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Formation of Nano- and Microspherules of Minerals in Ore Deposits Depending on Depth of Host Rock Occurrence

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Abstract—The cavitation and cavitation–ablation mechanisms of formation of mineral nano- and microspherules in hydrothermal fluids are considered. The formation conditions of nano- and microspherules were studied with regard to the depth of host rock occurrence on the basis of the theory describing the cavitation mechanism. It is shown that the temperature and pressure of hydrothermal fluid as functions of the depth of host rock occurrence may markedly affect the dimensions of cavitation bubbles, the temperature within them at the moment of greatest compression, and the time of bubble collapse in the fluid. The dimensions of nano- and microspherules produced by cavitation depend only slightly on the depth of host rock occurrence and are mainly controlled by the thermophysical properties of their constituents. Characteristic dimensions of nanospherules formed as a result of ablation from the surface of overheated material have been obtained.

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INTRODUCTION

The study of the origin and properties of natural nano- and microparticles (*Nanoparticles*…, 2001) may provide insights into fundamental processes within the Earth; increase our knowledge on the planet formation (Sobolev et al., 2000; Sobolev, 2002; Kamenetsky et al., 2004) and the processes in the atmosphere and ionosphere (Klumov et al., 2005), and furnish new information about extraterrestrial materials and conditions and mechanisms of mineral formation (Filimonova et al., 2003, 2004), in particular, about diamond synthesis (Galimov, 1973; Galimov et al., 2004).

In geology of ore deposits, attention is now focused on microspherules of refractory substances (Vernadsky, 1955) of different chemical compositions (for instance, aluminosilicate glass and native gold) and with obvious signs of melting, which are globular in shape, have dimensions from 10 to 100 μm, and are derived from hydrothermal fluids. Such globules were found in cavities and fractures of vein quartz at mesothermal gold deposits (Gamyanin et al., 1999).

According to the hypothesis put forward by Novgorodova et al. (2003b), local temperature and pressure fluctuations in medium-temperature hydrothermal fluids that lead to the melting of microparticles may arise as a result of cavitation phenomena, when fluid fills fractures and cavities opening slightly in mineralization zones during tectonic movements. The transition from the regime under which hydrothermal fluids slowly percolate through channels in host rocks to a fast filling of cracks leads to a substantial drop in the local pressure; boiling up of fluid; and, afterwards, to cavitation compression of the released vapor bubbles during pressure recovery and filling up of the slightly open space. Applying a simplified model that did not consider specific values of the cavitation bubble radius, Novgorodova et al. (2003a) showed that interaction of a collapsing cavitation bubble with refractory particles of micrometer dimensions (quartz, gold) in hydrothermal fluids may cause their melting if the maximum radius of the bubble equals ~1 cm. Adushkin et al. (2004a, 2004b) developed a unidimensional and spherically symmetric internally consistent theory that describes the cavitation mechanism of mineral nano- and microspherule formation in hydrothermal fluids taking into account both the typical dimensions of cavitation bubbles and their evolution and the dynamics of particle heating in cavitation bubbles. The theory serves as a basis for estimation of the maximum dimensions of cavitation bubbles and the size of globules that are formed due to the melting of particles of different mineral compositions under cavitation effects in hydrothermal fluids. In particular, the cavitation mechanism may lead to the formation of mineral and metallic nanospherules in hydrothermal fluids. At the same time, nanospherules might be formed as a result of cavitation related to the ablation of overheated material from the surface of nano- and microparticles. However, no theoretical description of this cavitation–ablation mechanism of nanoparticle formation has yet been presented.

The calculations were performed by Adushkin et al. (2004a, 2004b) at definite basic parameters (temperature, pressure, and density of the hydrothermal fluid) consistent with results of fluid inclusion studies in min-

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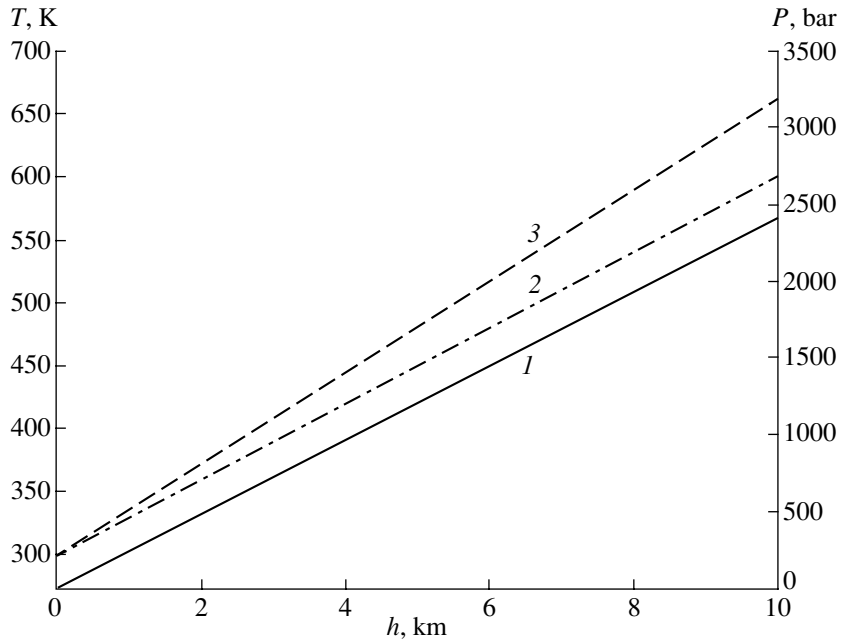

Fig. 1. Pressure (line *1*) and temperature (lines *2*, *3*) at $a = 30$ and 36, respectively, versus the depth.

erals (Bortnikov et al., 1998; Gamyanin et al., 1999; Novgorodova et al., 2003b). However, the aforementioned basic parameters of the fluid may also depend on the depth of host rock occurrence. Therefore, the problem of formation of nano- and microspherules with regard to the depth of host rock occurrence is certainly of interest. The objective of this study is to develop further this line of research and to consider the cavitation–ablation mechanism of formation of nanospherules.

The article consists of two sections. The results of investigations pertaining to the conditions of formation of mineral nano- and microspherules in hydrothermal fluids (through the cavitation mechanism) depending on the depth of host rock occurrence are given in the first section. The second section is focused on the cavitation–ablation mechanism of formation of nanospherules and the typical sizes of nanospherules formed due to ablation of overheated material from the surface of microparticles. Possible applications of the results of this research are also discussed.

FORMATION OF NANO- AND MICROSPHERULES DEPENDING ON THE DEPTH OF HOST ROCK OCCURRENCE

In terms of the cavitation mechanism, the equilibrium temperature and pressure of hydrothermal fluids are decisive for cavitation bubble compression and, consequently, for the formation of nano- and microspherules. These equilibrium parameters of fluid, in turn, depend on the depth of host rock occurrence.

Available data on the properties of the Earth's crust suggest that the Earth as a whole is in a state of hydrostatic equilibrium (Ershov et al., 1994). In this case, the variation of pressure P_0 with depth h (<10 km) may be calculated from the mass of the overlying rock column (Koronovsky and Yakushova, 1991):

$$P_0(h) = P_n + \rho_0 g_0 h = 1 \text{ bar} + 240h, \quad (1)$$

where $P_n = 1$ bar is the normal atmospheric pressure, $\rho_0 = 2.4$ g/cm^3 is the average rock density at a depth of $h < 10$ km, and $g_0 = 10$ m/s^2 is the acceleration of gravity (the variation of g_0 with depth is omitted).

The relationship between temperature (T_0) and depth is equivocal because the geothermal field depends not only on the depth of measurements but in many cases on the latitude of the locality. Nevertheless, at a depth $h < 10$ km, the relationship $T_0(h)$ may be regarded as linear (Ryzhenko et al., 2000) and approximated by the formula

$$T_0(h) = 300 \text{ K} + ah, \quad (2)$$

where the coefficient a varies according to the locality. In Eqs. (1) and (2), the h value is measured in kilometers. The variation of pressure (line *1*) and temperature (lines *2* and *3*, at $a = 30$ and 36, respectively) with depth h is shown in Fig. 1.

The equilibrium values $T_0 = 523$ K and $P_0 = 1.5$ kbar accepted for the hydrothermal fluid by Adushkin et al. (2004a, 2004b) fit with a sufficient accuracy formulas (1) and (2) at $a = 36$ and correspond to $h = 6.25$ km (Fig. 1).

Let us consider the variation of the extreme parameters of the cavitation bubble (the radius and the pressure and temperature of gas in the bubble) with depth of occurrence of rock that hosts hydrothermal fluid at $a = 30$ and 36.

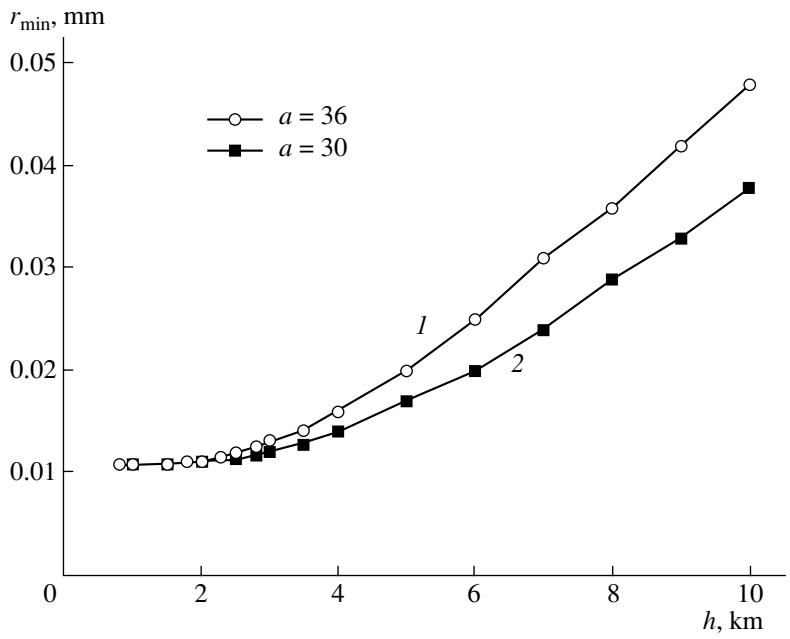

Fig. 2. Radius r_{min} of the cavitation bubble of initial radius of 1 mm at the moment of its greatest compression versus the depth of host rock occurrence at different a values. Curves *1* and *2* correspond to a = 36 and 30, respectively.

The dynamics of the bubble compression was calculated by a numerical method in the approximation of an uncompressible liquid applying the Rayleigh–Plesset equation (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 radius of the bubble; η and σ are the viscosity and surface tension of the liquid, respectively; $\dot{R}$ and $\ddot{R}$ are the first and second time (t) derivatives of the bubble radius; P_0 is the external pressure; and ρ_0 is the fluid density. The pressure $P(R)$ inside the bubble as a function of its radius R is determined with the equation of the adiabatic process for a nonideal gas with the adiabatic exponent $\gamma = 4/3$.

Figure 2 shows variations of the cavitation bubble radius r_{min} at the moment of its maximum compression versus the depth h and the value of the parameter a when the initial radius of the bubble r_0 equals 1 mm. Curve *1* corresponds to a = 36, and curve *2*, to a = 30. As follows from Fig. 2, the bubble experiences the maximum compression $r_0/r_{min} = 10$ when $h < 2$ km. At this depth, the discrepancy between the curves at different a values is minimal. As the depth grows, r_{min} increases, the more greatly the higher the value of the parameter a, that is, the higher the equilibrium temperature of the fluid (in our case, a = 36; curve *1*). Such behavior of r_{min} is explained by the fact that the equilibrium fluid pressure P_0 increases with depth linearly, whereas the T_0-dependent pressure of saturated vapor in the bubble $P_s(T_0)$ rises almost exponentially; in other words, as h increases, the difference $P_0 - P_s(T_0)$, which controls the evolution of the bubble, will decrease, while r_{min} will rise.

The relationship of the time t_0 of cavitation bubble collapse (that is, the time of bubble size change from r_0 to r_{min}) versus h for different a is given in Fig. 3. As can be seen from the figure, the collapse time diminishes as the depth becomes greater because it is determined by the increasing P_0. The fluid temperature T_0 and the saturated vapor pressure $P_s(T_0)$ virtually do not affect t_0; therefore, curves *1* and *2*, at a = 36 and 30, respectively, are nearly identical.

The solid nano- or microparticles within a bubble or at its surface start to melt when their melting temperature (T_m) is achieved. For example, T_m of gold and quartz are equal to 1350 and 1883 K, respectively (Adushkin et al., 2004a, 2004b).

Figure 4 shows the evolution of the maximal temperature (T_{max}) in the bubble (curves *1*, *2*) at the moment of its greatest compression and the time t_h during which the melting temperature of gold is exceeded ($T > 1350$ K, curve *3*) depending on h. Curves *1* and *3* correspond to a = 36, and curve *2*, to a = 30. It is seen from Fig. 3 that the relationships $T_{max}(h)$ and $t_h(h)$ are not monotonic: the maximum on curve *1* is approximately similar to the minimum on curve *3*; i.e., the maximum possible heating temperature corresponds to the minimum duration when $T > 1350$ K. The position and value of the maximum of the curve $T_{max}(h)$ substantially depend on the parameter a. If a decreases, the value of the maximum increases and it shifts towards higher h.

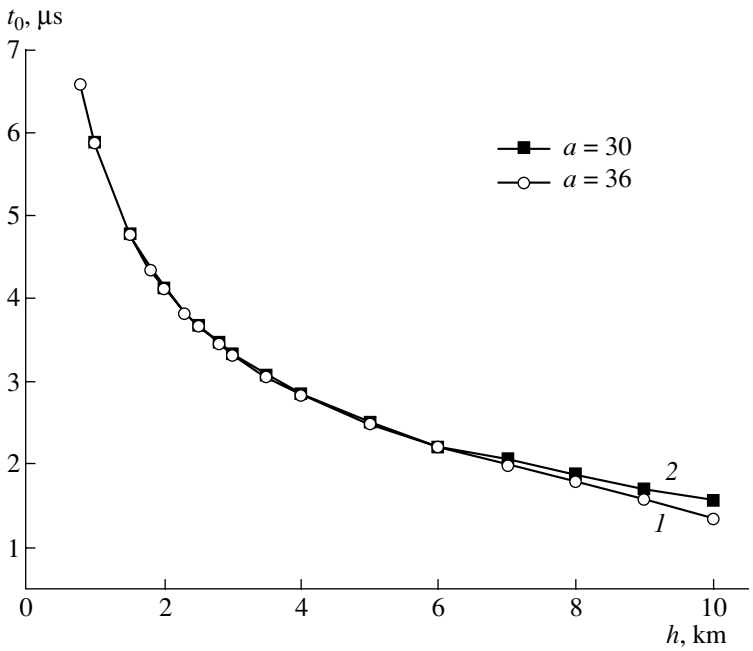

Fig. 3. Time of collapse (t_0) of a cavitation bubble of initial radius r_0 = 1 mm versus the depth at different a values. Curves *1* and *2* correspond to a = 36 and 30, respectively.

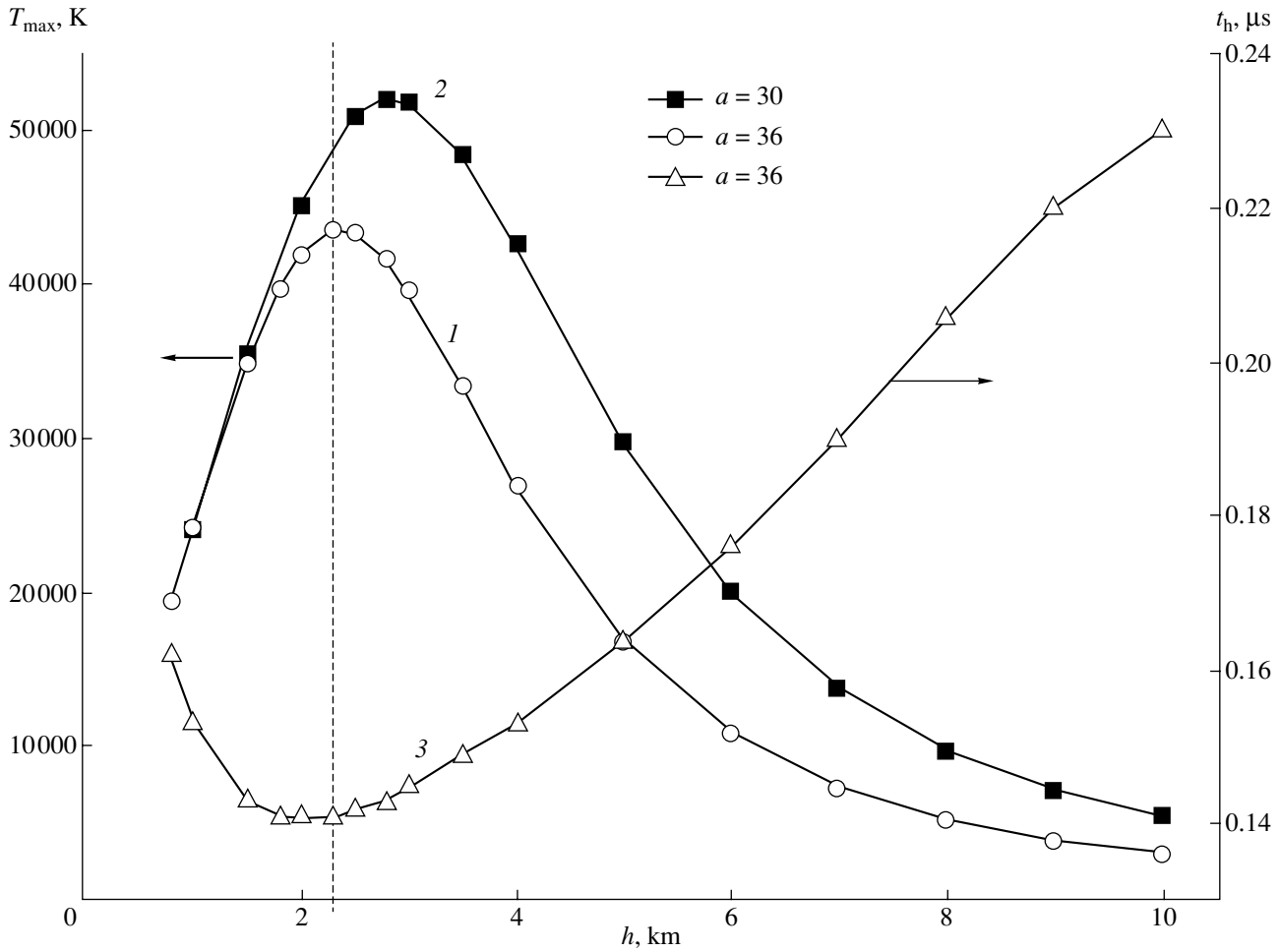

Fig. 4. T_{max} in the bubble at the moment of its greatest compression (curves *1*, *2*) and the time t_h when $T > 1350$ K (curve *3*) versus the depth. Curves *1* and *3* and *2* correspond to a = 36 and 30, respectively.

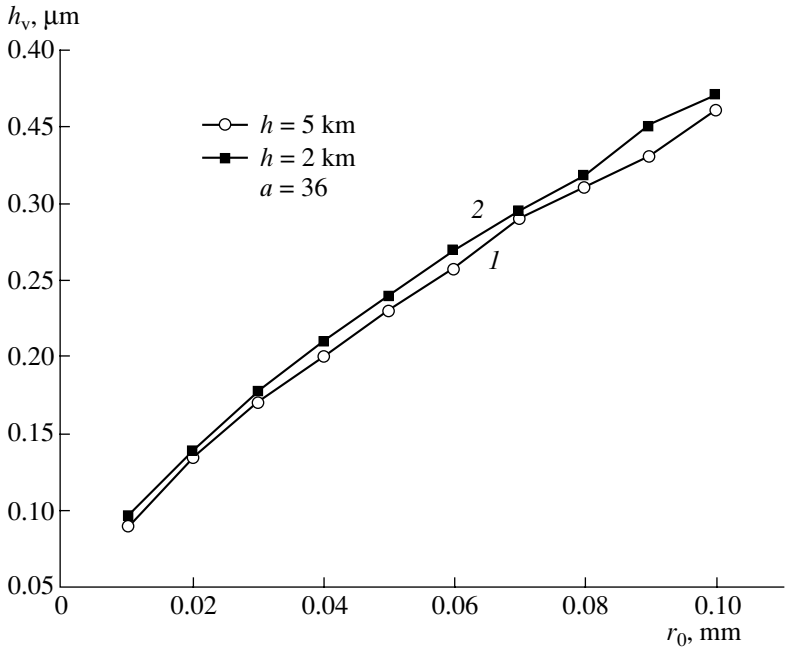

Fig. 5. Thickness of the surface layer (h_v) overheated above the boiling temperature of a quartz particle 2 μm in radius versus the initial radius of the cavitation bubble (r_0) at different depths: h = 5 (curve *1*) and 2 km (curve *2*) at a = 36.

Such high values of $T_{max}(h)$ as given in Fig. 4 are certainly beyond the scope of application of the calculated model. However, it may be expected that curves *1* and *2* in Fig. 4 correctly demonstrate the qualitative behavior of T_{max} as a function of h.

The spherical symmetry of the heat conduction problem was assumed to simplify calculations of the heating dynamics of a solid nano- or microparticle interacting with a cavitation bubble. A spherical nano- or microparticle with $r_p \ll r_{min}$ is located within the contracting bubble; the thermal effect of the particle on the bubble may be ignored. The time-dependent temperature distribution within the particle $T_p(r, t)$ is described by a thermal conduction equation; the change of temperature induced by melting is not taken into consideration. The initial temperature within the particle is supposed to be constant and coinciding with the temperature in the surrounding bubble. The temperature on the particle surface is controlled by the temperature of the surrounding vapor. The condition of symmetry is set at the particle center. The calculated melting dynamics of a solid nano- or microparticle during collapse of a cavitation bubble of 1 mm in initial radius at different depths of host rock occurrence shows that the maximum radius of a particle that melts completely under these conditions depends but slightly on h; r_p equals 2.2 and 19 μm for quartz and gold particles, respectively. The thermophysical parameters of quartz and gold accepted for calculations are as follows: density is 2.14 and 19.3 g/cm^3, respectively; heat capacity is 0.74 and 0.13 J/(g K); and heat conductivity is 0.07 and 3.17 W/(cm K).

The absence of a maximum r_p at a depth of ~2.5 km, where $T_{max}(h)$ is the highest (Fig. 4, curves *1*, *2*), is accounted for by the fact that the duration of high temperature in this region is minimal (Fig. 4, curve *3*). The particle has no time to heat up sufficiently, despite the fact that the temperature at its surface may be several times higher than its boiling temperature. It should be noted that the increasing duration of the high-temperature state with depth becomes a more significant factor for particle melting than the drop in T_{max} (Fig. 4, curves *1*, *3*). Therefore, the r_p values of 2.1 μm for quartz and 17.5 μm for gold at a depth of 2.5 km are lower by 10–15% than at a depth of 9 km, where r_p is 2.3 μm for quartz and 21μm for gold.

If the initial radius r_0 of a cavitation bubble diminishes, the maximum radius of a microparticle r_p necessary for its complete melting will decrease.

CAVITATION–ABLATION MECHANISM OF NANOSPHERULE FORMATION

As was already mentioned, a temperature markedly exceeding the melting and even the boiling temperature of a nano- or microparticle may be reached for a short time in the cavitation bubble during its collapse. For instance, the time t_v when the temperature exceeds the boiling temperature of quartz (T > 3223 K) during the collapse of a cavitation bubble 1 mm in initial radius varies from 10 to 20 ns depending on the depth of occurrence of the host rock. A thin melt film at the surface of a particle heated above the boiling temperature may turn out to be in the overheated metastable state.

The breakdown of this metastable state is of explosive nature (Skripov, 1972) and gives rise to ablation, i.e., to the ejection of nanosized drops of melted overheated film into the surrounding liquid. The subsequent cooling of nanosized drops in hydrothermal fluid is supposed to bring about the formation of nanospherules of various mineral compositions.

The modeling of the dynamics of particle heating during cavitation bubble collapse taking into consideration the particle melting and evaporation and the ablation of substance from its surface is a complicated multidimensional problem requiring advanced computer facilities. However, the size of drops formed as a result of ablation of nano- or microparticle substance may be estimated approximately from the maximum thickness of a surface layer overheated above the boiling temperature of the nano- or microparticle.

The maximal thickness of the overheated layer was determined from the dynamics of the temperature profile within the particle, which was calculated according to the procedure described above. The calculation was performed for a quartz particle 2 μm in radius and a cavitation bubble 1 mm in initial radius. The calculations made it evident that the maximum thickness of the layer h_v overheated above the boiling temperature of the given microparticle is about 400 nm for different depths within the range $h < 7$ km. As the depth increases to $h > 7$ km, the thickness of the layer sharply declines, and it reaches zero at $h > 9.5$ km because at this depth the maximum temperature in the bubble drops below the boiling temperature of quartz.

The relationship between the thickness of a surface layer h_v over a quartz particle 2 μm in radius overheated above the boiling temperature and the initial radius of the cavitation bubble at different depths $h = 5$ and 2 km at $a = 36$ is shown in Fig. 5 (curves *1* and *2*, respectively). As follows from the graph, the relationship of h_v versus r_0 is close to linear, while characteristic h_v values are within the range 100–400 nm. Note also that a variable h within the range considered only weakly affects h_v.

Thus, it may be expected that the maximum size of nanodrops formed as a result of ablation of overheated material from the surface of larger nano- or microparticles (the cavitation–ablation mechanism) amounts to 100–400 nm.

CONCLUSIONS

This research continues the study of mechanisms of nano- and microparticle formation driven by cavitation in hydrothermal fluids in the Earth's crust, particularly, at ore deposits (Adushkin et al., 2004a, 2004b). It has been shown that temperature and pressure, varying with depth of host rock occurrence, may considerably affect the dynamics of cavitation bubbles in fluids. For instance, as depth increases, the maximum compression of a cavitation bubble monotonically declines, whereas the maximum temperature in the bubble, achieved during its collapse, reveals a maximum at a certain depth, which is controlled, among other factors, by temperature gradients in the host rock.

Nevertheless, the dimensions of nano- and microspherules formed due to cavitation in hydrothermal fluids depend only slightly on the depth of host rock occurrence and are mainly determined by the thermophysical properties of the material of which they are composed.

Since the temperature in a compressed cavitation bubble may exceed by several times not only the melting but also the boiling temperature of a nano- or microparticle, a thin melt film on its surface may occur in the overheated metastable state. The breakdown of this metastable phase gives rise to the ejection of the overheated layer into the surrounding liquid in the form of nanosized drops of the melt. The subsequent cooling of the nanosized drops in the hydrothermal fluid may lead to the formation of nanospherules of variable mineral composition.

The estimations performed indicate that cavitation–ablation may result in the formation of nanospherules varying from 100 to 400 nm in size.

Further studies of cavitation effects on the formation of nano- and microparticles in the Earth's crust, particularly, at ore deposits, will require advanced experimental techniques and numerical methods that would allow researchers to solve multidimensional problems based on the theory describing the cavitation–ablation mechanisms of nano- and microparticle formation. Development of these techniques is necessary for solving the problems concerning the cavitation melting and ablation of polymineral nano- and microparticles. Heterogeneous thermal expansion of particles and variable strength of their constituents may cause cavitation fragmentation and breakup of particles into monomineral fractions. Such a process may be applied to the concentration of ores and minerals with production of nanosized fractions of pure materials.

The study of the origin of ore deposits also requires researchers to take into consideration the cavitation and cavitation–ablation mechanisms of nano- and microparticle formation because the rapid ascent of fluids from the mantle towards the Earth's surface, as well as the formation of micrometer-sized inclusions of primary terrestrial melts in olivine crystals, may be accompanied by cavitation phenomena.

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