# Cavitation Mechanism of Formation of Nano- and Microsize Particles of Minerals in Ore Deposits

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Abstract—Cavitation is shown to be a rather common and important physical effect in the processes of formation of nano- and microsize particles of natural origin. We tested the so-called cavitation hypothesis of the formation of mineral microspherules  $10-100 \ \mu m$  in size on the basis of a cavitation model that takes into account the characteristic values of the radius of a cavitation bubble and its evolution and thermal interaction with a solid mineral particle placed inside the bubble. We demonstrate that the model explains the appearance of the microspherules in accordance with the data of observations. An analogous cavitation mechanism can lead to the formation of mineral nanospherules in hydrothermal fluids. Another mechanism that can result in the formation of mineral nanospherules is the ablation process. This process is realized as a release into the ambient fluid of a superheated layer taking the form of small nanosize drops of melted substance in the case when the temperature in the compressing cavitation bubble exceeds the boiling temperature of the substance of the drops, the boiling temperature corresponding to the external pressure in the hydrothermal fluid. We discuss the conditions of experiments on melting of refractory materials in the process of their interaction with cavitation bubbles; such experiments are important from the viewpoint of identification of mechanisms of formation of mineral nano- and microspherules in the Earth's crust.

#### INTRODUCTION

At present, significant attention is being paid to the study of properties and processes of formation of nanoand microsize particles in nature (see, e.g., Nanotechnology Research Directions..., 2000; Lakhno, 2001; Nanoparticles and the Environment, 2001). Such research can increase our knowledge of the mechanisms and conditions of mineral formation. The investigation of nanosize structures can provide new information about the interstellar substance, deflation of the rock mass, etc. Nanosize components are considered to be the main structural elements in solid-state chemistry (Sergeev, 2003). However, in many situations, physical processes are of paramount importance in the formation of nano- and microsize structures. For example, more than thirty years ago, Galimov (1973) predicted the possibility of diamond synthesis in the cavitation process. In 2003, this possibility was confirmed in experiments (Galimov et al., 2004), the particles formed in the cavitation process being an aggregation of nanosize crystallites. The diamond crystals were 10-30 nm in size. The idea of the cavitation mechanism of diamond formation is the following (Galimov, 1973). A narrow canal cavity of varying cross section is formed as a result of the fast motion of fluid going up from the mantle to the Earth's surface. When the canal cavity dilates or opens up, the pressure decreases, resulting in phase separation of the fluid, which strati-

Novgorodova *et al.*  $(2003_1)$  have put forth a cavitation hypothesis of the formation of mineral microspherules (Vernadskii, 1955) which are ball-shaped precipitations from the hydrothermal fluids with different mineral compositions (aluminosilicate glasses, native gold) and of 10-100 µm in size. These ball-shaped precipitations were discovered in caverns and cavities of gangue quartz from mesothermal gold deposits up to a depth of 700 meters (Gamyanin et al., 1999). The microspherules have certain features of melting that mean their presence during a definite time under temperatures and pressures far exceeding their average values for mineral-forming fluids. The essence of the hypothesis is that the local fluctuations of pressures and temperatures in the hydrothermal fluids, which are sufficient for melting of refractory microsize particles, are due to cavitation effects when caverns and cavities opening up in the zone of mineralization are filled by the fluid during tectonic movements. The transition from the regime of slow percolation of the hydrothermal fluids in canals of country rock to fast filling of the cavities leads to a significant decrease in the local pressure; bubble formation; and, finally, to cavitation compression of the bubble, the re-creation of the pressure, and complete occu-

fies into an essentially liquid phase and a gas phase existing in the form of gas bubbles. When the fluid goes into the narrowing of the canal cavity, the pressure is reestablished and the bubbles collapse. The pressure inside the collapsing bubbles filled by gas loaded with carbon is sufficient for diamond synthesis.

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pation of the space opened up. During the compression of cavitation bubbles, pressures and temperatures of the order of hundreds of kilobars and ten thousand degrees Kelvin, respectively, develop; supersonic cumulative microjets and shocks are formed; and high-temperature chemical reactions occur (see, e.g., Margulis, 1995; Margulis and Margulis, 2000). Novgorodova et al.  $(2003_2)$  showed within a simplified model that the interaction of the collapsing bubble with microsize seeds of quartz 10  $\mu$ m in size and gold 50  $\mu$ m in size in the hydrothermal fluids can result in their melting if the maximum radius of the bubble during the cavitation process is of the order of 1 cm. This simplified model did not analyze, however, the characteristic values of the cavitation bubble radius, which can be much smaller than 1 cm.

Thus, cavitation appears to be a rather common and important physical effect in the processes of formation of nano- and microsize particles of minerals in ore deposits. The direction of this investigation is along the lines of other investigations, such as sonoluminescence (see, e.g., Margulis, 2000), that are associated with cavitation, are actively developing, and are of great significance for the progress of modern science and technology.

Since the microspherules are formed as a result of melting of some seeds of minerals present in ore deposits, their size may not exceed the characteristic size of the seeds. It is obvious that the characteristic size of seeds necessary for the formation of microspherules 10–100  $\mu$ m in size should exceed 10  $\mu$ m. Usually, the seeds of minerals are large nanosize particles, while the presence of the seeds  $10-100 \,\mu\text{m}$  in size is more likely an exception than the rule. This is confirmed, for example, by Filimonova et al. (2003) and also by the observations of nanosize particles of moissanite (Filimonova et al., 2004). In accordance with these investigations, the conditions of the formation of nanosize particles of moissanite and associated nanosize particles of ore minerals can be created in the process of penetration of fluids into porous rock of rhyolite and their spontaneous supercooling and supersaturation. To analyze the cavitation hypothesis, the possibility of formation of spherules of different composition of both nano- and microsize should be studied. It is necessary to determine the characteristic size of cavitation bubbles that appear in the hydrothermal fluids. The purpose of this paper is to investigate the possibility of the formation of nano- and microspherules of different composition in hydrothermal fluids as a consequence of cavitation effects and to estimate the maximum sizes of such spherules.

# EVOLUTION OF THE CAVITATION BUBBLE

The results of investigations of fluid inclusions in minerals (Bortnikov *et al.*, 1998; Gamyanin *et al.*, 1999; Novgorodova *et al.*, 2003<sub>1</sub>) allow the following values to be used as the basic parameters of a hydro-thermal fluid: the temperature  $T_0 = 523$  K, the pressure

 $P_0 = 1.5$  kbar, and the fluid density  $\rho_0 = 0.8$  g/cm<sup>3</sup>. The immiscibility of the fluid into liquid and gas phases is thought to occur in mesothermal hydrothermal systems. The liquid is usually a mixture of water with NaCl and CO<sub>2</sub> in solution, while the gas phase contains carbon dioxide and, perhaps, methane. In spite of the fact that the liquid phase may contain suspended fine solid particles of rock and ore minerals, which is observed in modern oceanic ore-forming systems, we do not take into account the nonsignificant change in the fluid density caused by its contamination by mineral particles.

Consider the evolution of the fluid pressure in the vicinity of the cavity opening up in the country rock during tectonic movements. After opening up of the cavity, the fluid bears down upon it, which leads to a sharp local decrease in pressure near and inside the cavity up to values less than the saturated vapor pressure of water  $P_s(T_0) = 39$  bar at the temperature  $T_0 = 523$  K. The fluid becomes a superheated one, which makes the fluid boil; i.e., gas bubbles appear.

The time of filling of an opening cavity L = 10 cm in size by the hydrothermal fluid can be estimated on the basis of the Bernoulli equation using the formula  $t_L = L/v_s \sim 100 \ \mu$ s, where  $v_s = 1500 \ m$ s is the acoustic speed in water. After the filling of the cavity by the fluid, the pressure inside it is reestablished not instantaneously but with the acoustic speed  $v_s$ , i.e., the pressure is reestablished up to the value of  $P_0$  at the time  $t_L$  after the cavity filling by the fluid. Thus, the time of existence of low pressure near the opening cavity being filled by the fluid is of the order of  $2t_L \sim 200 \ \mu$ s.

The bubble formation due to the local decrease in pressure during the boil-off of the hydrothermal fluid is random and occurs principally on nucleation centers, which are poorly moistened solids suspended in the fluid, gas bubbles, and coarse surfaces (Skripov, 1972). The critical radius of the cavitation bubble can be found with the aid of the formula  $R_c = 2\sigma/\Delta P \approx 15...20$  nm, where  $\sigma = 26 \text{ g/s}^2$  is the coefficient of the surface tension of the fluid,  $\Delta P = P_s - P_l$ ,  $P_s = 39$  bar is the saturated vapor pressure of water corresponding to the temperature  $T_0 = 523$  K, and  $P_l$  is the pressure in the fluid surrounding the bubble. Since the fluid pressure during the filling of the cavity is less than  $P_s$  (Kumzerova and Schmidt, 2002), we neglect  $P_1$  in comparison with  $P_s$  to estimate the critical radius. If the radius of the bubble exceeds the critical radius  $R_c$ , then the bubble expands. Otherwise, the bubble does not expand and, finally, disappears.

The rate of growth of the vapor bubble is determined mostly by thermal transport to the interface between different phases, the dynamical reaction of the fluid on the spherical expansion of the bubble, the viscous resistance of the fluid, and the evaporation processes at the interface between the phases. The consideration of the influence of these effects is carried out within a generalized inertial thermal scheme of vapor bubble growth (Avdeev and Zudin, 2002). The dependence of the bubble radius on time within this model is determined by the formula

$$R(t) = \frac{R_1(t)}{(1 + \alpha \tau^{3/4})^{1/3}},$$

$$R_1(t) = \frac{4}{3}R_0((1 + \sqrt{\tau})^{3/2} - 3(1 + \sqrt{\tau})^{1/2} + 2),$$
(1)

where  $\tau = t/t_0$ . The parameters  $t_0 = 0.06 \,\mu$ s,  $R_0 = 3 \,\mu$ m, and a = 0.47 are defined as follows:

$$t_{0} = \frac{\chi}{U^{2}} J a^{2}, \quad R_{0} = \frac{\chi}{U} J a^{2}, \quad a = \frac{8}{27 \psi^{3}},$$
  
$$\psi = 1 + \sqrt{\frac{\pi}{2}} \left(\frac{1}{\sqrt{1-N}} - 1\right),$$
 (2)

where  $U = \sqrt{(2/3)(\Delta P/\rho_0)}, N = (\rho_g/\rho_0)Ja, Ja =$  $\rho_0 C_p \Delta T / (\rho_o L) \approx 3, \Delta T = T_0 - T_s (P_l) \approx 120$  K is the overheating of the fluid,  $T_s(P_l) \approx 400$  K is the saturated vapor temperature corresponding to the pressure  $P_l$  = 2.5 bar in the fluid surrounding the bubble,  $\rho_g =$ 0.08 g/cm<sup>3</sup> is the saturated vapor density inside the bubble,  $C_p = 4.86 \text{ J/(g K)}$  is the specific isobar heat of the fluid,  $\chi = 0.0015$  cm<sup>2</sup>/s is the temperature conductivity, and L = 1700 J/g is the heat of the phase transition. As follows from formula (1), the maximum radius of the cavitation bubble during its expansion and existence under low pressure  $(t \sim 200 \,\mu s)$  is  $R_{\text{max}} \approx 0.5 \,\text{mm}$ . In the process of expansion, several bubbles can unite, forming one bubble of a large size. This mechanism of bubble unification can increase the rate of their growth significantly, leading to the appearance of bubbles even several centimeters in size, although the formation of bubbles several millimeters in size is more probable.

The reestablishment of the pressure in the cavity up to the value of  $P_0 = 1.5$  kbar after its complete filling by the fluid triggers the process of cavitation bubble compression, which leads to an increase in the pressure and temperature inside the bubble. The evolution of the bubble boundary during its compression under the action of the external pressure  $P_0$  in the approximation of an incompressible fluid is described by the Rayleigh–Plesset equation (Naugol'nykh and Ostrovskii, 1990; Margulis, 2000):

$$R\ddot{R} + \frac{3}{2}\dot{R}^{2} = \frac{1}{\rho_{0}} \left\{ (P(R) - P_{0}) - \frac{4\eta\dot{R}}{R} - \frac{2\sigma}{R} \right\}, \quad (3)$$

where R(t) is the bubble radius,  $\eta$  is the fluid viscosity, and  $\vec{R}$  and  $\vec{R}$  are the first and second derivatives of the bubble radius with respect to time.

Since during the bubble compression the speed of its boundary is rather large, the processes of evaporation and condensation do not occur inside the bubble (Mar-

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gulis and Margulis, 2000). Consequently, the pressure P(R) inside the bubble as a function of its radius R is determined by the adiabatic process equation and the van der Waals equation of state and takes the form

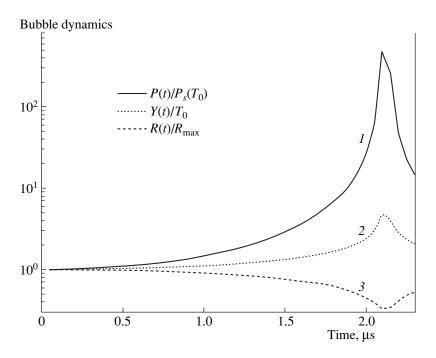
$$P(R) = P_{c} \left\{ \left( P'_{s} + \frac{3}{V'_{s}^{2}} \right) \left( \frac{3V'_{s} - 1}{3V' - 1} \right)^{\gamma} - \frac{3}{V'_{s}^{2}} \right\},$$

$$V' = V'_{s} \left( \frac{R}{R_{\max}} \right)^{3},$$
(4)

where  $P_c = 225$  bar is the critical pressure of the liquidgas transition for water,  $P'_s = P_s(T_0)/P_c$ ,  $V'_s$  is the vapor specific volume at the temperature  $T_0 = 523$  K and the pressure  $P_s(T_0) = 39$  bar normalized to the critical magnitude,  $\gamma = 4/3$  is the ratio of specific heat, and  $R_{\text{max}}$  is the maximum radius of the cavitation bubble. Since  $R_{\text{max}} \approx 1$  mm is more than one order of magnitude larger than the average size of the seeds (nano- and microsize particles) of the ore located inside the bubble or on its surface, one can neglect their influence on the process of compression of the cavitation bubble.

Figure 1 presents time dependences of the pressure  $P(t)/P_s(T_0)$  (curve 1), the temperature  $T(t)/T_0$  (curve 2), and the bubble radius  $R(t)/R_{max}$  (curve 3) normalized to their initial values, calculated with the aid of formulas (3), (4) for  $R_{\text{max}} = 1 \text{ mm}$ ,  $T_0 = 523 \text{ K}$ , and  $P_s(T_0) =$ 39 bar. The effects of viscosity and surface tension in the Rayleigh-Plesset equation are not significant on the time scales (of the order of microseconds) in which we are interested. The bubble compression from  $R_{\text{max}}$  to the minimum radius  $R_{\min} = 0.3$  mm occurs at the time  $t_m \approx$ 2.1 µs. The maximum magnitudes of the temperature and the pressure at the instant of collapse are  $T_{\text{max}}$  = 7030 K and  $P_{\text{max}} = 1450$  kbar, respectively. The magnitudes  $t_m$  and  $R_{\text{min}}$  are approximately proportional to the initial radius of the bubble, while  $T_{\text{max}}$  almost does not depend on  $R_{\text{max}}$ . The gradual increase in pressure inside the cavity during its filling from the value of  $P_s = 39$  bar to  $P_0 = 1.5$  kbar can result in a delay of the collapse of the bubble of several microseconds, the changes in the maximum magnitudes of temperature and pressure in the bubble being nonsignificant.

Equation (3) describes periodic pulsations of a spherical cavitation bubble. In actual fact, the influence of such factors as translatory motion of the fluid surrounding the bubble, inhomogeneity of the field of pressures inside the fluid, and morphological and thermal instabilities of the bubble boundary can lead to the violation of the spherical form of the bubble and its partition into several smaller bubbles in the phase of the expansion after the collapse. Therefore, in subsequent calculations, we consider only one period of the cavitation bubble pulsations (Fig. 1).



**Fig. 1.** Time dependences of pressure  $P(t)/P_s(T_0)$  (1), temperature  $T(t)/T_0$  (2), and bubble radius  $R(t)/R_{\text{max}}$  (3) normalized to their initial values for  $P_s(T_0) = 39$  bar,  $T_0 = 523$  K, and  $R_{\text{max}} = 1$  mm.

## DYNAMICS OF PARTICLE HEATING IN THE CAVITATION BUBBLE

The necessary condition of the transition of solid particles (seeds) inside the bubble (or on its surface) to melted drops is an increase in the seed temperature up to values exceeding the melting point of the mineral  $T_m$ , which is equal, for example (under the conditions of a hydrothermal fluid and a pressure  $P_0 = 1.5$  kbar), to  $T_m = 1350$  K for native gold and  $T_m = 1883$  K for quartz. Since, in the process of compression of a bubble with  $R_{\text{max}} = 1$  mm, its temperature exceeds the value of 1000 K only during 1  $\mu$ s and the value T > 2000 K for less than 0.2  $\mu$ s, the dynamics of the heating of the solid seed in its interaction with the cavitation bubble requires additional consideration.

The calculation of the characteristic length of the heated zone using the formula  $l = \sqrt{\chi t}$  shows that, at the time  $t = 0.2 \,\mu$ s, the width of the melted layer on the surface of a quartz seed with the temperature conductivity  $\chi = 0.04 \,\mathrm{cm^2/s}$  is not more than  $l \sim 1 \,\mu$ m. At the same time, a significant increase  $T_{\max} \approx 7000 \,\mathrm{K}$  over the melting point of quartz can provide conditions sufficient for larger magnitudes of the thickness of the melted layer on the surface of a solid seed.

To simplify the calculations of the heating dynamics of a solid seed that interacts with the cavitation bubble, let us assume spherical symmetry of the problem. A spherical seed with the radius  $r_p \ll R_{\text{max}}$  is placed in the center of the compressing bubble. We neglect the thermal influence of the seed on the bubble. The temperature distribution  $T_p(r, t)$  inside the bubble in dependence on time is described by the heat conduction equation written in spherical coordinates (temperature variations due to the melting are not taken into account):

$$\frac{\partial T_p}{\partial t} = \frac{\chi}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_p}{\partial z} \right), \tag{5}$$

where *r* is the radial coordinate. Initially, the temperature inside the seed is supposed to be constant and coincident with the temperature of the bubble surrounding the seed  $T_p(r, 0) = T_0$ . The temperature evolution on the surface of the seed  $T_p(r_p, t) = T(t)$  is determined from Eq. (3) by the change in the temperature of the surrounding vapor T(t) (Fig. 1). The condition of symmetry  $\partial T_p(0, t)/\partial z = 0$  is assumed to be fulfilled at the center of the seed.

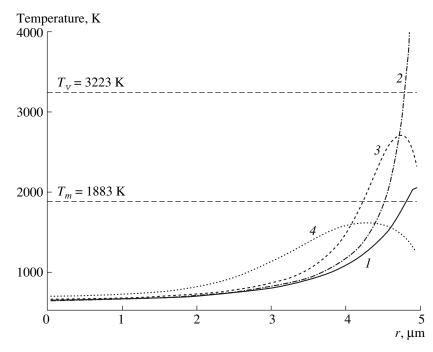
The solution of Eq. (5) corresponding to the above boundary conditions can be represented in the form of an infinite series (Karlsrow and Eger, 1964):

$$T_{p}(r,t) = \frac{2}{rr_{p}} \sum_{n=1}^{\infty} (-1)^{n+1} \exp\left(-\frac{\chi n^{2} \pi^{2} t}{r_{p}^{2}}\right) \sin\left(\frac{n\pi r}{r_{l}}\right)$$

$$\times \left(\frac{T_{0}r_{p}^{2}}{n\pi} + \int_{0}^{t} \exp\left(-\frac{\chi n^{2} \pi^{2} t_{1}}{r_{p}^{2}}\right) T(t_{1}) dt_{1}\right).$$
(6)

In Fig. 2, temperature profiles inside the seed are shown calculated on the basis of formula (6) for a quartz seed with radius  $r_p = 5 \,\mu\text{m}$  at different instants of time near the instant of the bubble collapse  $t_m = 2.1 \,\mu\text{s}$ .

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**Fig. 2.** Temperature profiles inside a quartz seed with a radius of  $r_p = 5 \,\mu\text{m}$  at different instants of time,  $t = 0.99t_m(1)$ ,  $t = t_m(2)$ ,  $t = 1.01t_m(3)$ , and  $t = 1.05t_m(4)$ , where  $t_m = 2.1 \,\mu\text{s}$  is the instant of the bubble collapse.

The figure shows that a temperature wave resulting in the melting of the mineral propagates inside the seed toward its center. Subsequent cooling of the seed surface leads to the appearance of a recrystallization wave also moving toward the center of the seed, following the melting wave. In spite of the fact that the temperature on the surface of the seed exceeds the melting point of quartz  $T_m = 1883$  K by more than 4 times at the instant  $T_m$ , the width of the region where the temperature exceeded  $t_m$  during the heating (the width of the melting region) is about 200 nm in this case. Note that, in reality, the melting point of quartz can differ from the value  $T_m = 1883$  K because of the change in the external pressure in the cavitation bubble during its compression. However, calculations carried out on the basis of Clausius-Clapeyron equation show that the change in the melting point at the boundary of the melting region is not very large (less than 3 K) and does not influence significantly the final magnitude of the width of the melting region. A similar statement applies to other substances considered in this paper (table).

The melting region can occupy the whole volume of a seed for quartz seeds of smaller sizes or seeds consisting of less refractory materials. This implies that the whole seed is melted as a result of its interaction with a compressing cavitation bubble. In Fig. 3, the dependence of the maximum radius  $r_p^{\text{max}}$  of a seed sufficient for its melting as a result of interaction with the cavitation bubble on the initial bubble radius  $R_{\text{max}}$  is presented. Figure 3 shows that this dependence is not very strong. For example, a 100-fold increase in the bubble radius  $R_{\text{max}}$  (from 10 µm to 1000 µm) results in a tenfold increase in the magnitude of  $r_p^{\text{max}}$  (from 250 nm to 2.5  $\mu$ m). Note that, for the seeds with radii  $r_p$  <  $r_p^{\max}(R_{\max})$ , not only their complete melting is possible but also significant superheating corresponding to temperatures higher the melting point.

Substance	Quartz	Gold	Iron	Galena	Stibnite
Chemical formula	SiO <sub>2</sub>	Au	Fe	PbS	$Sb_2S_3$
Density, g/cm <sup>3</sup>	2.14	19.3	7.8	7.3	4.6
Thermal capacity, J/(g K)	0.74	0.13	0.44	0.2	0.36
Thermal conduction, W/(cm K)	0.07	3.17	0.8	0.34	0.24
Melting point, K	1883	1336	1808	1387	819
Size, µm	5	42	12	16	30

Properties and calculated sizes of microspherules of different mineral composition

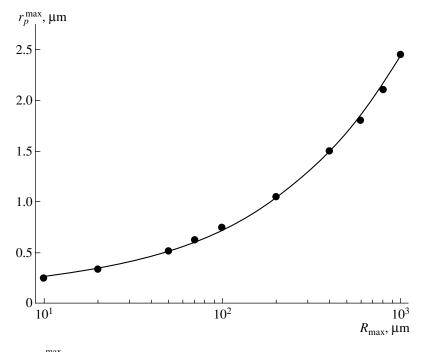


Fig. 3. The maximum radius  $r_p^{\text{max}}$  of the quartz seed sufficient for its melting as a result of interaction with a compressed cavitation bubble vs. the initial bubble radius  $R_{\text{max}}$ .

The sizes (diameters) of seeds calculated with the aid of formula (6) that are necessary for their complete melting as a result of interaction with a compressing cavitation bubble of the initial radius  $R_{\text{max}} = 1 \text{ mm}$  are given in table. Comparison of the calculated sizes of the microspherules (table) with the results of investigations of microspherules in ores of hydrothermal genesis (Gamyanin et al., 1999; Novgorodova et al., 2003<sub>1</sub>) shows a good agreement and indicates the adequacy of the cavitation model of microspherule formation although this model is simplified and needs some refinements. More consistent consideration of the dynamic processes on the bubble boundary, the real equation of state, and the process of thermal transfer from the ambient medium to the seed will be carried out in future papers.

Note that the considered cavitation mechanism of formation of spherical (or almost spherical) particles can result in the creation of mineral nanosize particles in the hydrothermal fluid. First of all, the maximum magnitudes of the seed sizes that are necessary for their complete melting are presented above (table). Naturally, if the sizes of the seeds are in the nanometer range, then, as a result of interaction with a compressing cavitation bubble of the initial radius of  $R_{max} = 1$  mm, the solid seeds are transformed into melted drops, which become, finally, solids transforming into nanospherules.

Another mechanism of formation of nanosize particles as a result of cavitation is possible. Since the temperature in the compressed cavitation bubble can exceed by several times not only the melting point but also the boiling temperature of a mineral seed, which corresponds to the external pressure in the hydrothermal fluid (Fig. 2), the thin layer of melted substance on the surface of the seed can be in a superheated metastable state. The process of disintegration of the metastable state can have an explosive character and lead to ablation. This process implies a release of a superheated layer in the form of fine nanosize drops of the melted mineral. Subsequent cooling of the nanosize drops in the hydrothermal fluid should result in the formation of nanospherules. To detect the nanospherules, it is necessary to study thoroughly samples of ores that contain mineral microspherules. Their detection will serve an additional confirmation of the validity of the cavitation hypothesis of the formation of microspherules in the Earth's crust.

# CONCLUSIONS

Thus, cavitation is an important physical effect in the processes of formation of nano- and microsize particles of minerals in ore deposits. We have tested the cavitation hypothesis of the formation of microspherules of different mineral composition 10–100  $\mu$ m in size. For this purpose, we have used the cavitation model, which takes into account the characteristic values of the radius of cavitation bubble, its evolution, and the thermal interaction with a solid mineral particle (seed) placed inside the bubble. This model is shown to

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allow us to explain the appearance of microspherules with sizes according with the data of observations. The cavitation mechanism of the formation of spherical (or almost spherical) particles can result in the creation of mineral nanosize particles in hydrothermal fluids. If the sizes of the seeds are in the nanometer range, then the solid seeds are transformed into melted drops as a result of the interaction of the seed with the compressed cavitation bubble. These melted drops become, finally, solids transforming into nanosize particles of spherical (or almost spherical) form. Another mechanism of the formation of nanospherules of different mineral composition is the process of ablation. This process implies a release of a superheated layer in the form of fine nanosize drops of the melted substance of the seed in the surrounding liquid. It occurs when the temperature in the compressed cavitation bubble exceeds the boiling temperature of the substance of the seed, which corresponds to the external pressure in the hydrothermal fluid.

The identification in detail of the mechanisms of formation of mineral nano- and microspherules requires an experimental investigation of the possibility of melting of refractory materials as a result of their interaction with cavitation bubbles under conditions close to those existing in the Earth's crust. For this purpose, it is necessary to perform laboratory modeling of the pressure evolution corresponding to the opening up of cavities and their filling by fluid: a sharp decrease in the fluid pressure (water containing particles of refractory materials with an initial temperature of the order of 250°C) from the initial value of 1.5 kbar to a value less than 50 bar (the saturated vapor pressure of water corresponding to the temperature 250°C) and subsequent reestablishment of the initial pressure level at a time of the order of 200 µs (the estimated time of the cavity filling). Existing and planned experimental installations for investigation of cavitation phenomena, for example, the SKGP test facility on the base of the EKAP installation at RFNC-VNIITF (Simonenko et al., 1997; Simonenko, private communication, 2001), enable a necessary evolution of the pressure in a liquid to be obtained (with somewhat smaller magnitudes of the pressure amplitude). The observation of the processes of bubble formation in a cavitation chamber will allow us to find the maximum and minimum sizes of bubbles formed and to follow their evolution. The investigation of the form and composition of nano- and microsize particles interacting with the cavitation bubbles will allow us to determine the characteristic sizes of newly formed particles and their chemical composition.

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### REFERENCES

- A. A. Avdeev and Yu. B. Zudin, "Vapor Bubble Growth in the Spinodal Region (Generalized Inertial Thermal Scheme)," Teplofiz. Vys. Temp. 40 (6), 971–978 (2002) [High Temp. 40 (6), 905–911 (2002)].
- N. S. Bortnikov, G. N. Gamyanin, V. A. Alpatov, *et al.*, "Mineralogy, Geochemistry and Origin of the Nezhdaninsk Gold Deposit (Sakha-Yakutia, Russia)," Geol. Rudn. Mestorozhd. **40** (2), 137–156 (1998) [Geol. Ore Deposits **40** (2), 121–138 (1998)].
- L. G. Filimonova, N. V. Trubkin, and N. S. Bortnikov, "Nanoparticles of Ore Minerals in the Disseminated Polymetal Mineralization of the Dukat Ore District, Northeastern Russia," Dokl. Akad. Nauk 392 (4), 521– 525 (2003) [Dokl. Earth Sci. 392 (7), 1043–1046 (2003)].
- L. G. Filimonova, N. V. Trubkin, and N. S. Bortnikov, "Moissanite Nanoparticles in Disseminated Mineralization of the Dukat Ore District, Northeastern Russia," Dokl. Akad. Nauk **394** (4), 540–543 (2004) [Dokl. Earth Sci. **394** (1), 137–140 (2004)].
- E. M. Galimov, "Cavitation as a Mechanism of Natural Diamond Synthesis," Izv. Akad. Nauk SSSR, Ser. Geol., No. 1, 22–37 (1973) [in Russian].
- E. M. Galimov, A. M. Kudin, V. N. Skorobogatskii, *et al.*, "Experimental Corroboration of the Synthesis of Diamond in the Cavitation Process," Dokl. Akad. Nauk **395** (2), 187–191 (2004) [Physics-Doklady **49** (3), 150–153 (2004)].
- G. N. Gamyanin, Yu. Ya. Zhdanov, and A. S. Syromyatnikova, "Composition and Structural Features of Endogenous Spheroids in Gold Deposits of North-East of Russia," Zap. Vseross. Mineral. O-va 128 (5), 71–75 (1999).
- G. Karlsrow and D. Eger, *Thermal Conduction of Solids* (Nauka, Moscow, 1964) [in Russian].
- E. Yu. Kumzerova and A. A. Schmidt, "A Numerical Simulation of Nucleation and Dynamics of Bubbles Formed under Drastic Depressurization of a Liquid," Zh. Tekh. Fiz. **72** (7), 36–40 (2002) [Tech. Phys. **47** (7), 829–833 (2002)].
- V. D. Lakhno, *Clusters in Physics, Chemistry, Biology* (NITS "Regular and Chaotic Dynamics," Izhevsk, 2001) [in Russian].
- 11. M. A. Margulis, *Sonochemistry and Cavitation* (Gordon and Breach, London, 1995).
- M. A. Margulis, "Sonoluminescence," Usp. Fiz. Nauk 170 (3), 263–287 (2000) [Phys.-Usp. 43 (3), 259–282 (2000)].
- I. M. Margulis and M. A. Margulis, "Dynamics of Single-Bubble Cavitation," Zh. Fiz. Khim. 74 (3), 566–574 (2000) [Russ. J. Phys. Chem. 74 (3), 483–492 (2000)].

- 14. *Nanoparticles and the Environment*, Ed. by J. E. Banfield and A. Navrotsky (Mineralogical Society of America, Washington DC, 2001).
- Nanotechnology Research Directions: IWGN Workshop Report. Vision for Nanotechnology R&D in the Next Decade, Ed. by M. C. Roco, R. S. Williams, and P. Alivisatos (Kluwer Academic Publishers, Dordrecht, 2000).
- K. A. Naugol'nykh and L. A. Ostrovskii, *Nonlinear Wave Processes in Acoustics* (Nauka, Moscow, 1990) [in Russian].
- M. I. Novgorodova, G. N. Gamyanin, Yu. Ya. Zhdanov, *et al.*, "Microspherules of Aluminosilicate Glass in Gold Ores," Geokhimiya, No. 1, 83–93 (2003<sub>1</sub>) [Geochem. Int. **41** (1), 76–85 (2003<sub>1</sub>)].
- M. I. Novgorodova, S. N. Andreev, A. A. Samokhin, and G. N. Gamyanin, "Cavitation Effects in the Formation of Mineral Microspherules in Hydrothermal Solutions," Dokl. Akad. Nauk **389** (3), 669–671 (2003<sub>2</sub>) [Dokl. Earth Sci. **389A** (3), 429–431 (2003<sub>2</sub>)].
- G. B. Sergeev, *Nanochemistry* (Mosk. Gos. Univ., Moscow, 2003) [in Russian].
- V. A. Simonenko, V. N. Nogin, N. G. Karlykhanov, and G. N. Kovalenko, "Scaling Analysis for Single-Bubble Cavitation," J. Acoust. Soc. Am. **102**, 3185–3187 (1997).
- 21. V. P. Skripov, *Metastable Liquid* (Nauka, Moscow, 1972) [in Russian].
- 22. V. V. Vernadskii, *Selected Works (Vols. 1, 2)* (Akad. Nauk SSSR, Moscow, 1955) [in Russian].

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