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Hydrothermal Noble Opal: Structure and Genesis

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Abstract—The results of the study of hydrothermal noble opal are discussed. It has been established that hydrothermal opal differs in its nanostructure and formation conditions from exogenic noble opal. The former is composed of smaller globules without any structuring of closely packed nanoparticles characteristic of exogenic opal. In the course of formation, hydrothermal opal is affected by pneumatolytic annealing related to the effect of high-temperature vapors under an elevated pressure. At the same time, the thermal effect results in the formation of two-dimensional photon zones in the chaotic opal matrix. These photon zones are produced by grids, the cells of which arose from a thermal effect similar to what related to Benard cells. Precisely, these structured blocks and thin films lead to spectral dispersion of light and appearance of iridescence.

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INTRODUCTION

As is known, noble opal is a gem variety of the wide family of amorphous and poor crystallized minerals of hydrous silica. It has a typical play of colors in the visible spectrum that was named opalescence. Contemporary investigations showed that exogenic noble opal is a classic photon crystal, the photon band gap of which is in the visible range of electromagnetic radiation (Baryshev et al., 2004; Kavtareva et al., 2007; Romanov et al., 2007). As has been established for exogenic opal, opalescence (photon energy-band structure) appears in the resultof diffraction of electromagnetic waves on a three-dimensional lattice formed by spherical or icosahedral silica particles. These particles, which are identical in size and ordered according to the law of face-centered or hexagonal packing, create the special and readily recognizable nanostructure of noble opal (Sanders, 1964; Deniskina et al., 1987).

Despite the fact that 95% of natural noble opal are produced from ancient weathering mantles (exogenic deposits), hydrothermal deposits related to volcanic rocks are known in many regions worldwide. They are not important but they attract interest with regard to their genesis. Nevertheless, hydrothermal opal is poorly documented and some of its features have not been studied yet. In particular, this concerns the nanostructure and the true parameters of the formation environment of some noble opal varieties.

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In the 1980s, the occurrence of noble opal hosted in the Upper Cretaceous altered volcanic rocks of the Severyanka Formation was discovered in the northern Primorye. Some authors consider this opal to be an analogue of the exogenic noble opal from Australia (Tishkina et a., 2003; Tishkina and Lapina, 2004). However, our preliminary studies have already shown that this is not the case (Vysotsky et al., 2008). In this paper we discuss the results of the study of hydrothermal opal from Primorye as compared to iridescent opal from Cenozoic andesite of Eritrea.

EXPERIMENTAL

The nanoscale (10^{-6}–10^{-9} m) structure of noble opal was studied with Solver and NTEGRA Aura NT-MDT (Zelenograd, Russia) atomic force microscopes (AFM). In the study of the nanostructure, NSG10 cantilivers with a radius of tip rounding of 10 nm and a resonance frequency of 190–325 kHz were used. The calibration of the device and the adjustment of the recording procedure were performed on a diffraction grid with a spacing of 3 μm and a matrix of synthetic opal; samples of Australian natural noble opal were used for comparison. The microstructure was studied on a JEOL/EO JSM-6490 and EVO 50 XVP Zeiss SEMs using samples coated with gold.

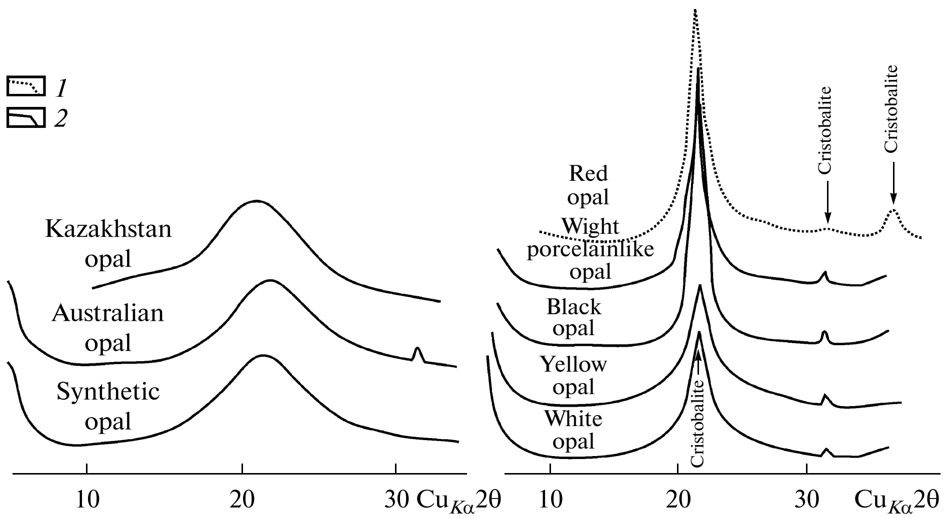

Fig. 1. X-ray diffraction patterns of the A-type (left) and C-type (right) noble opal. C-type opal: (*1*) Eritrea, Africa and (*2*) Raduzhny deposit, Primorye, Russia.

The atomic–molecular (10^{-10} m) structure of opal was investigated with DRON-3 and D8 DISCOVER diffractometers (Cu_{K_α} monochromatized radiation).

Both fresh chips that had not undergone any preliminary treatment and polished surfaces etched by diluted hydrofluoric acid were studied. Noble opals different in color and transparency—white porcelain-like, yellow, light brown, translucent, and dull—were involved in the examination. Red–orange and green–light blue opalescence was observed in the samples.

RESULTS

Atomic–molecular structure of opal. A study of the structural varieties revealed that worldwide most noble opals are attributed to the A type according to Jones and Segnit (1971) or type I according to Smith and Thrower (1978). They consist of identical spherical particles of SiO_2 150 to 450 nm in diameter and ordered according to the law of face-centered or hexagonal packing. The space between these particles is filled with amorphous silica. The X-ray diffraction patterns of this opal show a broad fuzzy peak in the region of the major extremum of α-cristobalite (4.1 Å) that was recorded for synthetic and Australian and Kazakh natural opals (Fig. 1). No other reflections of α-cristobalite or other minerals were observed.

The X-ray diffraction study of opal from Primorye and Eritrea indicated that the mineral is composed of α-cristobalite because pronounced peaks are noted in the region of the major extremum (4.1 Å). The X-ray diffraction patterns (Fig. 1) comprise a wide set of reflections of α-cristobalite, whereas reflections of other minerals are absent. The crystalinity of the samples studied is variable; some of them contain quite great amounts of amorphous silica along with α-cristobalite, while others are practically free of it.

Thus, iridescent opal from Primorye and Eritrea belong to another structural type: C-opal according to Jones and Segnit (1971) or type III according to Jones and Segnit (1971). It is composed of octahedral nanocrystals of α-cristobalite. It is suggested that preciselythis opal is associated with lava flows (Deniskina et al., 1987). This type of opal was described in active hydrothermal systems (Jones and Renaut, 2007).

Among opals from Primorye, CT-opals are also identified (Fig. 2); however, no iridescent varieties have been established. The X-ray diffraction patterns of intercalating opal and chalcedony are shown for comparative purposes. As is shown in Fig. 2, the presence of α-quartz is a specific feature of chalcedony.

It should be noted that opals from Primorye contain inclusions of feldspars, clay, and other minerals. Due to the extremely low concentration, the characteristic reflections of these minerals are not detected in the X-ray diffraction patterns.

Nanostructure of opal. Exogenic and hydrothermal opals are clearly distinguished at the nanoscale. As was previously stated and illustrated in Figs. 3a and 3b, exogenic opal consists of randomly oriented blocks composed of globules ~200 nm in size, which are closely packed in compliance with the hexagonal or cubic law.

Hydrothermal noble opal has an absolutely distinct nanostructure. Silica globules range from 40 to 60 nm in size. Occasionally, they occur as agglomerates up to 200–300 nm in size, but in any case, their spatial arrangement does not correspond to the closest packing (cubic or hexagonal).

At the same time, the photon energy-band structure occurs in such opal as clearly indicated by opalescence. This phenomenon is probably caused by the presence of cellular layers (Figs. 4a–4c). Such layers

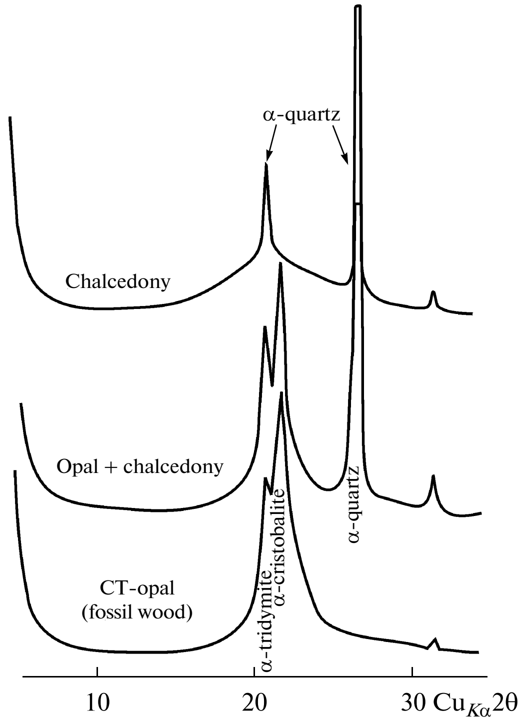

Fig. 2. X-ray diffraction patterns of CT-opal, chalcedony, and fine opal–chalcedony intercalation.

are formed by a grid with strictly ordered cells. The size of the cells in noble opal varies within λ/2 of visible light (150–300 nm). If the cell size is larger (we have found layers with a cell size of about 500 nm), opalescence is not observed.

As is seen in Fig. 5, the cells of the grid are formed by fine (40–60 nm) chaotically arranged globules. In the cell nodes, these globules occur as agglomerates comparable in their size with the cell itself, whereas the walls may be twice as thin. In some cases, a hexagonal shape of the cells is documented, though the primary shape is frequently obscured as a result of the high degree of diagenesis of hydrothermal opal. In slightly diagenetically transformed opal, the concentrically zonal arrangement of globules probably marks the conduits of the hydrothermal solution (Fig. 5c). In completely altered opal, such feeders are usually filled with clay minerals.

As is seen in Fig. 6a, the cellular structure does not penetrate deeply within opal. The grid is most likely a monolayer and its thickness is comparable with the cells in size. From above and below, this grid is covered by continuous opal layers with a chaotic packing of globules (Figs. 6a, 6b). As a result, a thin film of two-dimensional photon crystal providing the effect of opalescence is formed.

Diagenesis. Unmetamorphosed varieties of hydrothermal noble opal with spherical globules are not frequently found among the samples from Primorye. The particles of opal from the Raduzhny deposit are usually deformed and become disk-, cone-, or rectangular-shaped (Vysotsky et al., 2007). As a rule, spherical nanocrystals are closely amalgamated with one another. They occur as clusters consisting of two–three and more intergrown particles, which cannot be broken without corruption. When this occurs as a result of chemical etching, the surface of globules is never smooth. Piliform, acicular, or bumpy relics of undissolved material are always retained at the surface. Occasionally, transition from a granular to vitreous texture is recorded.

DISCUSSION

The aforementioned data unambiguously indicate that hydrothermal opal and exogenic noble opal differ in their nanostructure and formation conditions. If globules are present, they are intergrown and consti-

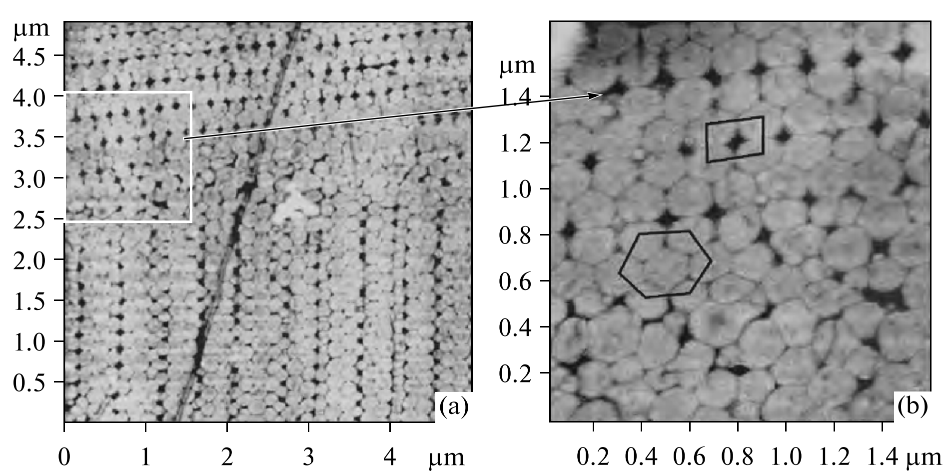

Fig. 3. AFM image of exogenic white noble opal from Australia: (a) boundary of blocks, (b) alternation of layers with hexagonal and cubic packing.

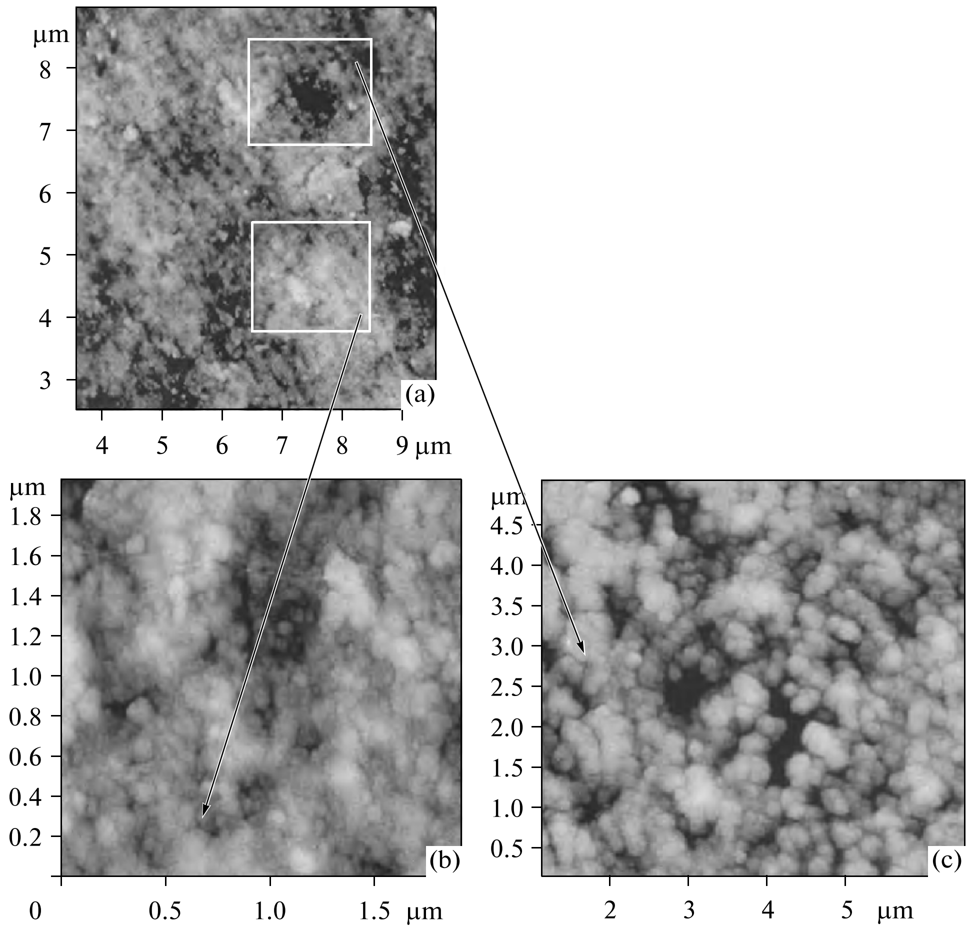

Fig. 4. AFM images of hydrothermal noble opal from Eritrea, Africa: (a) cellular grid, (b) disordered globules, (c) feeding conduit.

tute a comprehensive whole with intergranular silica. The disk-shaped fragments consisting of smaller flattened nanoscale individuals show that in some cases globules were deformed as a result of opal transformation. Occasionally, transition from a granular to vitreous texture is recorded. This all, in combination with the presence of crystalline phases, provides evidence that opal was affected by high temperatures. As follows from the experiments, a similar result may be reached through thermal processing of opal with superheated water vapors (Kazantsev et al., 1978; Kalinin et al., 1981). In this case, globules are sintered sustaining strong siloxane bonds. The elevated vapor pressure leads to complete devitrification of amorphous silica, structuring disturbance of globules, and loss of iridescence. Even partial devitrification of amorphous silica results in a volume change that leads to bulk defects and fracturing, which are characteristic of opal from the Raduzhny deposit.

Two-dimensional photon crystals within the chaotic opal matrix are the most intriguing feature of hydrothermal noble opal. These photon crystals are based on a grid with a cell size comparable with $\lambda/2$ in the visible light range. The hexagonal shape of the cell recorded in some samples and the cell ordering according to the laws of the closest packing furnish serve as evidence for its nonrandom formation.

Similar structures are formed as a result of thermal convection and are known in physics as Benard cells. If a liquid is heated from below, then convection starts at a certain critical temperature; i.e., the hot lower layers of the liquid expand, become lighter than the cold upper layers, ascend, then cool and descend again. The convection cells resembling honeycombs, i.e., vertical hexagonal cylinders closely adjoining one another (Benard cells), form in the liquid. The movement of the liquid is stabilized by its viscosity, because the friction force acts in the opposite direction. The liquid ascends within the cell along its axis, spreads at the upper edge, descends along the lateral sides, gathers in the center of the lower edge, and ascends again (Fig. 7). A dynamically ordered structure forms. If a drop in the temperature leads to coagulation in the liquid, then the precipitating globules will accumulate at the cell perimeter to form an ordered lattice with cells identical in size. The size of these cells will probably

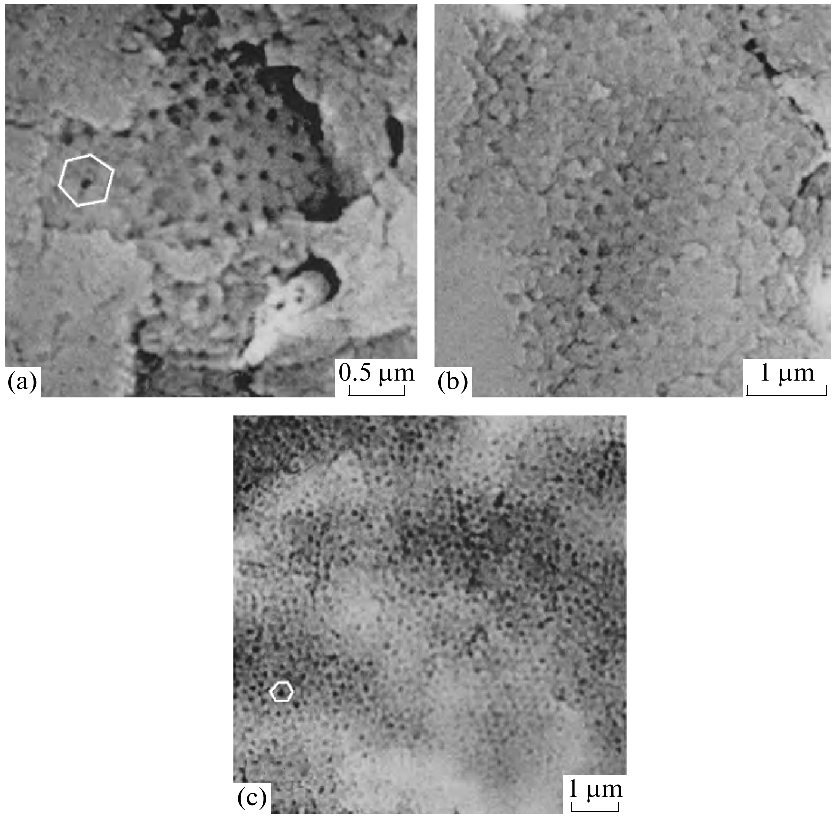

Fig. 5. SEM images of noble opal from the Raduzhny deposit, Primorye, Russia: (a, b) grid in opal overlain by a continuous layer of chaotically packed globules, (c) hexagonal motif of the grid cells.

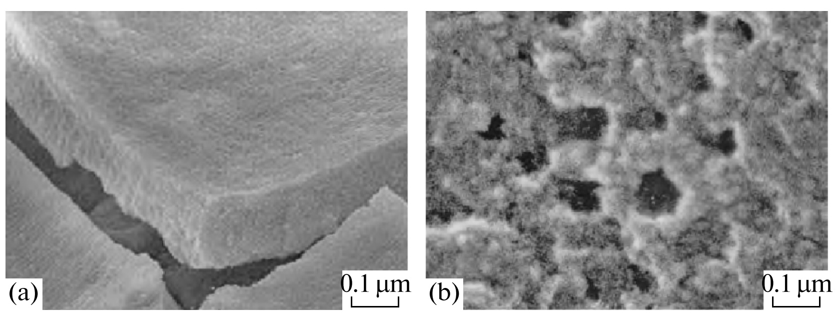

Fig. 6. SEM images of hydrothermal noble opal from the Raduzhny deposit, Primorye, Russia: (a) cellular grid at the surface of the block with a chaotic packing of globules, (b) hexagonal cells.

depend on the *PT* conditions of the hydrothermal system.

CONCLUSIONS

Thus, hydrothermal opal of the Raduzhny deposit differs in its nanostructure and formation conditions from exogenic noble opal. It is composed of smaller globules and does not reveal any structuring of nanoparticles according to the law of the closest packing typical of exogenic noble opal. In the course of formation, opal was affected by pneumatolitic annealing related to the effect of high-temperature vapors under an elevated pressure.

At the same time, the thermal effects led to the formation of two-dimensional photon energy-bands in the chaotic opal matrix. These photon energy-bands are created by grids, the cells of which were probably formed in a way similar to the formation of Benard convection cells.

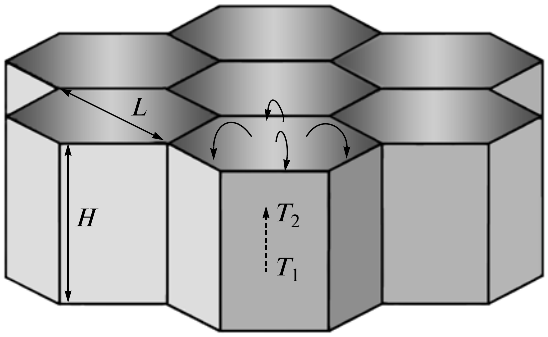

Fig. 7. Model of a Benard convection cell. $T_1 > T_2$ is the temperature difference, L is the linear dimension of the cell, and H is the height of the cell.

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