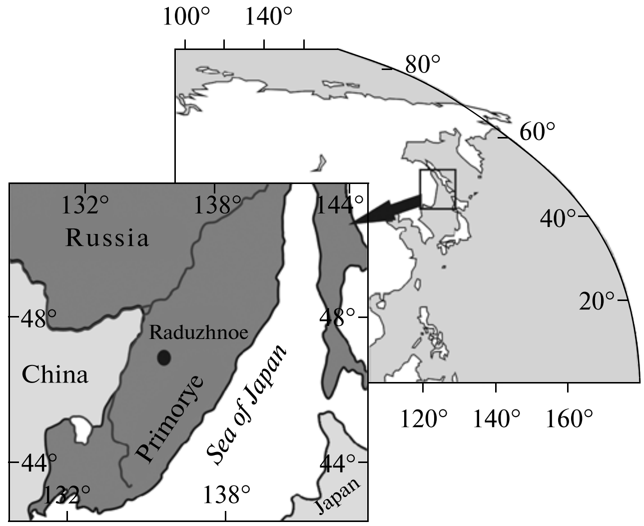

Fig. 2. Position of the Raduzhnoe deposit (Northern Primorye).

Primorye as compared with the iridescent opals from the Cenozoic andesites of Ethiopia.

METHODS

The nanoscale (10^{-6} to 10^{-9} m) structures of the precious opals were studied using a Solver and NTEGRA Aura NT-MDT atomic-force scanning microscope (AFM) (Zelenograd). The nanostructure was studied using NSG10 cantilevers with a spike radius of 10 nm and a resonance frequency of 190–235 kHz. The calibration of the device and the adjustment of the survey technique were carried out using a diffraction lattice with a period of 3 μm and a synthetic opal matrix. Samples of Australian natural precious opals were used for comparison. The microstructure was studied on gold-sputtered samples using scanning electron microscopes (SEM JEOL/EO JSM-6490 and EVO 50 XVP Zeiss).

The study of the opal structure at the atomic–molecular level (10^{-10} m) was conducted using XRD DRON-3 diffractometers and a D8 DISCOVER device (CuK_α monopchromatic irradiation).

Both fresh chips and polished surfaces preliminarily etched with diluted hydrofluoric acid were examined. The collection included precious opals with different appearances: white porcelaneous, yellow, light brown translucent, dull, and other varieties characterized by red-orange and green-blue opalescence.

RESULTS

The opal structure at the atomic–molecular level. It was established that most of the precious opals around the world are ascribed to group A after [15] or to group I after [20]. They usually consist of ball-like uniform silica particles (globules) from 150 to 450 nm in diameter, which are ordered according to the law of the face-centered cubic or hexagonal packing. The interstices between the globules are filled with amorphous silica. In the X-ray patterns, these opals yield a wide diffuse maximum in the region of the main peak of α-cristobalite (4.1 Å), which was also obtained by us for synthetic and exogenic Australian (Fig. 3) and Kazakhstan natural opals. However, other lines of α-cristobalite (or other minerals) are absent.

The X-ray analysis of opals from the Primorye deposits showed prominent peaks in the region of the main peak (4.1 Å); i.e., they are composed of α-cristobalite. The X-ray patterns (Fig. 3) contain only its lines, while the lines of other minerals are absent. Various opals differ in their crystallinity indices: one samples, in addition to α-cristobalite, contained a fairly great amount of amorphous silica, while other samples practically lack it. Similar X-ray patterns were obtained for Ethiopian opals.

Thus, the iridescent opals from the deposits of Primorye and Ethiopia are ascribed to another structural type—K-opals or group III according to classifications [15] or [20], respectively. They are composed of octahedral nanocrystals of α-cristobalite. Precisely such opals are considered to be associated with lava flows [4] and were also described in modern hydrothermal systems [16].

The third group—CT-type opals—was also identified among the opals from Primorye (Fig. 3); however, they show no iridescence. These opals replace

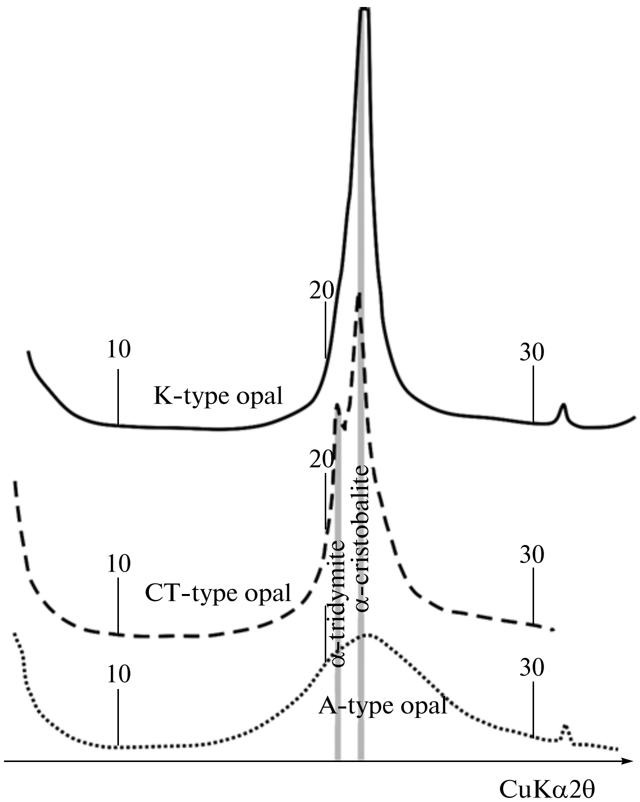

Fig. 3. X-ray patterns of precious opals of the A type (Australia), CT type (pseudomorphs after wood), and K type (the Raduzhnoe deposit).

paleowood. In their X-ray pattern, they show two distinctly expressed peaks corresponding to two minerals: α-cristobalite and α-tridymite.

Detailed studies revealed that the precious opals of Primorye contain inclusions of feldspars, clay, and some other minerals. However, their concentrations are too low to yield the characteristic reflections in X-ray patterns.

Nanostructure of opals. Exogenic and hydrothermal opals have distinctly different nanostructures. As was repeatedly mentioned and seen in the presented figures (Figs. 4a, 4b), the exogenic opals consist of randomly oriented blocks made up of globules (~200 nm in size) densely packed according to the hexagonal or cubic law.

Precious opals of hydrothermal genesis have a sharply different nanostructure. They consist of silica globules 40–90 nm in size, which sometimes form sinters up to 200–300 nm in size. However, in any case, their arrangement is inconsistent with the laws of closest packing (cubic or hexagonal).

However, these opals contain a photonic band gap, which distinctly follows from the presence of cellular layers (Fig. 5). The latter are created by sheet with strict short- and long-range ordering. The unit cell size in the precious opals varies within the λ/2 spectra of visible light (200–350 nm). For greater cells (we found layers with a cell size of about 500 nm), opalescence is not observed.

As is seen in Fig. 5a, 5b, and 5c, the sheet cells consist of small (40–90 nm) chaotically arranged globules. In the points of these cells, the globules are united in sinters, which are comparable in size with the cells, whereas their walls can be two times thinner. In some cases, they form hexagonal cells; however, the high diagenetic transformation of hydrothermal opals often obliterates their initial shape. In the lower grade

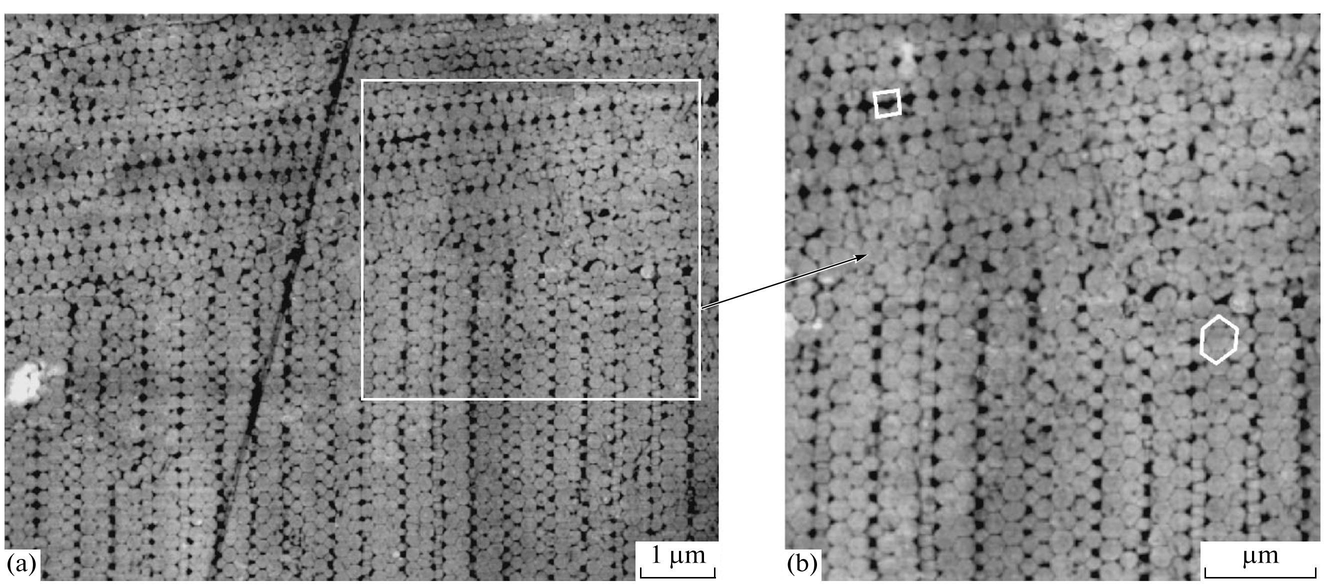

Fig. 4. White precious opal of exogenic origin (Australia):
(a) the boundary of blocks; (b) alternation of layers with hexagonal and cubic packing. AFM image.

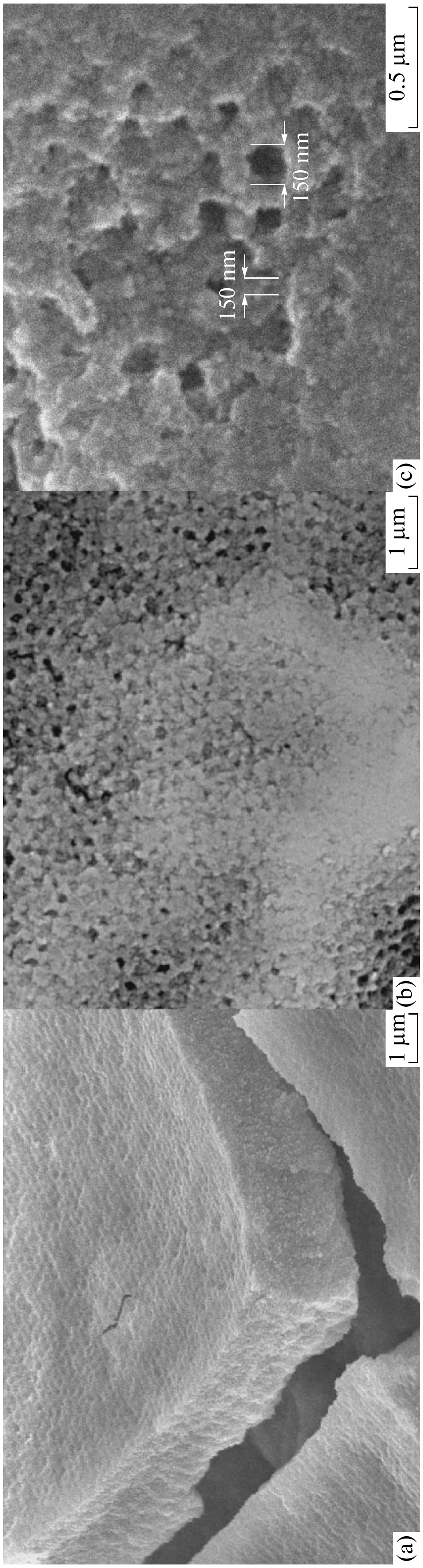

Fig. 5. Precious hydrothermal opal, Raduzhnoe deposit, Primorye:

(a) plane two-dimensional cellular sheet; (b) fragment of a sheet; (c) hexagonal motif of a cellular sheet. SEM image.

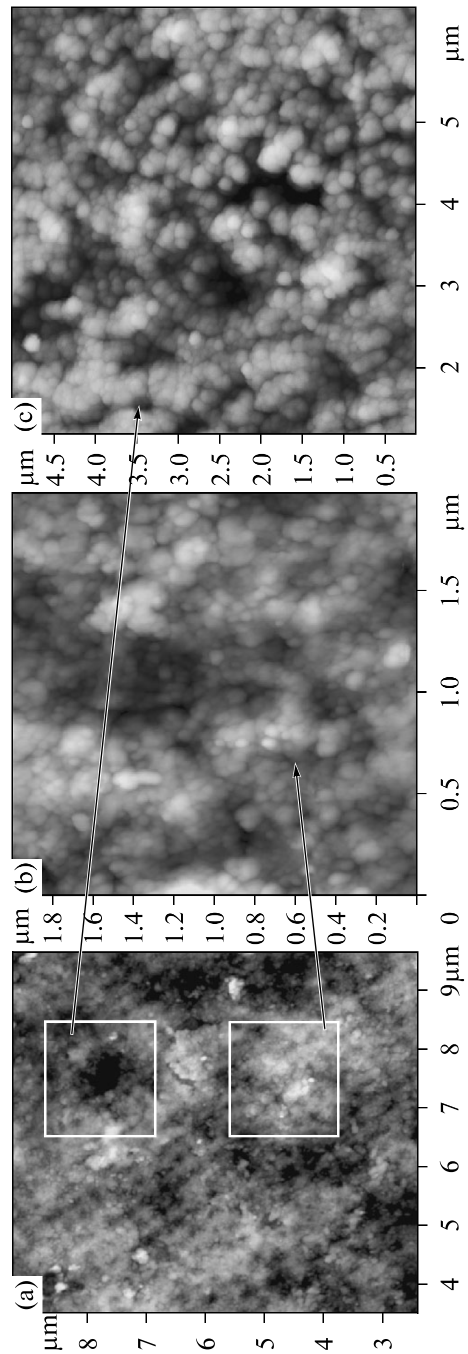

Fig. 6. Precious opal, Eritrea (Africa):

(a) cellular sheet in a hydrothermal opal; (b) absence of globule ordering; (c) channel on the surface of a hydrothermal precious opal. ASM image.

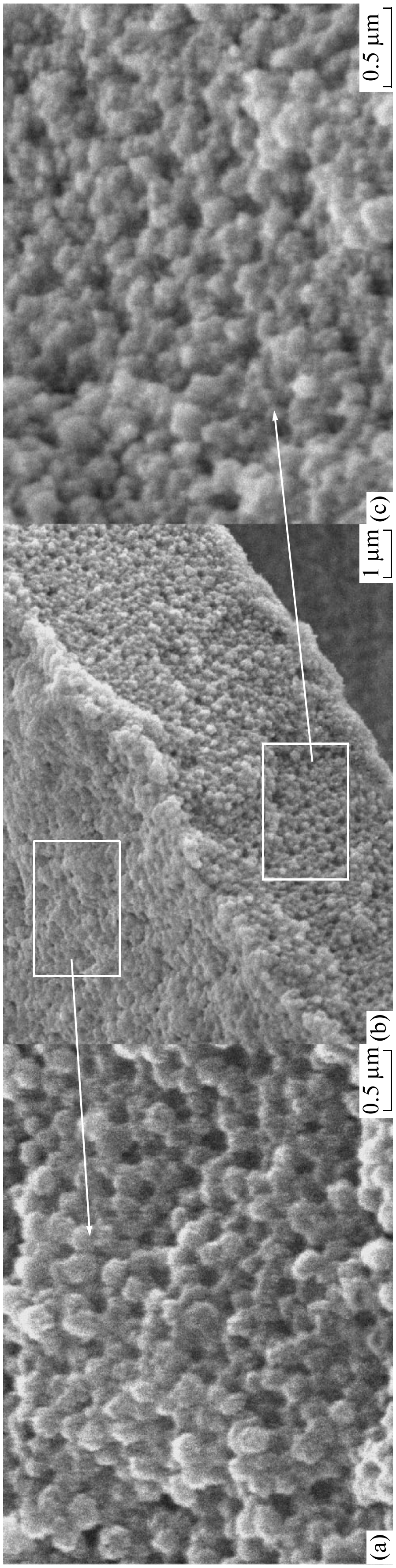

Fig. 7. Packages of films in a precious hydrothermal opal, Raduzhnoe deposit, Primorye:
(a) chaotically packed globules of a package surface; (b) ordered cellular layers on the lateral section of samples; (c) hexagonal motif of packing of the globules of a lateral section. SEM image.

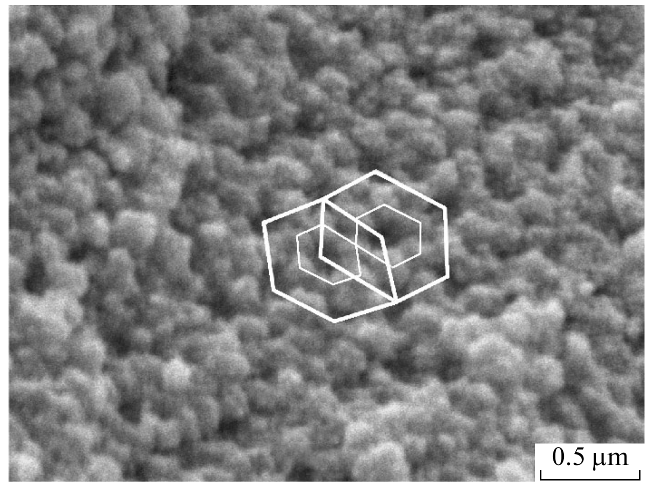

Fig. 8. Fragment of a two-level photonic lattice.
The diameter of the internal hexagon is 300 nm, while that of the external hexagon is 600 nm.

opals, the globules sometimes show concentric zoning, which probably marks the channels for transportation of hydrothermal solutions (Fig. 6c). In the diagenetic opals, these channels are typically filled with clay minerals.

Up to now, two types of photonic blocks have been identified: thin single films and their packages. In the thin films, the cellular structure is not propagated deep inside the opal (Fig. 5a). They are characterized by a one-layer sheet with a thickness comparable with the cell size. As was shown previously [3], these single sheets from the bottom and top are overlain by opal layers with chaotic globule packing. This results in the formation of a thin film of two-dimensional photonic crystals providing the opalescent effect.

These packages are volumetric (about 3 μm thick) with ordered sheets oriented perpendicularly to the surface plane (Fig. 7b). The package's surface is composed of chaotically arranged globules. However, the lateral section demonstrates an ordered structure with fragments of cubic and hexagonal packing. The upper cellular layer is underlain by at least two ordered layer sheets (Fig. 7b). In this sample, the globules are approximately 90 nm in size, while the cells (holes) are approximately 200 nm. Judging from this example, the periodicity of the optical superlattice in the packages is provided by the combination of the cristobalite globules and the holes between them and could have a more intricate configuration than common closest

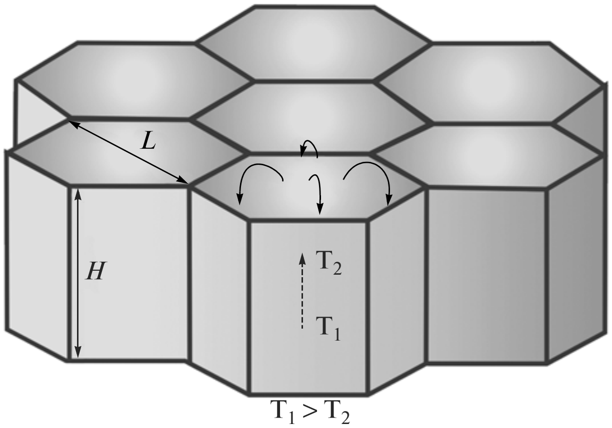

Fig. 9. Model of a convection cell according to the principle of the Benard cell.
$T_1 > T_2$ is the temperature gradient, L is the linear size of the cell, and H is the cell's height.

packings. For instance, Figure 8 demonstrates that the globules and cells form a two-level hexagonal lattice. The size of the internal hexagon formed by the globules is two times less than the external hexagon consisting of cells. Note that the globules themselves represent a cluster of small spheroids with a size of no more than 50 nm.

Diagenesis. Unmetamorphosed varieties of hydrothermal precious opals with spherical globules are scarce among the Primorian samples. The opal particles from the Raduzhnoe deposit are typically deformed and have a diskoid, conic, or rectangular shape [3]. Spherical nanoparticles are usually tightly "welded" with each other. They form clusters of two, three, and more globules, which cannot be broken without the violation of their integrity. When such a violation is caused by chemical etching, the surface of the globules is never smooth and always contains filiform, acicular, or knobby residues of incompletely dissolved material. Sometimes, we observe a transition from a granular to glassy structure. All these facts, together with the presence of the crystalline phase, indicate that the opals were subjected to high temperatures.

DISCUSSION

The presented data unambiguously indicate that hydrothermal opals differ from exogenic precious opals in terms of their nanostructure and formation regime. In the globular domains, the opal particles are tightly intergrown and represent a single cluster with intergranular silica. The presence of diskoid fragments consisting of small flattened nanoparticles [3] indicates that, in some cases, the spheroids were deformed during the opal transformation. Occasionally, the granular structure grades into a vitreous structure. All this, in addition to the presence of the crystalline phase, indicates that the opals experienced a high-temperature impact. As was shown by the experimental data, a similar result can be reached by the thermal treatment of opal with superheated water vapor [7, 8]. In this case, the globules are welded with each other with the formation of strong siloxane bonds. An increase in the vapor pressure provokes the complete devitrification of the amorphous silica, the disturbance of the structural arrangement of the globules in the blocks, and the loss of iridescence. Even the partial devitrification of amorphous silica leads to volume changes, thus causing volumetric defects and fracturing, which are typical attributes of the opals from the Raduzhnoe deposit.

However, the most interesting feature of hydrothermal precious opals is the presence of two-dimensional photonic crystals within the chaotic opal matrix. These photonic crystals are based on a periodic sheet, whose cell size is comparable with the light wavelength in the visible range. The hexagonal configuration of the cells recorded in some samples, as well as the ordering of the cells according to the closest packing law, indicates its nonchaotic formation.

Similar structures are formed by thermal convection and are known in physics as Benard cells. If the liquid temperature from the bottom is increased, there will be some critical temperature at which convection will appear: the warmer lower layers of the liquid expand and become lighter than the colder upper layers and float upward, where they are cooled and again descend, etc. This produces convection cells, which are similar to bee's cells: vertically arranged tight hexahedral cylinders (Benard cells). The movement of liquid is stabilized by its viscosity, since the strength of friction is directed against it. The liquid ascends inside cell along its axis, is spread along the upper plane, descends along the lateral sides, accumulates along the lower base toward its central part, and again ascends (Fig. 9). This process produces a dynamically ordered structure. If the temperature gradient causes coagulation, thus formed globules are allocated the along cell perimeter to form an ordered lattice with similar cells.

At present, three mechanisms are proposed to generate the thermal convection by heating from below. The first, the Rayleigh mechanism, is triggered by the buoyancy force, which is generated by the volume expansion of liquid due to its heating [14]. The second mechanism is provoked by the difference of surface tension forces due to their dependence on the temperature–thermocapillary effect [17, 18]. The third mechanism is related to the excitation of thermoelectric effect [5] in liquids with a dielectric constant high enough to prevent the compensation of the volume charge arising in the liquid.

However, the sizes of Benard cells obtained in experiments are much more than the sizes of cells established by us in the hydrothermal precious opals. It is known [14] that heating the liquid film–base open system from below with a temperature gradient oriented normally to the base results in the formation of stationary periodic structures (Benard cells) at the expense of convection movement. Their sizes vary from hundreds of microns to a few millimeters, and they fill the entire surface of the base. The temperature gradient in this case is insignificant (up to hundreds of degrees), while the thickness of liquid layer does not exceed one millimeter. High-density liquids, if the thickness of their layer is no more than a millimeter [18] and they lie on heated bases, could reveal the thermocapillary effect [17], which also leads to the formation of Benard cells with sizes up to a few millimeters. Top heating with a temperature gradient from 1000 to 10000°C causes the transformation of solids into a melt. This process is accompanied by the appearance of the thermoelectrical effect perpendicular to the surface [11–13], thus providing convection stirring from the top downward. As a result, periodic structures with sizes up to tenths of millimeters are formed at a melt depth of hundreds of microns.

If precious hydrothermal opals are formed in fissures, it is necessary to take into account the great pressures of overheated vapor saturated in nanometer silica granules at a low temperature gradient (no more than 200°C). The sizes of the granules in precious hydrothermal opals vary from tens of nanometers to a few hundred nanometers, which is significantly less than the previously observed Benard cells formed according to one of the three aforementioned mechanisms. This can be related to the insignificant width of the fissures in the rocks, the high pressure, the rate of the overheated vapor passage, and the vertical temperature gradient. Such a combination of parameters should accelerate the formation of Benard cells. The regimes of operation of the hydrothermal vents that transfer to the Earth's surface liquids of different density and composition could change with time depending on the amount of overheated vapor in the eruption. This must lead to a change of the formation conditions and sizes of the Benard cells. As was noted, in one sample of precious hydrothermal opal, we observe the formation (at different levels) of either individual layers with a plane periodic structure alternating with amorphous silica layers or a set of planes with periodic packing of the granules in the vertical and (with high probability) horizontal planes. It is necessary to suggest in this case that the regime of the hydrothermal vent periodically changed with time, and individual ejections of hydrothermal vapor alternated with weak diffusion transfer of vapor from a source with elevated contents of silica granules. In the former case, the layer with periodic alternation of the structures was formed, while the increase of the silica density in the vapor and the decrease of its rate and pressure led to the formation of the disordered silica layer. Then, the vent began to operate periodically and with a high frequency, ejecting portions of overheated vapor variably saturated with silica. The process of the formation of the ordered structures repeated in each subsequently forming layer, which led to the formation of a pile of ordered layers. The cell size depended on both the pressure of the overheated vapor and the degree of its saturation with silica granules.

CONCLUSIONS

Thus, the hydrothermal iridescent opals from the Raduzhnoe deposit differ in the nanostructure and regime of their formation from exogenic precious opals. They are made up of smaller globules, and the nanoparticles in them are not arranged in closest packing, which is typical of exogenic precious opals. During their formation, they were subjected to pneumatolytic annealing—the influence of high-temperature vapor at elevated pressure.

At the same time, the influence of the thermal effects promoted the formation of two- and three-dimensional photonic band gaps (photonic crystals) in the chaotic opal matrix. Precisely these structured blocks and thin films are responsible for the dispersion of light and the production of the iridescence. The band gaps consist of sheets whose cells were formed in response to the thermal effect by the mechanism of Benard cells. The mechanism of the formation of the photonic band gaps is complicated by the disequilibrium conditions: the large pressures of the overheated vapor, the variable degree of saturation with nanosize silica granules, the relatively low temperature gradient, and the pulsed character of the process. The self-organization led to the formation of complex two-level ordering structures, which cause the spectral dispersion of light and the formation of the iridescence.

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