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GEOCHEMISTRY

Dynamics of the Formation of Globular Silica Particles according to Dynamic Light Scattering

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Abstract—For the first time, the dynamics of the origination and growth of monodispersion spherical silica particles is studied by dynamic light scattering in the real-time mode. Experimental changes in the particle size and intensity of scattering during their formation and growth indicate the hierarchical formation of silica globules under various mechanisms of aggregation of particles.

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The globular structure of amorphous substances was first identified in 1964, when J. Pence [1] found that precious opal is composed of regular spherical silica particles, which, as was established later, are also composed of smaller spherical particles [2, 3]. A similar internal globular structure has been identified in many natural X-ray amorphous materials and still attracts attention from mineralogists, material scientists, and, finally, nanotechnologists [4, 5]. Amorphous nanostructural materials have been studied in recent years. Opal-like materials were experimentally synthesized from quartz and other compounds [5–7]. As a result, various theoretical genetic models were offered for spherical particles and opal-like structures of various degrees of order [6–9]. However, basic problems related to deciphering the formation mechanism, control of processes, and, correspondingly, management of the particle size remain open. Advances in solution of these problems became possible after elaboration of the continuous registration of synthesized particles in the real-time mode [10].

In this work, we first present the results of experimental study of the dynamics of the formation and growth of globular silica particles by dynamic light scattering. The principle novelty is the indication of different mechanisms of formation of globules at different stages of the process, which had not been proposed by any previous genetic model.

The experimental device was assembled on the basis of a Photocor Complex modified spectrometer with an integrated flow cell [10]. In the experiments, the maximum registered radius of silica particles is 55 nm; their content is 2 wt %; the temperature is 30 ± 0.1°C; the scattering angle is $90° \pm 0.01°$; and the laser wave length λ is 661 nm. The accumulation time of the correlation function is 60 s; the duration of pump work is 50 s; and its production is 250 ml/min, which corresponds to more than quadruple renovation of the flow cell over the accumulation time of the correlation function.

Our data on the variable intensity of light scattering and particle sizes are shown in Fig. 1, which demonstrates three temporal zones (stages) with various character of change in the size of silica particles and the corresponding values of intensity of light scattering, which is logically related to the features of the processes of formation of globules.

Zone 1 spans the initial period of formation of primary particles and their further aggregation before the formation of experimental silica particles (duration of 15–17 min). The intensity of scattering remains at the level of the base line during the entire extension of the zone. The zone continues to the outburst of scattering intensity and corresponding particles ~30 nm across. The formation of these particles is preceded by a series of processes including hydrolysis of ethoxy groups of tetraethoxysilane, which provide conditions (i) for polycondensation of the solution and formation of branched polymer chains and, further under conditions of oversaturation of solution, (ii) for the formation of stable clusters (quatarons or clusters of a hidden phase), which are believed to be the primary protoparticles for the formation of globular particles through a series of consecutive stages [9, 11]. According to the model of [9], experimental particles 30 nm in size registered at the end of the second stage can be formed at the second level of fractal aggregation of quatarons. The first level forms particles 2.2 to 8.9 nm in radius depending on the size of the initial primary clusters (quatarons). At a typical hierarchical aggregation, a

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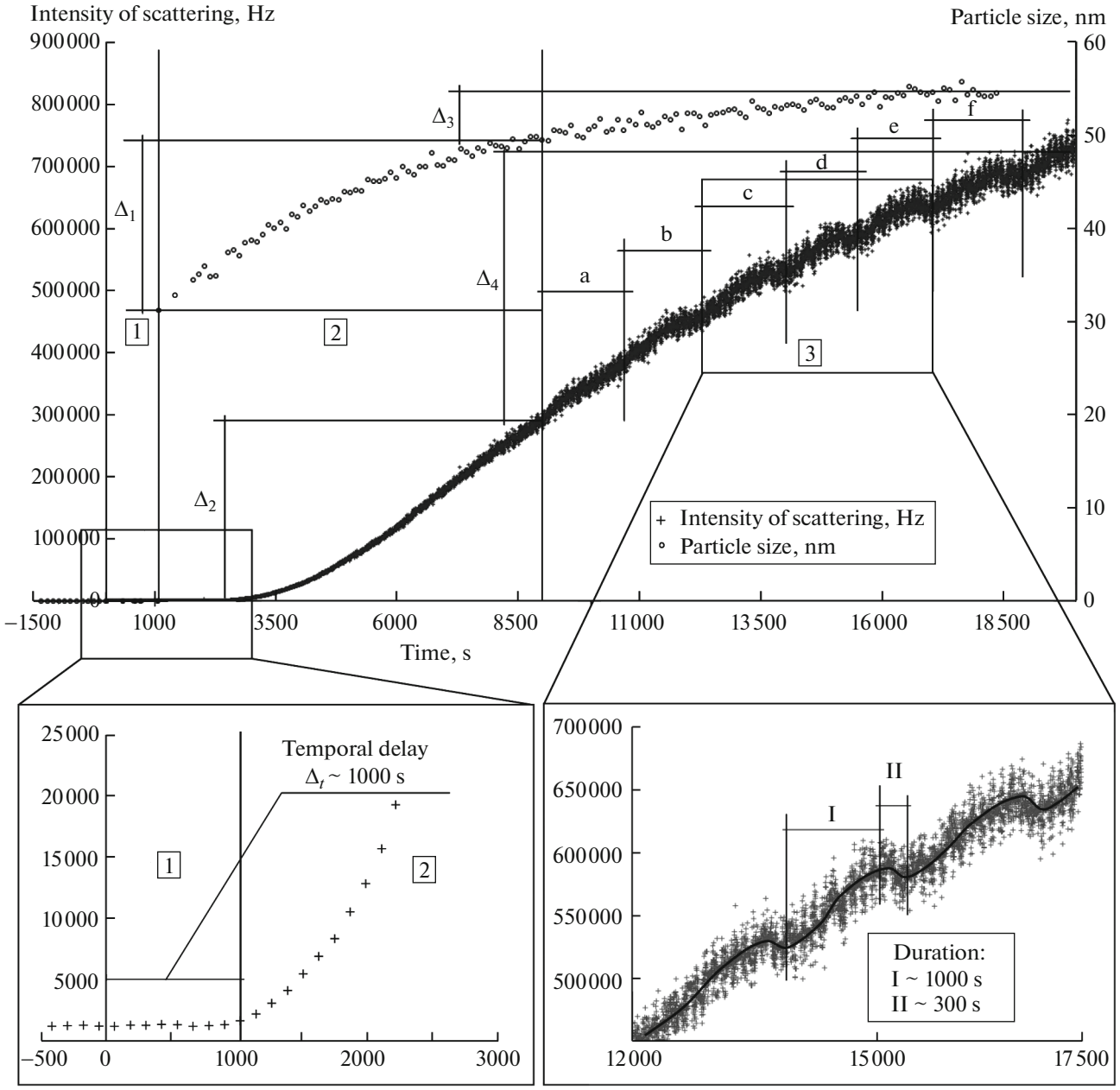

Fig. 1. Variation in the size of silica particles in time during their formation and growth and accompanying intensity values of light scattering. For symbol explanations, see text.

radius of 30 nm is possible only at the fourth level. Registration of smaller particles in this area is impossible by dynamic scattering owing to the physical features of the forming clusters, which, being fractal structure, do not change the intensity of the scattered light.

In zone 2, the size of silica particles increases to ~50 nm and the increase in the intensity of light scattering is explosive. The analysis of the correlation of the particle size and corresponding intensity of light scattering in zone 2 shows that, in this interval (Fig. 1), the particle sizes increase relatively weakly and Δ_1 is $50.0 - 30.0 = 20$ nm (66% of the initial value), whereas the intensity of light scattering increases almost by 230 times and $\Delta_2 = 350000 - 1500 = 348500$ (≈23000%). According to theoretical calculations, the increase in the intensity of light scattering during particle growth by 66% should be no greater than 36%. This significant dissonance between the increase in intensity and the calculated (judging from the increase in the particle size) value indicates the sharp increase in the amount of forming globular particles 50 nm across (by more than 100 times) or, most likely, the rather high partial and (or) mass concentration of particles, the

size of which cannot be registered experimentally. This means that the size of globular particles at this stage increases along with these particles; i.e., the mechanism of formation of particles changes. It is suggested that, in this zone, the cluster–cluster fractal aggregation of particles dominant at the first stage is replaced by cluster–cluster aggregation, when clusters of the second and first levels are aggregated. The clusters of the first aggregation level in this case are the particles that resulted from fractal aggregation of precrystallization clusters of finite size, the radius of which is <0.6 nm. Thus, according to calculations, the size of these clusters (first level of aggregation) is 4.4 nm [9].

Zone 3 marks termination of particle growth. In this zone, we also observe a mismatch between the increase in intensity and the particle size (the real intensity is also higher than calculated). However, this mismatch is significantly lower than in zone 2. The intensity increases by 270% instead of the calculated 20%, which is related to exhaustion of the initial substances. As a result, primary particles (quatarons) are formed more slower and are much more rapidly consumed during aggregation process. Correspondingly, this zone is characterized by dominant aggregation processes of already formed globules and primary particles; i.e., they follow cluster–quataron aggregation, which explains the decrease in the rate of growth of silica globules. At the final stages of the aggregation process, this zone almost loses the features of fractal aggregation and the particles are transformed to spherules with a relatively smooth division boundary.

It is interesting that a striking oscillation process in zone 3 is manifested against the background of a decelerated rate of increase in the intensity of scattering. The duration of oscillations of the intensity of scattering is the same all the time and, for the intervals in Fig. 1, is as follows: a ≈ 1600, b ≈ 1600, c ≈ 1700, d ≈ 1500, e ≈ 1600, and f ≈ 1800 s. It is suggested that the character of oscillation is caused by various effects of the simultaneous growth of silica globules, formation, and aggregation of particles on the intensity of scattering. The increase in the particle size makes a greater contribution to the increase in light scattering than the increase in their mass concentration. The aggregation of particles with the formation of finite spherules leads to a rapid increase in the intensity (uplift on curve I). Correspondingly, a significant decrease in the concentration of primary particles and the components of the hydrolysis reaction results in a decrease in the intensity of scattering (fall on curve II). The next accumulation of primary particles and their further aggregation again lead to an outburst of intensity and, finally, experimental oscillation of a correlation character.

Thus, the principles of experimental formation of monodispersion spherical silica particles (globules or structural units of precious opal) have been established for the first time during real-time dynamic light scattering. This allowed us to reveal the temporal zones of different mechanisms of aggregation of particles at different stages. This significantly modifies our ideas on the processes and mechanisms of formation of structural units of opal-like materials. To observe the processes at the initial stages of formation of phase-isolated particles, the experiments should be repeated using other analytical methods (e.g., X-ray free electron laser).

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