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FIBROUS NOBLE OPALS: ELECTRON AND ATOMIC-FORCE MICROSCOPY AND SPECTROMETRY DATA

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Abstract. The work deals with results of study of hydrothermal noble opals. It has been established that hydrothermal opals are composed of multiple clusters: chaotic packs, fibers and grid layers. An effect of the water saturation coefficient on the opal optical properties was considered.

Synthetic noble (opalescent) opals have well-known structure adequate to the law of face-centered cubic or hexagonal close packing [1]. The same structure is characteristic [2, 3] for the majority of natural noble opals, in particular opals from exogenic deposits that associate with residual sedimentary or volcanic rocks. Other type of opal deposits is hydrothermal (fibrous noble opals by Fritsch E. et al [4].) wich is not uncommon in the world; though constitute no more than 5% of the total volume of opal mining [5]. Deposits of such opals locate in Mexico, Slovenia, Germany, Ethiopia, and USA; the only deposit in Russia, “Raduzhnoe”, also belongs to this type. Hydrothermal opals strongly differ from the exogenic amorphous opals of Australia and Brazil [6, 7, 8]. This opals consist of mainly crystobalite, rather than amorphous silica like exogenic opals. Study of their nanostructure shows that they are made up of great number of chaotically packed globules [7, 9, 10]. Globules spatial position in the internal structure disaccords (Fig. 1) with the law of face-centered cubic or hexagonal close packing.

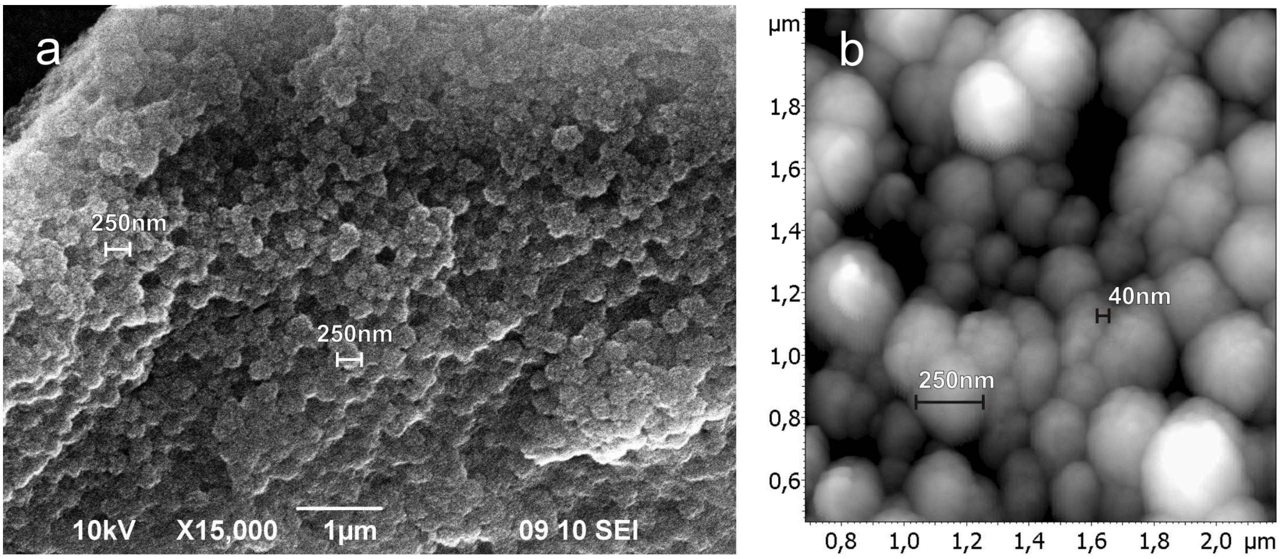

Figure 1. Supramolecular hydrothermal noble opal images: a- layers of flattened globules under EM JSM-6490LV, b- internal structure of globules under AFM Solver NT-MDT.

As it is shown on Figure 1, large (~250nm) flattened globules (Figure 1a) are composed of chaotically assembled small (30-50nm) particles (Fig. 1b) and are placed in a quantity of layers. Recenly fibrous structures have been discovered in hydrothermal opals of Mexico [4, 10].

The ordered layers-grids, detected earlier by Vysotsky's team [8] in the structured clusters, may form a repeated pattern (fig. 2a) with the thickness sometimes more than 3 microns (Fig. 2b). Depending on an angle of cutoff, the ordered grid can be shown on a surface, settle down at an angle (Fig. 2a) or perpendicular to a surface plane (Fig. 2b). Figure 2b demonstrates lateral cut of a package where the ordered structure with fragments of cubic and hexagonal packing is seen. But more often, singular layers-grids occupy a position between layers of the chaotically packed opal globules (Fig. 2c, d). On Figure 2c, lateral cut exposes a single-wall grid, which thickness (30-50 nm) is comparable with a globule size; the distance between layers is 1.5-2 μm. The globules are soldered among themselves, their initial form is deformed. On Figure 2d, a singular layer-grid is apparent in the "window" of randomly packed opal matrix; size of globules and cells (apertures) in this sample approximates 90 and 150-200 nm, respectively.

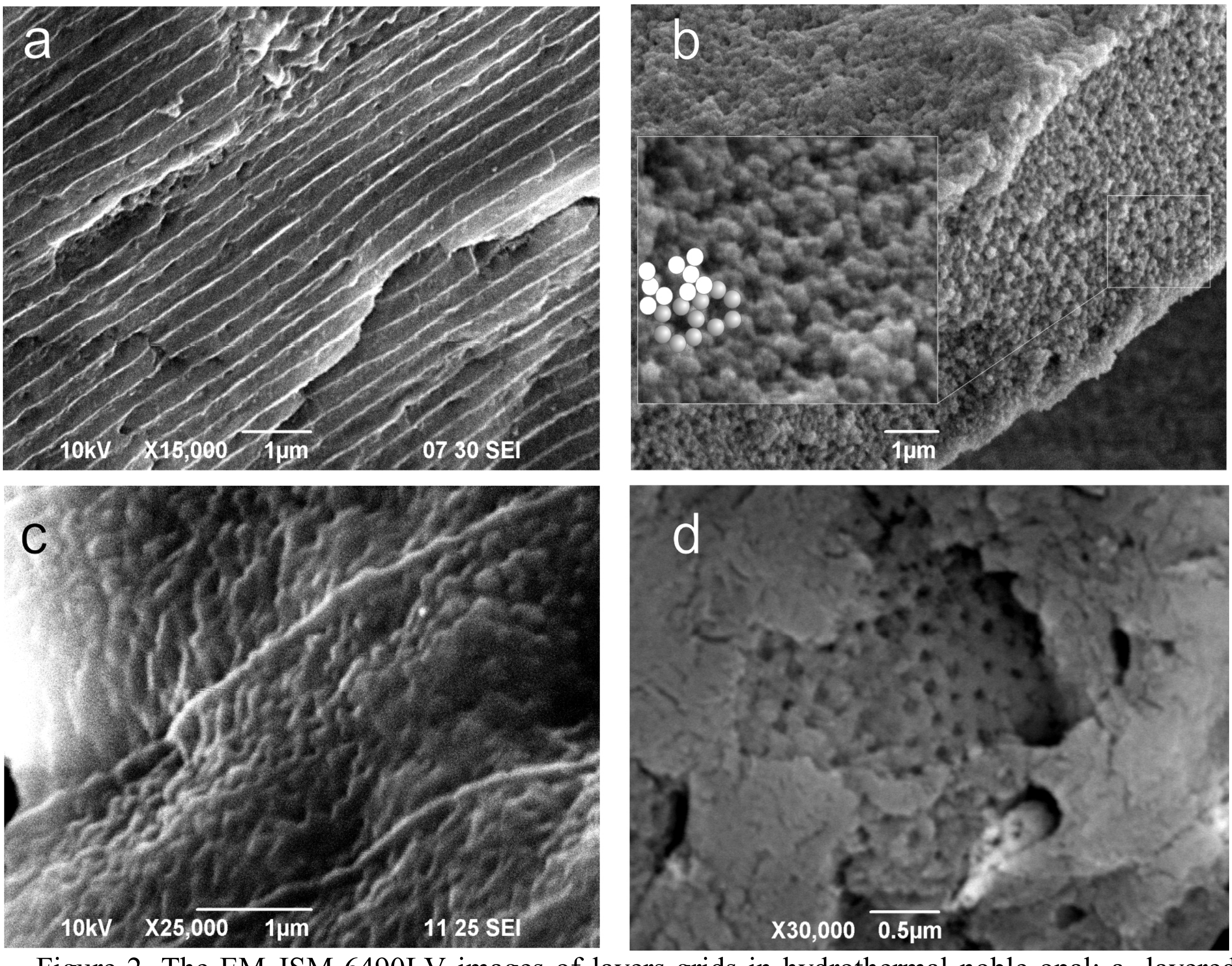

Figure 2. The EM JSM-6490LV images of layers-grids in hydrothermal noble opal: a- layered clusters, b- fragments of cubic and hexagonal pack (cutoff), c- singular layers-grids in chaotically packed opal globules, d- singular layer-grid is apparent in the "window" of randomly packed opal matrix.

Opal structure in its total volume does not have an ideal (homogeneous) uniform packing at all, but represents an aggregate of unstructured and structured or, as the extreme case, only structured blocks. Borders between blocks are not crystallographic. Blocks connect by means of dislocation lines or adjoin to each other with saving the integrity and structure continuity. Silica globules in hydrothermal opals are often metamorphosed and soldered together. Our further investigations have revealed that there are several degrees of crystallization. The opalescent hydrothermal opals are notable for weakly metamorphosed structures.

When studying one of noble opal samples from the Wollo province deposits, Ethiopia, we have find out zones of tubular/fiber structure (Fig. 3). On Figure 3в and 3c there are seen parallel - oriented tubules. It is worth to notice that sample preparation provides a long being of samples in the water and then in the solution of hydrofluoric acid. Image of the same place of the sample (Fig. 3d) made in a month, when the sample has dried out, showed more compressed structure that was apparently bound with a degree of water saturation. Such effect has never been noticed before.

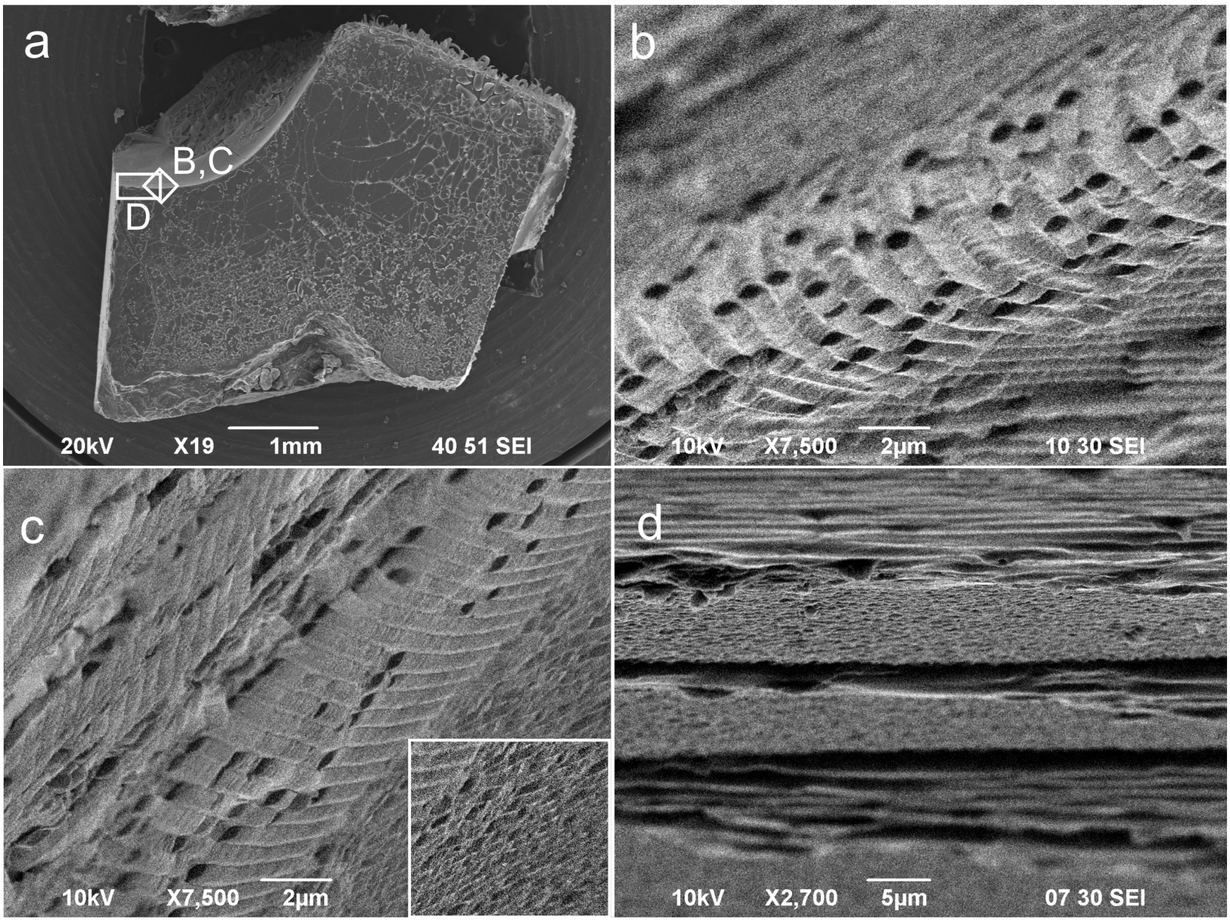

Figure 3. The EM JSM-6490LV images of hydrothermal noble opal: a – general view of the sample; b - tubules; c and d - lateral side of the layered block, the combined image of the same place made at different depth of sharpness. Top of the sample is polished, lateral sides are natural chips.

To confirm the effect, opals saturated with water have been analyzed with the help of spectrophotometer to observe changes of their optical properties. Zones with the brightest opalescence were chosen. Comparison of reflectance and transmittance spectra of dry opals and opals that were soaked in water for two months revealed that exogenic Australian and synthetic opals remained practically unsaturated. Their reflection factor value (Fig. 4c) was reduced without change of spectra form, and the transmittance remained practically unchanged. The transmittance constancy testifies that the water did not penetrate through the sample. This is because both the synthetic and exogenic opals represent the aggregates of the most densely packed silica globules.

Hydrothermal opals from the "Raduzhnoe" deposit exhibited absolutely different optical characteristics. The Figure 4 shows that hydrothermal opal (b, e, f) saturated with water has a sharp decrease in the reflectance and increase in transmittance of the system. This is because when the pores between the silica globules are filled with water, refractive index is changed ($n = 1$ for air and $n = 1.33$ for water). The reflectance decreases at the water - silica boarder, thus increasing the transmittance of the system. Therefore, we observe only decreasing of reflectance, whereas the transmittance of the sample does not change. Minor changes in the reflectance and transmittance spectra for Wollo opal (Fig. 4 d) can be explained by the denser packing of general structure and higher degree of metamorphism. In this case pore size becomes smaller and water does not pass through.

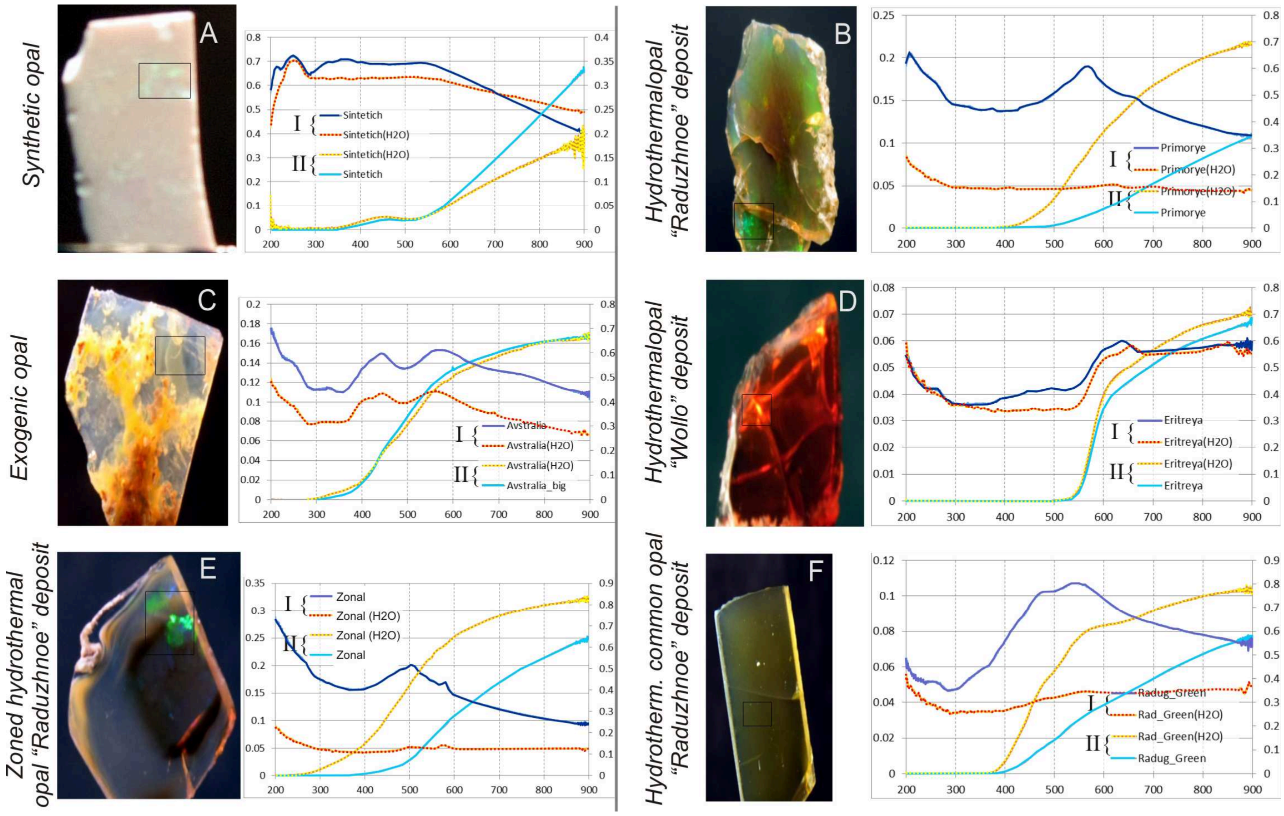

Fig. 4. Reflectance (I) and transmittance (II) spectra of the dried opals (solid line) and opals saturated with water (dashed line), Hitachi U-3010.

Summary

Combined facts about the hydrothermal opals allow several conclusions:

1. Hydrothermal opals are composed of blocks possessing various properties: a –blocks of chaotically packed globules (predominate), b - layers-grids-containing blocks (randomly occur), c - spongy blocks (extremely rare).
2. Layers-grids represent a photon zonal structure responsible for the light decomposition.
3. Spongy areas of the structure are consisted of tubules that absorb liquid while opals are soaked in water or acid solutions and that are closed by drying, when they loose water. Diameter of a tubule makes 800-900 nanometers.
4. On saturation with water, sharp decrease of reflectance factor and the increase of system transmittance are observed, that testifies a consistency of transmittance coefficient.
5. Highly metamorphosed hydrothermal opals demonstrate minor changes in the reflectance and transmittance spectra due to their dense structure.

Acknowledgment

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