On the possible mechanism of the diamonds formation in Kamchatka mantle wedge.

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Key Points:

- Poro-elastic calculations show that the rapid heating of a Fe and Mn enriched carbonate-silica aggregate in a carbonatized mantle wedge by magma can temporarily pressurize fluid to the PT stability conditions of the diamond. This mechanism can explain the discovery of diamonds in volcanic rocks in Kamchatka. The high content of native Ni and Mn in Kamchatka diamonds is a signature of a high CO fraction in reduced carbonic fluid.

Abstract

Various geodynamic mechanisms can lead to the penetration of siliceous carbonates into the mantle wedge. Their thermal decomposition in the “mantle olivine autoclave” can be a mechanism for the formation of diamond erupted in subduction zone of Kamchatka. Using the theory of poro-elasticity, we showed that rapid heating of a mixture of sideritic dolomite and silica at 150-200°C can lead to an increase in pressure by 2-3 GPa. With the initial parameters $P = 2$ GPa and $T = 830^\circ\text{C}$, the carbonic fluid produced during the reaction would get into the PT stability field of the diamond. The growth of diamond in the PT field of metastable graphite can be enhanced by microparticles of native Ni and Mn formed by the thermal decomposition of gaseous carbonyls. The corresponding abundant microinclusions of Ni and Mn are found in Kamchatka diamonds.

1 Introduction

Finding diamonds in active volcanoes in subduction zones is contrary to the generally accepted models of their formation, which require equilibrium PT parameters in the mantle edge [Erlach and Hausel, 2002]. Recently in Russia a new example of such discoveries on the 2012-2013 eruption of Tolbachik volcano (Kamchatka) was published [Silaev et al., 2015]. These diamonds were discovered together with pyroclastics, but not inside it, and their natural origin has not yet been recognized by the global diamond community. In the Avachinsky volcano (Kamchatka) carbonado-like diamonds cemented predominantly with porous silica are described in avachites (basalts with olivine - plagioclase phenocrysts assemblage) [Kaminsky et al., 2016]. These diamonds with respect to the high content of Ni and Mn are similar to those of Tolbachik volcano. For both [Kaminsky et al., 2016], a mechanism of diamond formation with the chemical deposition from the vapor phase (CVD) was proposed. However, relatively large diamonds from Avacha bear the features of strong deformations, such as dislocation kink-bands and twinning [Kaminsky et al., 2016], as in minerals formed upon impacts. At the same time, smaller diamond grains that appear to be in a mechanical shadow have no manifestations of strong deformations. In general, these observations indicate significant deviator stresses at the time of diamond formation [Kaminsky et al., 2016]. Regardless of the actual mechanism for the formation of Kamchatka diamonds, it is clear that the carbonic fluid phase was involved.

2 Carbonates in the mantle wedge

Decarbonatization reactions in the upper mantle are the most probable source of carbonic fluid. Carbonates react with silicates (silica) and generate CO_2 and other components (hydrocarbons) in secondary reactions with water and mantle iron-containing minerals buffering $f\text{O}_2$. Several basic reactions determine the carbonate-silicate interaction. In general (neglecting contribution of alkalis) the carbonate is represented by dolomite $(\text{Ca,Mg,Fe})\text{CO}_3$. It decomposes on aragonite and magnesite at high pressure:

Carbonated iron free lherzolite upon heating releases CO_2 by the following reaction [Gudfinnsson and Presnall, 2005]:

The line of this equilibrium has a gentle slope in the PT space – the equilibrium pressure is in the range 1.5-2.5 GPa at $1000 < T < 1400^\circ\text{C}$. Iron-free dolomite reacts with silica (in the form of stable polymorph coesite) at higher parameters [Luth, 1995]:

Pressure of equilibrium is in the range 3-5 GPa at $1000 < T < 1400^\circ\text{C}$.

The presence of iron in the dolomite significantly changes the parameters of the decarbonatation reaction [Martin and Hammouda, 2011].

The equilibrium line of the reaction in the PT space is rather steep – at $850 < T < 1200^\circ\text{C}$ pressure increases from 1.5 to 6.5 GPa, i.e., it is essentially a reaction mediated by the temperature. These parameters are determined for intrinsic $f\text{O}_2$ buffered by the presence of FeCO_3 (and partially carbon). In more reduced conditions, the equilibrium shifts toward lower temperatures.

Below, we estimate the possible range of pressure increase in a fast (before fluid loss and viscous relaxation) closed system decarbonatation of a mixture of iron-bearing dolomite and silica when heated by basaltic magma at $150\text{--}200^\circ\text{C}$. Calculations in the poro-elastic approximation demonstrate that the PT conditions of diamond stability can be temporarily achieved in the fluid.

Figure 1. Equilibrium diagram of the decarbonation reactions in the upper mantle.

Decarbonatization of sideritic dolomites is plotted in accordance with experimental data by Martin and Hammouda [2011], dolomite plus silica reaction parameters are from [Luth, 1995]. Cross-hatched rectangle outlines PT parameters of the eclogitic diamonds [Smiths et al., 2015].

Important geotherms for cratons, continent and mantle adiabat are shown. Filled circle corresponds to the starting point of silica-dolomite mixture in the mantle wedge under Tolbachik volcano accepted in this paper, open circle corresponds to parameters of the CO_2 oversaturated

mantle xenolith from Panonian plain [Creon et al., 2016] (numbers are heat flux on the surface [Davies, 2013]).

3 Physical model

In Figure 1, the possible starting point of the carbonate-silica mixture in the PT parameter space is located at $P=2$ GPa and $T=830^{\circ}\text{C}$ near the intersection of the continental geotherm and the equilibrium line of reaction (4). Dashed lines bracket PT parameters of the craton lithosphere, where typical diamonds are formed. For example, the hatched rectangle represents the conditions of the crystallization of eclogite diamonds from Yakutya [Smith et al., 2015]. The CO_2 release will increase the fluid pressure limited by the equilibrium parameters of the PT reaction (3) (Figure 1) and can reach the diamond stability field. Among the variants considered above, this situation is possible only for dolomite containing siderite.

The overpressure of 2.4 GPa is recorded in coesite inclusions in zircon from the exhumed eclogites partially transformed into quartz ($D=15$ mkm) [Korsakov et al., 2007], it gives an example of a similar effect caused by an increase in volume during a phase transition. The pressure in inclusions was fixed near the equilibrium level at low T ($P=2.2$ GPa, $T=500^{\circ}\text{C}$, [Swamy et al., 1994]). The complete transition is inhibited by its large volume effect and low compressibility of the host zircon (bulk modulus $K_{\text{zircon}}=230$ GPa).

The subducting plate beneath the Tolbachik volcano erupting diamonds is located at a depth of 190-200 km (lithostatic pressure of about 6 GPa) [e.g., Seliverstov, 2007]. The pyroxenite source of basaltic magma at a depth of about 100 km or at a lithostatic pressure of about 3 GPa was proposed on the basis of geophysical and general geochemical data [Nikulin et al., 2012]. This assumption was confirmed by our estimate of the pressure in the source of the Tolbachik lava with the formation pressure of chrome-diopside 2.7-3.2 GPa [Simakin et al., 2015].

Figure 2. Schematic view of the subduction zone under Kamchatka. On the surface position of Tolbachik volcano is labeled. Under Central Kamchatka depression (CKD) Crust – Mantle transition by the seismic data is unclear [Levin et al., 2014]. It can be interpreted as a manifestation of the densification processes (grnulite and probably eclogitic stages of metamorphism) of the thickened crust in the zone of Kronotsky paleo-arc accretion (similar to

the interpretation for Izu-Bonin arc crust in [Tatsumi et al., 2007]). Position of the subduction fluid flux melting and of the partially carbonatized zones (light purple) are shown.

The presence of carbonates, silicious ooze and coal in the mantle wedge beneath Eastern Kamchatka can be anticipated in connection with the recent accretion of the Kronotsky paleoarc (see references in [Simakin, 2014]). Large masses of these sedimentary rocks may be cleaved from the accreted island and dragged beneath Kamchatka and form a sedimentary plume several million years ago [Simakin, 2014]. These rocks could be emplaced in the mantle above the level of basaltic magma generation at a depth of 60 – 70 km (see Figure 2). The conditions of magma generation in Avacha are less clear, distance to the slab is only 120 km there. The temperature in the mantle wedge on Kamchatka was predicted to be much higher than 830°C at $P = 2$ GPa (depth 67 km) [Portnyagin and Manea, 2008]. However, the heat flux near the North Pacific coast of Kamchatka is low in the range 42-47 mW/m² [Davies, 2013], which corresponds to a low geotherm. This is probably the effect of a thickening of the crust in the accretion zone, and therefore our assumed starting point [2GPa, 830°C] seems reasonable. Similar PT parameters are expected in the oceanic plate (with the age of 100-120 million years [Davies, 2013]) near Kamchatka. It is predicted that the temperature at a depth of 60 km is about 700°C [McKenzie et al., 2005].

The intersection of the stable silica-carbonate mixture by hot magma may cause decarbonatisation and sudden increase of the fluid pressure to stability parameters of diamond (see Figure 1). When heated, part of the carbonate decomposes and an additional volume ζ of CO₂ is formed. To evaluate the mechanical respond to this reaction with increasing of the system volume, the deformation of solid phases and porous rocks will be taken into account within the framework of the theory of poro-elasticity [e.g., Detournay and Cheng, 1993].

3.1 Poro-elasticity equations

Let us assume that the spherical domain of the silica-carbonate aggregate with radius R_0 has porosity ϵ_0 and is under confining pressure P_0 . It is assumed that this region is bounded by a mantle rock with zero porosity. The poroelastic approximation is valid in a short time limit. For internal reactive volume we can write constitutive equations as:

$$\sigma_{RR}(r) + \alpha \delta_{ij} P_l(r) = \lambda \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + 2\mu \frac{\partial u}{\partial r} \quad (1) \text{ for the radial component of stress}$$

$$\sigma_{\phi\phi}(r) + \delta_{ij} P_l(r) = \lambda \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + 2\mu \frac{u}{r} \quad (2) \text{ for the tangential component of stress}$$

$$P_{fl} = M \left(\zeta - \alpha \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) \right) \quad (3) \text{ for the fluid pressure}$$

After inserting (3) into (1) and (2)

$$\sigma_{RR}(r) + \alpha M \zeta = (\lambda + M \alpha^2) \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + 2\mu \frac{\partial u}{\partial r} \quad (4)$$

$$\sigma_{\phi\phi}(r) + \alpha M \zeta = (\lambda + M \alpha^2) \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + 2\mu \frac{u}{r} \quad (5)$$

For the shell we can write:

$$\sigma_{RR}(r) = \lambda_2 \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + \mu_2 \frac{\partial u}{\partial r} \quad (6)$$

$$\sigma_{\phi\phi}(r) = \lambda_2 \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) + 2\mu_2 \frac{u}{r} \quad (7)$$

It can be shown (see in the textbooks) that in the case of mechanical equilibrium, the spherically symmetric displacements in the sphere and the shell can be expressed as:

$$u_i = a_i r + b_i / r^2, i=1,2 \text{ for the internal domain and shell respectively}$$

At the uniform fluid addition $\zeta(r) = \zeta_0$ constant $b_1=0$ and volumetric strain within inclusion is constant

$$e_{kk} = \frac{\partial u}{\partial r} + 2 \frac{u}{r} = 3a_1 \quad (8)$$

Three unknown constants (a_1, a_2, b_2) require the definition of three boundary conditions. These conditions are 1) equality of radial displacements on the boundary $r=R_0$: $u_1(R_0)=u_2(R_0)$ 2) equality of the radial components of stresses at the boundary: $s_{RR,1}(R_0)=s_{RR,2}(R_0)$ and 3) vanishing of the radial component of the stress in the shell at infinity $s_{RR,2}(\infty)=0$.

Solution is:

$$a_1 = \frac{\alpha \zeta M}{3(\lambda + M\alpha^2) + 2(\mu + 2\mu_2)}, b_2 = \frac{\alpha \zeta M R_0^3}{3(\lambda + M\alpha^2) + 2(\mu + 2\mu_2)}, a_2=0 \quad (9)$$

Finally, substituting the expressions for the displacements into (3) and (6, 7) we obtain formulas for the excess fluid pressure in the inclusion (ΔP_{fl}), the maximum tangential stress in the shell on the boundary with the inclusion (τ_{max}) and the mean stress in the mixture (ΔP_s):

$$\Delta P_{fl} = \frac{\zeta M ((2 + K/K_2)/3 - \nu_2(4 - K/K_2)/3)}{(2 + K/K_2)/3 - \nu_2(4 - K/K_2)/3 + M(1 + \nu_2)\alpha^2/3K_2} \quad (10)$$

$$\tau_{max} = \frac{\alpha M \zeta (1 - 2\nu_2)}{(2 + K/K_2)/3 - \nu_2(4 - K/K_2)/3 + M\alpha^2(1 + \nu_2)/3K_2} \quad (11)$$

$$\Delta P_s = \frac{2\zeta M \alpha K_2 (1 - 2\nu_2)}{(K + M\alpha^2)(1 + \nu_2) + 2K_2(1 - 2\nu_2)}, \quad (12)$$

where K and K_2 are the bulk moduli of the inclusion and the shell, respectively and ν_2 is Poisson's ratio of the shell. It should be noted that the maximum shear stress in the shell and the overpressure do not depend on the inclusion mixture Poisson's ratio ν , which is explained by the hydrostatic inclusion state.

The Biot's module M can be defined experimentally, with some micromechanical model or approximately taken as [Detournay and Cheng, 1993]

$$M = K/(\varepsilon K/K_f + \alpha - \varepsilon) \quad (13)$$

Biot's constant α for isolated pores is:

$$\alpha = \frac{3\varepsilon(1-\nu)}{2-4\nu+\varepsilon(1+\nu)} \quad (14)$$

Equations (9-14) completely define the solution as a function of the parameters (ε , ζ) characterizing the progress of the reaction in a closed system.

3.2 Material parameters

We use San Carlos olivine parameters for approximating surrounding rock properties. Its bulk modulus at ambient conditions 130 GPa, Poisson's ratio 0.25, at $P=2$ GPa and $T=830^\circ\text{C}$ $K=125.6$ GPa [Liu et al., 2005] rising to $K=135.3$ at $P=5$ GPa and $T=1100^\circ\text{C}$. Physical properties of the reactive mixture at the upper mantle PT parameters can be estimated only approximately since mineral composition and texture have not known and changes in the course of the decarbonatisation reaction. Low-Quartz has the contrasted with other minerals properties: bulk modulus increases from $K=51.7$ GPa at $P=2$ GPa and $T=830^\circ\text{C}$ to $K=70.8$ at $P=5$ GPa and $T=1100^\circ\text{C}$ [Swamy and Saxena, 1994]. Poisson's ratio at the ambient conditions is only 0.1. Coesite has the following parameters: $K=99.4$ GPa at $P=2$ GPa and $T=830^\circ\text{C}$ and $K=121.62$ at $P=5$ GPa and $T=1100^\circ\text{C}$ [Swamy and Saxena, 1994]. Coesite Poisson's ratio at the ambient conditions is 0.196 [Pabst and Gregorova, 2013]. Polycrystalline dolomite properties are incomplete, temperature dependence of the bulk modulus is unknown. Bulk modulus at ambient conditions $K=93.7$ GPa, $K'P=4.71$ or at pressure $P=2$ GPa [Bakri and Zaoui, 2011] and $T=830^\circ\text{C}$ K is expected to be about 100 GPa. Dolomite Poisson's ratio at the ambient conditions is 0.268. Diopside at $P=2$ GPa and $T=830^\circ\text{C}$ has bulk modulus equal to $K=116.3$ GPa [Li, Neuville, 2010] and at $P=5$ GPa and $T=1100^\circ\text{C}$ $K=127.8$ GPa. Poisson's ratio at the ambient conditions is 0.242.

Thus assuming initial dolomite – low-quartz mixture (75/25 by weight) we get average bulk modulus equal to 87.9. After quartz-coesite transition average K of this mixture will be around 100 GPa. Surrounding rocks are expected to be stiffer with bulk modulus around 130 GPa. Porous rock property is complex function of the properties of its constituents, rock texture and porosity. For the initial guess in our hypothesis we tentatively fix bulk properties at the values close to the presented above.

4 Results of calculations

First we consider the analytical solution of the simplified problem. It is assumed that the fluid formed at the decarbonatisation reaction fills the spherical inclusion in an infinite elastic medium. Solving the equations (6-7) with the boundary conditions $S_{RR} = -\Delta P$ at $r = R_0$ and $S_{RR} = 0$ $r=\infty$, we can express the relative increase in the inclusion volume due to the excess pressure above the confining pressure P_0 (to within linear terms in $P-P_0$)

$$dV/V = \frac{(1+\nu)(P-P_0)}{2K_s(1-2\nu)} \quad (15)$$

Suppose that before the start of the reaction there was a fluid with a corresponding porosity ε_0 , then the total volume of CO_2 at pressure P is equal to $V_{fl} = (0.733X_Q/V_0 + \varepsilon_0\rho_{fl}(P_0, T_0))/\rho_{fl}(P, T)$. The porosity or the total relative initial void volume at the initial pressure P_0 is equal to $V_{por}^0 =$

210 $0.401X_Q/V_0 + \varepsilon_0$ (here V_0 is the volume of the unit mass of the mixture, X_Q is the mass fraction of
 211 the reacted silica).

212 We assume that when the dolomite reacts, the pressure follows an equilibrium path
 213 $P=P_{eq}(T)$. This dependence was taken from [Martin and Hammouda, 2011] and it is linearly
 214 extrapolated to pressures lower than that of coesite stability (see Figure 1). Since the volumes of
 215 fluid and void are equal

$$(V_{fl}(P, T) - V_{por}^0)/V_{por}^0 = \frac{(1 + \nu)(P - P_0)}{2K_s(1 - 2\nu)} \quad (16)$$

217 This equation was solved numerically for $\nu=0.26$, $K_s=96$ GPa, $P_0=2$ GPa and the solution
 218 is displayed in Figure 3. It can be noted that an increase in the initial porosity results in a
 219 decrease in the fluid pressure. However, in the entire range of used initial porosity values and the
 220 corresponding different mass ratios of the initial fluid and the released CO_2 , a PT stability field
 221 of the diamond is achieved. In this simplified micromechanical model, the average stress in the
 222 rock containing the inclusion does not change, and the maximum shear stress is sufficiently high
 223 $1.5 P_{fl}$.

Figure 3. Fluid pressure as a function of the weight fraction of the reacted silica (in the initial mixture dolomite plus silica) is calculated with simplified micromechanical model. We assume that decarbonation reaction follows equilibrium trajectory $P=P_{eq}(T)$. Initial porosity (ε_0) filled with CO_2 fluid at $P_0=2$ GPa is indicated in legend. Thick dashed line depicts diamond stability boundary.

230 To obtain a more realistic representation of the stressed state of the reacting mixture and
 231 host rocks, a complete pore-elastic solution (equations (9-14)) is used. The theory of
 232 porouselasticity has been developed for engineering applications and usually does not operate
 233 with such great variations in fluid pressure as in our case (approximately from 2 to 5 GPa).
 234 Under the simulated conditions, the compressibility of the fluid (calculated by [Duan and Zhang,

2006]) varies linearly from the pressure in the range $7.9 < K_{fl}(P_{eq}(T)) < 21.4$ (GPa). In the calculation of ζ we use the density of the fluid at the initial pressure $P_0=2$ GPa. The fluid compressibility was iteratively calculated at the midpoint to the pressure corresponding to the current stage of the reaction, expressed in the mass fraction of the reacted silica (see Figure 4). With this choice, the estimated fluid pressure appears to be close to the micromechanical estimate (see Figure 4a).

Figure 4 Results of calculations of different mechanical parameters at the decarbonatization progress, each curve is calculated at the different initial porosities labeled on the plots a), b) P_{fl} , fluid pressure as a function of the reaction progress c), d) P_s , solid pressure (mean stress) within reacted inclusion e), f) τ , deviatoric stress at the boundary of the inclusion in the host rocks. Discontinuities on the plots are connected with α -quartz - coesite transition. Left column

displays results calculated with the first poroelastic model for Biot's coefficient α (the lowest values), right column is obtained for more well connected pore space with larger values of α as a function of porosity.

First, we calculate P_{fl} , the average stress in the reacting matrix, the maximum shear stress in the host rocks before the pressure in the matrix reaches the α -quartz-coesite transition level of 2.4 GPa. At this condition $\zeta=0.356 X_Q$ and $\varepsilon=\varepsilon_{react} + \varepsilon_0=1.126 X_Q + \varepsilon_0$, where X_Q is weight fraction of the reacted silica. At zero initial porosity ($\varepsilon_0=0$), the heating to $T < T(6.5 \text{ GPa})$ transforms the mixture into a metastable state, since formally at any degree of reaction the pressure will rise above the equilibrium value, i.e. the reaction can't begin. Practically with a low porosity, the degree of decarbonatation will be small due to a rapid increase in pressure along the equilibrium line. The release of the fluid is accompanied by an increase in the maximum deviatoric stress in the enclosing rocks to 6 kbar (at given values of the parameters). With a small initial porosity of not more than 3 vol%, the diamond stability conditions will be reached before the coesite transition. Further heating leads to the transition of α -quartz to coesite at an average stress in the matrix of about 2.4 GPa. A decrease in volume during the formation of coesite causes additional porosity, depending on the amount of unreacted α -quartz ($X_{0Q}-X_Q$), up to linear terms in X_{0Q} and X_Q total porosity is $\varepsilon=1.126 X_Q + \varepsilon_0 + 0.125(X_{0Q}-X_Q)$. In Figure 4a, the calculated fluid pressure is displayed as a function of the total porosity with an initial silica content of $X_{0Q}=0.2$. Coesite transition leads to a decrease in the fluid pressure and a shift of the curves $P_{fl}(\varepsilon, \varepsilon_0)$ to the larger porosities. In Figure 4, the equilibrium parametrization $P(T_{eq})$ is used, but in fact, under the conditions of the coesite transition, decarbonatation equilibrium can not be hold. The drop in pressure at a constant T will shift the mixture into a nonequilibrium field. Probably, the coesite transition will lead to an acceleration of the decarbonatation reaction, which can cause high shear stresses in the host rocks above the shear strength. This can lead to explosive destruction of these rocks and a rapid invasion of the fluid with diamonds into magma. With such an "explosion" deformations of large diamonds with the formation of kink-bands [Kaminsky et al., 2016] are expected. The exsolution of silica from carbonic fluid, subsequently transformed into quartz, which binds Avacha diamonds [Kaminsky et al., 2016], can also be explained by an abrupt pressure drop of several GPa at the failure of host mantle rocks.

It should be emphasized here that the elastic problem does not have its own spatial scale, and therefore the results obtained are equally valid for a large quartz-carbonate domain, for small inclusions and even for several grains. It can be expected that the system has a small size, since only then is rapid heating possible on contact with the magma. At sufficiently large spatial and temporal scales, the viscous relaxation of elastic stresses and the drop in excess fluid pressure become important. An additional argument in favor of the small size of the system in the Kamchatka case is the fact that the findings of diamonds are rather sporadic and in general the geochemical signatures of the interaction of carbonates and basaltic magmas or melting of the carbonatized mantle are weak. Mineralogical evidences of the proposed mechanism of diamonds formation are considered next.

5 Geochemical evidences of the high pressure conditions at Kamchatka diamonds growth

Tolbachin diamonds have anomalously high content, Co (enrichment factor 5-50), Fe (1-2 orders), Ni (1-4 orders) and Mn (3-5 orders of magnitude), as compared to kimberlite diamonds [Silaev et al., 2015]. Absolute concentrations of Ni and Mn in Tolbachik diamonds are

86.3 ± 68.6 ppm and 1129.5 ± 1070.4 ppm, respectively. In diamonds from Avacha, numerous nanosized (about 50 nm) inclusions of Mn-Si (with traces of Ni and Fe) and Ni-Mn (with traces of Fe and Si) alloys were observed. At the average interparticle distance ca. 2 μm (estimated for rich Ni rich inclusions with a width of 50 nm in the images from [Kaminsky et al., 2016]) corresponds to a nickel content of about 60 ppm, which is analogous to the content of diamonds in Tolbachik. Diamond-bearing basalts from Tolbachik volcano have high concentrations of Pt (up to 3 ppm) and Co (up to 108 ppm) [Gordeev et al., 2014]. Avacha diamonds are also characterized by the presence of tungsten carbide (WC) with inclusions of native Mn-Fe-Ni-Co alloys [Kaminsky et al., 2016]. Altogether, these mineralogical data may indicate the formation of diamonds from a fluid enriched with different carbonyls or other organometallic compounds. Indeed, the siderophile transient elements (Mn, Fe, Ni, Co, PGE) and W are known to form carbonyls.

We have obtained preliminary experimental data on the solubility of Mn and Pt in a reduced carbonic fluid consisting of CO and CO₂ at P=0.2 GPa and T=800-1000°C and found that these solubilities are at least 250 and 15 ppm respectively [Simakin et al., 2016]. It is estimated that the solubility of nickel in the form of Ni(CO)₄ in the reduced carbonic fluid rises from 0.2 to 100 ppm with an increase in pressure from 0.2 to 1 GPa at T = 900°C. Our experimental data and thermodynamic calculations indicate the stabilization of carbonyls with increasing pressure and their thermal decomposition. For example, for nickel carbonyl, we calculated that at P=1 GPa and T = 1000°C, heating on 150°C releases about 60 ppm Ni (based on the weight of the initial fluid solution). Thermodynamic calculations for Ni have not been verified experimentally, solubility can be underestimated since solubility forms differing from Ni(CO)₄ are possible. In any case, at the low pressure anticipated for CVD diamond growth [Kaminsky et al., 2016], the solubility of Ni and Mn in the reduced carbon fluid would be small, and the simultaneous crystallization of carbon and metals corresponding to the observed metal concentrations in diamonds would be hardly possible. Existing experimental data do not allow unambiguous determination of PT parameters of formation of Kamchatka diamonds based on Ni and Mn concentrations, however, it seems that the pressure was at the level of several GPa.

It should also be emphasized here that carbon often precipitates as graphite when the fluid decomposes. We found graphite-like carbon formation at the disproportionation of CO (2CO = C + CO₂) at 0.2 GPa [Simakin et al., 2016]. Martin and Hammouda [2011] also observed graphite formed due to the disproportionation of CO at the decomposition of FeCO₃ (partially exsolved from (Fe,Mg,Ca)CO₃) in the PT field of diamond stability. In Kamchatka case, the crystallization of diamond (the cubic group of symmetry Fd3m) might be promoted by the presence of Ni and Mn particles with a similar cubic structure (Fm3m).

6 Conclusions

Unusual diamonds found in volcanic rocks of Kamchatka, were formed, certainly, from the fluid. We suggest that the formation of diamond occurs not at low pressure by the CVD mechanism, but rather at PT parameters of their stability. The presence of abundant inclusions of native Ni and Mn can be explained by the thermal decomposition of the corresponding gaseous carbonyls present in reduced carbonic fluid at high pressure. Theoretically, we demonstrated that fluid pressure at the reaction of silica and siderite dolomite caused by magma heating can temporarily increase by 2-2.5 GPa, thus achieving PT stability field of diamond. At the

mechanical failure of the pressurized rocks the fluid phase with diamonds is injected into the magma which transfers them to the surface.

Acknowledgments

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