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# Genetic Role of Calcium Content in Olivine Crystals of Ultramafic and Mafic Rocks

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**Abstract:** The results of genetic systematization of olivine compositions formed both under experimental conditions and its natural differences from rocks of basic and ultramafic compositions of various depth facies and formed in various geodynamic settings are presented. Similar work [53], performed in the 70s of the last century and has been actively cited to this day. Generalization of the subsequent accumulated data showed the error of one of the main conclusions in this work – the dependence of the CaO content in olivine on the hydrostatic pressure during its formation from the melt. According to experimental studies conducted in recent years, up to a pressure of 29 GPA, the content of calcium in olivine, which has grown from the main-ultrabasic melts, does not depend on the pressure and is not lower than 0.1 wt.% CaO. Experiments in solidus conditions involving fluid and natural data have demonstrated that one of the leading factors affecting the calcium content in olivine are metasomatic processes that lead to the removal of calcium from olivine crystals. The role of metasomatic transformations of olivine in terms of calcium content, despite the apparent insignificance of secondary changes in it, is clearly visible in the examples of basalts and gabbro of the modern oceanic crust and the same facies differences in ophiolite complexes. The wide development of metasomatic transformations of igneous rocks of various facies and ages indicates the need to take into account the calcium content in olivine as an equilibrium criterion when calculating temperatures and pressures for paragenesis involving olivine. Olivines, which are part of ultrabasic xenoliths carried out by sub-alkaline magmas, including those carried out by kimberlites, are overwhelmingly represented by low-calcium differences. Low levels of calcium in olivines from these mantle fragments suggest that magmatic melts of the main-ultramafic compositions are not in equilibrium with the mantle substance to depths of about ~ 200 km, and possibly more. Among the compositions of olivines from fresh effusive rocks, its inclusions and microlites are mostly represented by calcium-containing differences. Only in kimberlites, almost all the differences in its crystals (inclusions, microlites) in the rock are represented by low-calcium differences. Olivines included in diamonds are also overwhelmingly represented by low calcium differences. This suggests that the composition of kimberlite olivine is associated with metasomatic transformations, and the growth of diamonds from kimberlites is due to the fluid. Inside the natural single crystals of diamond, there are polymetallic films buried in the body of crystals. Similar films were formed on the faces of diamond crystals formed in the Lav pores (that is, almost on the surface of the day) in 2012-13 of the Tolbachinsky Fissure eruption. These data allow us to create artificial "soft" conditions (CVD, solution, etc.) for the growth of single-crystal diamond films on similar polymetallic or single-element films. For these purposes, elements such as zirconium, dysprosium, erbium, and others can be used.

**Keywords:** Calcium, Olivine, Equilibrium

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## 1. Introduction

Minerals of olivine group, being almost constant participants of mineral associations in the ultramafic and mafic rocks, are commonly used as indicators of its genesis.

There are two types of tools used for genetic mapping. These tools are based on the composition of olivine crystals – discriminatory diagrams and equations – binding compositions of olivine and other phases of association with the physical and chemical conditions of its formation. The most important genetic criteria regarding the content of

minor elements, as a rule, are synthesis of a large amount of data by element content in natural olivine varieties and discriminatory diagrams built on its basis. The elements forming the olivine lattice are the most significant genetic criteria in the form of equations for the calculation of temperature, pressure, oxygen fugacity, equilibrium with melts and other phases in the rock, melting degree, etc.

For olivine, due to the development of precision methods of local analysis, both groups of elements are in great demand. Among minor elements, the contents of Ni, Co, Mn, Cr, Ti, and Ca are usually used for genetic mapping. One of the most significant genetic indicators of olivine is probably the threshold of calcium oxide content (0.1 wt%) in its composition. This criterion was identified and presented in [53]. The authors explained it by the influence of crystallization depth – pressure. Ratio of calcium-containing and low-calcium (less than 0.1 wt% CaO) varieties of olivine was left unaddressed in the study results over the past period (experiments, field data) and often non-complying with the conclusion [53]. Based on a large amount of data synthesis on experimental research of melting systems involving olivine within a wide range of conditions, as well as on the results of classification of its natural varieties, the papers [40, 41, 42, 43] showed that the conclusion was irrelevant. However, involving experimental data and olivine natural varieties, there is a number of facts (as for calcium content) both confirming and strengthening the proposed explanation and inconsistent with it.

The aim of the present paper is to illustrate the collected facts and consider its possible explanations.

## 2. Genetic Criterion – Threshold CaO Content in Olivine

With the development of microanalysis, determination of local element content has become possible in mineral phase up to 3–4 decimal places. It gave an impulse to design of geothermometers using element content – admixtures in olivine. Based on interphase distribution of calcium according to experimental data, a number of geothermometers were proposed, for instance, geothermometer [50, 12]. In the paper [17], using precision determination of calcium contents, the dependence is proposed of H<sub>2</sub>O content in the melt on the value of  $K_d$  ol/m for CaO. Checking the relation of  $K_d$ -H<sub>2</sub>O by interphase calcium distribution over three experimental data arrays (310 points, 333 points and 115 points) used in the paper [43] has revealed the following: dependence of  $K_d$  ol/m for Ca on magnesium content in the melt reflects the curved dependence of magnesium and calcium content in the melt, equilibrium with olivine. This is due to poor relation of calcium content in olivine to its content in the melt (average value of correlation ratio over 3 arrays is 0.37) and it varies from one data sampling to another. Dependence of  $K_d$  ol/m for Ca on olivine composition, melt composition, P-T conditions has showed its rather high negative dependence

only on magnesium content in olivine (average over three data arrays is 0.62) and low (-0.23) negative association with water content in the melt. The dependence of magnesium content in olivine can be controlled by Fe<sup>2+</sup> content (very sensitive to oxygen fugacity), Mg content in the melt and variable value of  $K_d$  Fe/Mg ol/m. Such associations show the ambiguity of the proposed dependence of  $K_d$  ol/m for CaO on water content in the melt.

Threshold calcium content (0.1 wt% CaO) in olivine crystals is probably one of the most informative criterion for olivine genesis in ultramafic and mafic rocks. In the papers [40]; [41]; [42]; [43] based on the analysis of a large amount of experimental data on the crystallization of mafic and ultramafic melts, and rock melt of similar composition within a wide range of conditions, it was shown that olivine crystals equilibrium with mafic and ultramafic melt contain at least 0.1 wt% CaO in it, while the melt contains more than 3 wt% CaO. This conclusion was drawn based on the analysis results of the experimental data arrays that were built on the basis of experimental data by phase equilibria of igneous rocks (INFOREX system) [2] and author's own databases. Data selection is as follows: "dry" conditions, atmospheric pressure (~100 KPa) – 1033 experiments; "dry" conditions, pressure up to 17.5 GPa – 756 experiments; experiments with undersaturated fluid melt under pressure up to 3.5 GPa – 310 points; experiments with saturated fluid melt under pressure up to 12.5 GPa – 330 points. Experimental data array with available values of water content in the melt and pressure up to 6 GPa - 130 points (author's database). In addition, the data were supplemented by experimental results, not included in the above data selection and collected in [41] – 313 points and [43] – 40 points. These are mostly experiments on melting of peridotite, kimberlites, peridotite-carbonate and eclogite-carbonate systems under maximum pressure reaching values of 26 GPa.

However, a number of *exemptions* were revealed to specify regularity among the experimental results that make up ~2–7% of data selection where olivines are represented either by calcium-free or low-calcium varieties. In the first case, the calcium content was not analysed in olivine crystals and this practice, unfortunately, survived until the present time. It probably includes analytical errors if consider the period of low accuracy in determining calcium in olivine. In the second case, there may be multiple variants of presence of low-calcium varieties of olivine. Firstly, it is due to solidus conditions of its crystallization, or similar to subsolidus + fluid when the system under study contains practically no melt cementing mineral phases. Data from [33] (33 of 36 crystals are represented by low-calcium varieties), [19] where 3 of 4 olivine crystals are represented by low-calcium varieties and data from [29] (29 of 30 crystals are presented as low-calcium crystals) may serve as an example. The results obtained by [46] can be probably referred to this group of experiments on partial melting of peridotite (1.9 GPa) involving H<sub>2</sub>O-KCl (only 2 of 7 crystals are represented by calcium-containing ones thus related, according to the authors, to capture of clinopyroxene inclusions during analysis). Products of the melt quenching in these experiments

contain CaO less than 3%wt, in 5 cases of 6, that causes, in our view, formation of low-calcium varieties. A series of experiments presented in the paper [38] is an illuminating example of the influence of CaO low contents in the melt on its content in olivine and formation of low-calcium olivine in the solidus area; all the described analyses here (14 tests) are represented by low-calcium varieties. Local equilibria in the experimental system under study can cause formation of the two varieties of olivine. So, in the experiment (without melting) with fluid [8], olivine (around tablet of  $\text{CaCO}_3$ ) is represented by calcium-containing varieties, and as for the matrix it is calcium-free varieties. These experimental data on olivine formation in the solidus area suggest that reaching the melting temperature during the experiment and the presence of fluid (water) are not the reasons of low-calcium olivine formation. Experimental results over the recent years have revealed a few more affecting elements, along with calcium, in the melt on a particular occurrence of calcium in the crystals of olivine. Both calcium-containing olivine crystals and low-calcium varieties are formed in the melts during melting of peridotite-carbonate, peridotite-phlogopite-containing, potassium-rich kimberlite-like systems involving fluids [10, 11, 56, 57]. This data selection from four papers is represented by 40 analyses of olivine crystals where the proportion of low-calcium varieties ranges from 30 to 100%. These melts are characterized by CaO content of more than 4 wt% but wider variations of  $\text{SiO}_2$  (~6–46%wt.) and relatively high content of  $\Sigma$  alkali ~6–30 wt% with potassium predominance (kamafugite varieties). In case of moderate alkali contents in the melt (1–8 wt%) [14] all the analyses presented (10 crystals) refer to calcium-containing varieties. One of the options of low-calcium olivine formation in these experiments can be the influence of high alkali content in the melt. Data from [62] are apart from the experimental results analyzing the presence of low-calcium olivine. In this system, peridotite-fluid (water) with a small amount of local fluidized glass, through all 10 analyses of olivine crystals carried out, are represented by low-calcium varieties in association with low-calcium and high-calcium pyroxenes and garnets. Although CaO content in the melt varies within the range 11–16 wt%,  $\text{SiO}_2$  35–40 wt%,  $\Sigma$  alkali less 2 wt%. Such discrepancy might be due to several reasons. Due to restrictive evolution of the melting (glass), a subsolidus recrystallization of the starting material is probably occurred involving water and with the formation of low-calcium olivine. In experiments [29] on dehydration of serpentinite under milder conditions (2 GPa, 550–850°C) if compared to the experiments conditions [62] (10–13 GPa, 1350–1450°C) under solidus conditions, the following mineral association has been formed: olivine-low-calcium pyroxene-high-calcium pyroxene-garnet. In this series of experiments, olivine is also represented by a low-calcium variety (29 out of 30 indicated analyses) but garnet is represented more by calcium variety and mineral association contains clinocllore. In addition, another possible reason for the formation of low-calcium olivine in the experiments [62] may be non-equilibrium of olivine with the melt, as duration of the experiments was 24 hours whereas according to [2] olivine-melt equilibrium occurs when the experiments last over 48 hours.

The main condition for conducting experimental research

is obtaining equilibrium of compositions of coexisting phases. This suggests that crystals of calcium-containing olivine *are in equilibrium* with the melts of mafic and ultramafic compositions containing at least 3 wt% CaO and of normal and moderate alkalinity. The indicated above experimental data, together with the exceptions, suggests that pressure up to 29 GPa *does not affect* the calcium content in olivine crystals that are in equilibrium with the melts of mafic-ultramafic compositions. Thus, it makes the thesis [53] wrong on the effect of pressure on calcium content in olivine crystals and assumes looking for other causes of low-calcium varieties presence in the rocks known as of primary magmatic genesis. Moreover, we would like to draw the attention of the reader that the number of experiments on the interaction of peridotites with carbonatite melts under the mantle pressure with formation of calcium-containing olivine is constantly growing. One of the recent papers is [49] on interaction of peridotite with carbonatite melt under the conditions of 3.1 and 6.5 GPa where 10 olivine compositions contain 0.4 wt% and more CaO. In addition,  $\text{K}_2\text{O}$  in the melt is high enough and varies within the range ~10–15 wt% that should contribute to the formation of low-calcium varieties of olivine. Possible influence of potassium in the melt is compensated by high-calcium content in the melt (~20 wt% CaO). Summarizing the experimental data, we can assume that the presence of low-calcium varieties of olivine crystals under experimental conditions is due to the following melt composition: below 3–4 wt% CaO; ~less than 10 wt%  $\text{SiO}_2$ ; high content of alkali  $\Sigma$  ~10–30 wt% with a predominance of potassium. Border effects of  $\text{SiO}_2$  content and  $\Sigma$  alkali in the melt are to be specified by using a larger number of experimental data. It may be the integral index that takes into account the temperature values and CaO content in the melt.

This revised conclusion, based on experimental data, was used to consider possible genesis of some mafic and ultramafic rock compositions with a focus on alkaline varieties, as some published papers still refer to reasoning based on the conclusions [53].

## 2.1. Volcanic Rocks

Aspects are considered of CaO content in olivine generated by mafic lava, komatiites, meimechites, kamafugite rocks, carbonatites and kimberlites.

As a rule, *mafic lava* formed under different geodynamic environments, mainly on the ground surface within a wide range of age, contains largely calcium-containing crystals of olivine. Share of low-calcium olivine is growing with increasing metamorphic transformations. Share of low-calcium olivine is minor in the Quaternary lava, it does not extend beyond the first percent. Mafic lava of the modern second layer of the oceanic crust represented by ellipsoidal lava is typical for calcium-containing olivines. The only exception so far is young (six million years) shoshonites found in the Japan trench [24]. Analyses presented of olivine phenocrysts (6 crystals), represented by low-calcium varieties with rims of calcium-containing olivine, microliths are mainly represented by calcium-containing olivines. In the

lava of ophiolitic complexes, preservation of calcium-containing olivine depends on facies of metasomatic transformations in the rock and degree of its variability. However, in general, we can confidently state that low-calcium varieties of olivine in pillow lava of ophiolitic complexes are predominating. These data based on synthesis of experimental data suggest that there is a calcium removal from olivine crystals under metamorphic transformations and non-equilibrium with the melt of low-calcium olivines present in the Quaternary basalts.

*Komatiites and meimechites.* Komatiite lava, forming the part of the Precambrian greenstone belts, is usually altered and ranges from green schists to ~epidote-amphibolite facies, being consistent to hosting rocks. Quantitative correlations of high-calcium and low-calcium olivines vary within a wide range: there are both individual crystals of low-calcium olivine and complete lack of calcium-containing olivine but occurrence of new metasomatic calcium-free olivine. In Cretaceous komatiites of Gorgon island, practically not affected by secondary alterations, olivine crystals are slightly affected by secondary transformations – serpentinization in fractures and represented by calcium-containing varieties. Based on the data presented (188 tests) [20], these crystals have quite homogeneous composition of ~0.3–0.35 wt% CaO without any distinct differences between cores and edges of phenocrysts and microliths.

Meimechite genesis is studied in many papers in relation to bulk and phase compositions of these rocks. It can be referred to alkali-ultramafic Gulinsky massif. Compositions of olivine crystals indicated in publications are represented by calcium-containing varieties. Data from the paper [59] can be used as an illustration. Meimechites and dunites of Gulinsky plutonic rocks are of absolute age according to the data presented in [59] within the range of 231–245 million years. Crystals of olivine in meimechites are quite fresh and affected by serpentinization in fractures. It is represented by calcium-containing varieties (20 tests) of ~0.3–0.5 wt% CaO. These volcanics are formed from ultramafic alkaline magma, plutonic dunites can be olivine cumulates from this magma [59], which derivatives can be carbonatite melts [45].

*Kamafugite volcanics and carbonatites.* Kamafugite volcanism is not widely spread, mainly in the zones of large transstructural tectonic faults. Practically all occurrences, both spatial and genetic, are closely related to carbonatites. Data on the contents of CaO in olivines of uvanites (9 crystals) were used as examples [22]; mafurites (7 crystals) and uvanites (7 crystals) [30]; melilitites (25 crystals) [37]; kalsilitites and melilitites (7 crystals) [34]; carbonatites (5 crystals) [60]; calcite carbonatites (8 crystals, 5-monticellite, 3-olivine) [23]. These rocks are of Quaternary age. Only 5 crystals out of 68 presented analyses of olivine crystals are represented by low-calcium varieties. In most cases, higher calcium content was revealed at the edge parts of crystals. The sum of alkali in kamafugite rocks varies within the range ~3–9 wt% with predominance of potassium. Higher values of  $\Sigma$  alkali are recorded in the heated melt inclusions where it can reach 15–20 wt%.

In calcite carbonatites  $\Sigma$  alkali (by compositions of the melt inclusions) can reach 36 wt%; in the silicate melt inclusions ~9–16 wt%, sodium dominates over potassium in both groups.

*Kimberlites.* The upper age limit for kimberlite eruptions was considered to have taken place ~22–32 million years. However, kimberlite lava are found of the Quaternary period – Igwisi Hills volcanoes, Tanzania [64]. Almost all kimberlite lava regardless of its age (including the Quaternary ones) and location are typical for low-calcium crystals – phenocrysts of olivine, having the rim of calcium-containing varieties developed on its edges. Calcium-containing varieties are common for the microlithic phase of olivine. But there are cases where almost all the phenocrysts and microliths of olivine under study are represented by low-calcium varieties. For example, data on kimberlites of the Udachnaya Vostochnaya Pipe (Yakutia) [25] where single analyses (less than 10 tests) out of ~270 presented studies of phenocrysts and microliths, including marginal parts of microliths, are represented by calcium-containing varieties. Numerous publications on composition of olivine crystals, contained in diamond crystals, are also largely represented by low-calcium varieties. It can be illustrated, along with the previously data collected [41], by inclusions of olivine into microdiamonds of the Jubileinaya Pipe (Yakutia) [58]. There are some single findings of calcium-containing olivines contained in diamond crystals, see [41]. Olivine, formed within the melt polymineral inclusions out of minerals-phenocrysts in kimberlites, is represented by calcium-containing varieties. It can be illustrated using data on olivine from olivine phenocrysts of the Udachnaya Vostochnaya Pipe (Yakutia) [18] and crystals of olivine and phenocrysts of clinopyroxene and garnet from kimberlites of Lac De Grass (Canada) [5].

## 2.2. Plutonic Rocks

Data collected previously on hypabyssal bodies and major intrusive rock mass and xenoliths provided for the following generalizations by this group of rocks. Similar to effusive varieties with increasing age and extent of metamorphic transformations (facies level and volume fraction) of the rocks, the share of low-calcium olivines in mafic and ultramafic holocrystalline rocks is growing and can achieve 100%. Although there are examples of preservation of calcium-containing olivine varieties in the Precambrian rocks. Low-calcium varieties dominate considerably (3/1) in the mafic intrusive bodies (third layer) of the modern oceanic crust. In the Tertiary stratified rock of RAM island, along with the individual sites completely deprived of calcium-containing olivine, there are fragments of the complex where low-calcium and calcium-containing varieties of olivine are ~1. Whereas there is practically no calcium-containing varieties of olivine in the Precambrian stratified rock mass. Olivines of homoeogene xenoliths are represents by calcium-containing varieties. Olivines of ultramafic xenoliths, that for the most part are expected to be of mantle nature, are predominantly represented by low-calcium varieties of

crystals. Newly formed crystals of olivines from the melting zones of these xenoliths are represented by calcium-containing varieties.

Some selected data on a number of arrays can be found below, it allows to complement selections obtained previously.

There is a distinct difference in the proportion of low-calcium olivines in the complementary complexes of plutonic rocks and derivatives of this magma – volcanic rocks (though this distinction may not be widespread). The data [63] can be an example of the Miocene destroyed volcanic edifice in Fuerteventura island (Canary Islands) which involves stratified intrusive complex in its structure (peripheral volcanic focus?) and co-magmatic lava. Olivine crystals are almost not affected by secondary alterations while sometimes iddingsite can be found. In olivine crystals from intrusive complex, the share of low-calcium varieties is ~42% (150/364); in lava the proportion of low-calcium olivines among phenocrysts is ~27% (22/83). Gabbro xenoliths from Fuerteventura island [31] are represented by fresh varieties of rocks and contain predominantly low-calcium (8 of 9 given analyses of the crystals) varieties.

Differences in ratio of low-calcium and calcium-containing varieties of olivine in pillow lava (modern oceanic crust), where olivine phenocrysts are predominantly represented by calcium-containing varieties, and in gabbroid bodies of the third layer of the modern oceanic crust are quite resistant, appear already in the rocks of ~ 1 million years old, or possibly before this. Data on gabbroids from borehole U1309D sampled the Atlantis Massif [61] and gabbroids dredged out of the faults zone of Vityaz, the North Central Indian, Mid-Oceanic ridge [44] can serve as an example. Gabbroids of the Atlantis Massif are of ~1–1.3 million years, olivine crystals are affected by serpentinization and all the presented analyses of 39 crystals are represented by low-calcium varieties. Gabbroids of the Vityaz zone are more than 0.4 million years, slightly altered and contain an equal number of low-calcium and calcium-containing olivines (8/8). However, it is typical that low-calcium varieties of olivine crystals of gabbroids of the modern oceanic crust prevail. Examples include the following data (in the form of a ratio of low-calcium to the calcium-containing varieties): the ridge area of the Mid-Atlantic ridge [52] – 8/1; Kane ridge area of the Mid-Atlantic ridge [26] – 8/0; Parece Vela Basin (Philippine Sea) [47] – 28/1.

Indicator of the olivine composition preservation can probably be homoeogene inclusions of gabbroids in the mafic volcanics. Most of such inclusions, described in the literature, contain calcium-containing crystals of olivine. Xenoliths of lava, the Antilles, the East Pacific Rise, Iceland island and other are not the exceptions. Examples can include gabbro xenoliths from pikrite pillow-lava (subglacial eruption), Iceland island [21], ranges presented of CaO content in olivine crystals (7 samples) are within the range 0.34–0.45 wt%.

Intrusive varieties of carbonatite rocks are quite often included in alkali-ultramafic and alkaline complexes. Olivine

crystals in these rocks can be represented by low-calcium and calcium-containing varieties, wherein the first ones prevail. In the modern carbonatite lava (Ol Doiyo Lengai volcano), there are descriptions of xenoliths presented by forsterite-phlogopite ijolites with a minimum amount of glass that indicates the final crystallization of the near surface intermediate chamber [48]. In 5 tests of 2 crystals mentioned, CaO content is above 0.1 wt%, total alkali content in the heated melt inclusions is ~15–19 wt% with sodium prevailing.

### 3. Discussion

The collected experimental data allow generalizing and specifying its boundaries. Olivine crystals containing more than 0.1 wt% CaO are formed from mafic-ultramafic melts *with restrictions* by composition (CaO content more 3–4 wt%,  $\Sigma$  alkali less 10 wt%, SiO<sub>2</sub> more 10 wt%) regardless of pressure with values up to 26 GPa. Boundary values of the element content can be mutually dependent and need to be specified. Under experimental conditions with insignificant melting or without it (subsolvus and solvus areas of this material existence during the experiment) and involving fluid, formed olivine crystals are represented by low-calcium varieties containing less than 0.1 wt% CaO.

Such generalizations match well the data on the content of calcium in the olivine crystals of mafic and ultramafic volcanics (komatiites and meimechites). In komatiites, as a rule, of the Precambrian age, and being altered at the facies of green schists according to the host rock, sometimes calcium-containing olivines can be preserved [40]; [42]. In the Cretaceous komatiites of Gorgona island and Triassic meimechites of the Siberian platform (see above) olivines are represented by calcium-containing varieties only. Presence of a certain proportion of low-calcium crystals in the rocks that were slightly affected (facially and quantitatively) by secondary alternations (the Neogene-Quaternary age) indicates its non-equilibrium with the melt that formed this rock, and as a result, xenogenicity. Newly formed olivine crystals during metasomatic transformations of the rocks, in most cases, are represented by low-calcium varieties. Calcium-containing crystals are represented by individual analyses that is typical for intrusive rocks, for example, included in the ophiolitic complexes. However, in the literature there are single descriptions of metasomatite findings of ophiolitic complexes with a high content of calcium-containing varieties. So, in the peridotites and dunites of the Jurassic ophiolitic complex of the Central Pontide (Turkey), being subjected to serpentinization to various degree [6], the proportion of calcium-containing olivines (11 out of 72 tests) is ~15%.

There are cases describing findings of natural calcium-containing olivines, as a rule, contact metasomatites (skarns, hornstones). Examples include the following data: skarns – contact zones of intrusions of the South-Californian batholite (USA) with dolomites where olivines are represented by low-calcium forsterite and monticellite [1]; contact zone of Alta

Stock (Utah, USA) with dolomites – forsterites contain 0.04–0.11 wt% CaO [13]; contact zone of magmatic chamber melt with carbonates, volcanic area of the Colli Albani (Italy) – forsterite in endoskarns contains 0.44–1.01 wt% CaO, forsterite of exoskarns contains 0.09–0.31 wt% CaO [15]. An example showing the presence of calcium-containing olivines in hornstones is the data of [7] where fayalite in hornstones from the contact area of the Khibiny alkaline massif with metavolcanics contains 0.12–0.42 wt% CaO. It is interesting that in the examples given, contact metasomatites, olivine group members are represented by extreme members of this group, i.e. fayalite and forsterite. Although there are experimental data indicating the possible formation of calcium-containing olivine in the solidus area. Thus, the paper [16] presents the experimental results of study of the system peridotite + water in solidus area (under pressure 2.5 and 6.5 GPa and temperature of 680–800°C). The paper presents 14 analyses, only 4 of them are represented by low-calcium varieties that, in the light of generalizations obtained, finds no explanation.

The data collected suggest that the calcium content in volcanic olivines and coherent to it intrusive varieties (peripheral volcanic focus, etc.) will be different. The most practical contributing factors to calcium mobility in olivine crystals appear to be fluid and temperature to ensure these differences already at the stage of autometasomatism. Partly autometasomatism may explain wide development of low-calcium olivine varieties in the Tertiary stratified massif of Rum isle [41]. In gabbroids of the modern oceanic crust, both at the stage of autometasomatism during solidification of the melt and in the process of further metasomatic transformations, these processes affect almost all crystals of olivine. This can be related to large amounts of water fluid (various forms of the sea water) involved in the process. The existence of homoeogene inclusions with calcium-containing olivine suggests that the phenomenon is not widespread. It can be assumed that, similar to calcium, during autometasomatism, other chemical elements (for example rare and scattered ones) and in other crystalline phases become mobile. One can concede that due to autometasomatism, some petrochemically effusive and intrusive varieties of co-magmatic rocks in some formations will vary. That is probably what indicates the differences between these types of rocks in the classification of the TAS diagrams. Although the scale (both spatial and quantitative) of this phenomenon is unclear. In contact-metasomatic processes, the behavior of calcium in olivine crystals needs to be studied.

In kamafugite volcanics and carbonatites, alkali content often does not exceed ~10 wt% and olivine crystals are mostly represented by calcium-containing varieties. The presence of high-magnesium low-calcium olivines, based on the example of venancite lava of Italy, can be explained by the oxidation of primary less magnesia varieties [39]. In the paper [41] it is shown that these phases occur due to secondary transformations of primary olivine. In the heated melt inclusions from kamafugite volcanics and carbonatites,

$\Sigma$  alkali can achieve 20 wt% or more that should reduce the formation of primary calcium-containing olivines. Such discrepancy in the content of alkali in the primary melts of these rocks and the content of calcium in olivines requires detailed experimental study of mutual influence of silica, calcium and alkali in the melt, in particular, and independently, influence of potassium and sodium on calcium content in olivine crystals. So, calcite carbonatites of Kerimasi volcano, despite the content of alkali  $\Sigma$  up to 36 wt% with sodium predominance, olivine is represented by calcium-containing variety. Thus probably indicating the differences of the impact of sodium and potassium, that present in the melt, on calcium admittance from the melt into the olivine lattice and, perhaps, on some features of its structural position in the melt.

The most significant is the discrepancy between the conclusion based on experimental data on the growth of calcium-containing crystals of olivine from magmatic melts of mafic and ultramafic rocks, regardless of the pressure, and structure of olivine crystals from kimberlites and ones contained in diamonds of this rock. Almost all crystals, except for peripheral rim of olivine phenocrysts and microlithic phase, often calcium-zoning, are low-calcium irrespective of age and rock alteration. Identified restrictions on compositions of the melts (calcium, silica, alkali sum) that may give rise to low-calcium varieties of olivine crystals, do not apply to natural kimberlite melts according to the reconstructed structures of primary kimberlite melts listed in the paper [55]. In the studies on diamond crystallization [36], the seeded growth of diamond takes place in equilibrium kimberlite melt (probably, local equilibrium experiments) with olivine, which in 9 out of 14 presented analyses, is represented by calcium-containing variety. The papers [54, 55] consider the conditions of kimberlite magma generation and its role in the growth and dissolution of diamond crystals, while the paper [27]), summarizing a wide range of data, suggests the mantle-carbonatite concept that presents melts/dissolutions as the basic diamond-forming medium. In the experiments involving melting phase and diamonds [3, 54] olivine crystals are presented both as calcium-containing and low-calcium varieties; wherein according to the paper [54] in 2 out of 6 crystals studied it is low-calcium variety that can be explained, based on our conclusions, by potassium content in the existing melt of ~10–11 wt% K<sub>2</sub>O and, consequently, it falls into exceptions. Generally, it can be concluded that experiments involving *paragenesis of melt-diamond-olivine*, the latter is mainly represented by calcium-containing variety whereas olivines of phenocrysts in kimberlites and ones contained in diamonds are represented by *low-calcium variety and some findings of calcium-containing varieties among them are singularities*.

As a result, inconsistencies in olivine crystal compositions in kimberlite and contained in diamonds in the same rock along with the experimental results suggest the following: compositions of natural olivine varieties of kimberlites *are non-equilibrium* with the melts, with the possible exception of calcium-containing rim, and the diamonds have been

formed in *solid phase medium*. The most probable growth medium for diamond crystals under these conditions is a *fluid phase* that is consistent with the model of fluid metasomatism of the mantle substance. Experiments show the reality of diamond crystallization in the fluid [35, 9] under mantle P-T conditions. In the experiments from the paper [4] under conditions corresponding to ones of the upper mantle, diamond crystals were formed in the mixture of silicate melt, water fluid and carbonates. Moreover, presented compositions of olivine crystals (4 tests) are represented by calcium-free forsterite through wide variations of glass compositions. Lack of calcium in the olivine crystals may be explained by the presence of aqueous fluid in the system. Experiments also proved the possible growth of diamond monocrystals under "soft" conditions that is atmospheric pressure and temperatures below 100°C with graphite solution in solvent consisting of acids mixture in water (inventor's certificate no. 1522789, Dunin-Barkovsky et al., 1989). Micron and smaller diamond crystals that usually present in kimberlites could be formed similarly from a fluid.

In diamond crystals along with solid-phase monomineral inclusions there are polyphase melt inclusions with calcium-containing olivine, probably, the medium that corresponds to kimberlite melts bringing diamond crystals to surface and forming calcium-containing olivine rim around olivine phenocrysts. It is not clear either this rim is of diffusive nature or it is a new phase growing on low-calcium nuclei. Time of rim formation is limited to several years or months, and, probably, regardless of the formation type, it is quite constant in spite of the geological age of kimberlites. Thus, it also indicates the non-melt genesis of these olivine and diamond crystals. The number of publications is growing devoted to study of fluid mantle inclusions different from the compositions of kimberlite melts, see review [41]; [43]. These data are also argument in favor of fluid growth medium for diamond. It is fluid phase, judging by the data on compositions including olivines that formed the vast majority of diamond crystals in kimberlites under study. Individual cases of calcium-containing olivines in diamonds are well-known [41] but these exceptions indicate that diamond growth from the melt is a rare occurrence.

The papers [41]; [43], based on fluid genesis of diamond under natural conditions, suggest possible use of solid phase inclusions in diamond crystals (olivine, garnet, pyroxene, spinel, perovskite, etc.) as substrates for artificial heteroepitaxial growth of monocrystal diamond films by using CVD-technologies. The possible existence of regular intergrowth of diamond on contained olivine crystals is presented in the paper [32]. However, there is another group of phases: contained in diamond crystals and rimmed diamond crystals [28]. The phases are developed almost everywhere on diamond crystals, its formation range is wide enough: from mantle (there are multiphase films buried inside the diamond crystals [28]) to ones formed on the surface on diamond crystals from the pores in lava of the Tolbachik Fissure Eruption named after 50 years' anniversary

of the Institute of Volcanology and Seismology FEB RAS (TFE-50) (Kamchatka, 2012–2013) [51]. Based on opinion of the authors [28], the growth and dissolution of diamond crystals occur through the metallic membranes (films) that surrounds diamond crystal. Setting this possible crystal growth mechanism aside, it could be stated that the existence of buried films in the diamond crystal body is an indisputable proof of the reality of heteroepitaxial rise and growth of monocrystalline diamond at phases composing the films. These phases can be used as substrates for artificial growing of monocrystal diamond films using CVD or other technologies. Various metallic films are of interest during the first stage of study. Many phases in these films have face-centered cubic lattice with lattice constant close to diamond lattice of ~0.357 nm. Consistency of lattice parameters for diamond heteroepitaxial growth has significant impact on the perfection of a growing crystal due to small mechanical stress in the transition zone. Phases, composing the film, are represented by pure metals, its alloys and intermetallides. Classification of data on films (50 species) is presented in the paper [28]. Data on films on diamonds from lava of TFE-50 fall within this classification, but a set of elements and phases is greater, and with the studies, the number of mineral species that make up the film and new growing mineral phases, is expanding. The film composition, according to [28] consists mainly of the following elements: Au, Pd, Cu, Zn, Sn, Fe, Ni, Cr, W, as monoelement phases and forming bronze, brass, etc. Under experimental conditions [35] neogenic diamond crystals of 30–80 μm were found to be grown on platinum (in the cold part of the platinum ampulla). Platinum has a lattice spacing (cubic crystal system) of ~0.392 nm. But there are still some elements with high melting temperatures (over 1600 °K): zirconium (cubic crystal system, lattice spacing ~0.361 nm), dysprosium and erbium (hexagonal lattice spacing ~0.356 nm), which lattice parameters practically coincide with the lattice spacing of a diamond (0.357 nm). Study of the films of all the elements and various element compounds indicated as substrates for heteroepitaxial growth, using diamond seeds on its surface, will finally make possible production of cheap monocrystalline diamond films. By adding to it semiconducting properties, it will, in some cases, substitute such materials as Si, Ge, GaAs, GaN and form the basis for a new generation of field transistors, radiation detectors, quantum computers, etc. Such monocrystalline diamond films can be used to create 2D and 3D photonic crystals that are in great demand for optical processors.

Olivine crystals of ultramafic xenoliths carried out by alkaline basalts and kimberlites are represented, with few exceptions, by low-calcium varieties. A small number of exceptions available, where olivine is represented by calcium-containing variety, is quite satisfactory, and it can be treated as cumulates of magmatic systems. By supposing the mantle nature of xenoliths and considering the experimental data, where olivine is a main phase in the mantle, it is fair to say, that in the upper mantle down to the depths of 200–300 km, olivine is represented by low-calcium variety. Based on

the conclusion that olivine crystals, equilibrium with the melt of mafic and ultramafic composition, are represented, regardless of the pressure, by calcium-containing variety, it could be argued that the melting in the mantle within a wide range of pressure should be *non-equilibrium*. Calcium-containing olivine crystals from the melt stringers in xenoliths are the best proof here. In addition, it allows to state that coefficient  $K_d$  ol/m for Fe/Mg ratio is not an only criterion of equilibrium. *Equivalent and another important criterion is the boundary calcium content in olivine* and both of these criteria *should be used together*.

The role of water in removal of calcium from olivine lattice is an interesting issue. Based on the data collected on compositions of olivine from lava and intrusive bodies of oceanic crust, rock massif of Fuerteventura island, being stratified intrusive complexes, one can believe that for the removal of calcium from olivine the fluid, its ratio (water/rock) and temperature play a major role. Process of the removal begins during melt cooling, capturing solidus stage. Calcium removal from olivine crystals is the beginning of metasomatic transformations of the rocks. And it may be equivalent, based on the structural features of olivine, calcium is usually not included in the newly formed lattice of metasomatic olivines although there are exceptions. These processes are under control, probably due to structural position of calcium in the olivine lattice as well. This particular calcium mobility in olivine crystals and its relation to fluid is an urgent issue. It is also possible that the calcium and water content in olivine under mantle conditions are interrelated.

Using xenolith in lava of Ol Doinyo Lengai carbonatite volcano as an example, containing  $\Sigma$  alkali in the melt inclusions of 15–19 wt%, it may be assumed that in cases both of the effusive and intrusive varieties of the rocks, there is a mismatch with experimental data between the alkali content in the melt and calcium content in olivine, thus require further study. In particular, it is necessary to identify the reasons of differential impact of sodium and potassium on calcium's ability to enter the olivine lattice.

Concept on genesis of olivines of ultramafic mantle xenoliths that are predominantly represented by low-calcium varieties is presented by a wide range of opinions. Even if we assume that it is restitic genesis, then originally it should have been calcium-containing varieties but prolonged exposure in subsolidus area (in the presence of fluid?) should have resulted in the loss of calcium.

## 4. Conclusions

Classification of experimental data has provided for identifying the factors affecting the content of CaO in the olivine crystals generated from magmatic melts and formed in the solidus area involving fluid.

At this stage of the studies these are CaO, K<sub>2</sub>O, SiO<sub>2</sub> (?), H<sub>2</sub>O in the melt. During metasomatic processes water and temperature contributes to increase of low-calcium olivines and possible removal of calcium from olivine crystals.

Presence of a number of exceptions points to no more individual factors revealed.

In the majority of ultramafic and mafic rocks, subjected to metasomatic changes, olivine is represented by low-calcium varieties. It is clearly seen using the examples of modern oceanic crust and ophiolite complexes. Calcium-containing crystals of olivine can be formed in contact-metasomatic rocks thus contradicting the scheme assumed. But this phenomenon and its scope require further study.

In order to identify equilibrium of compositions within magmatic melt-olivine system, two criteria should be used – coefficient  $K_d$  ol/m for Fe/Mg ratio and CaO content in olivine.

Using these conclusions in relation to olivines of mafic and ultramafic rocks, in certain cases, it made clear its genesis. In particular, the non-equilibrium of the main phase of the mantle substance (olivine) has been revealed including diamond depth facies with the melts of mafic and ultramafic compositions, thus suggesting that kimberlite diamonds predominantly have metasomatic nature.

A number of substances has been specified that can be a basis for heteroepitaxial growth of monocrystal diamond films using CVD technologies, aqueous solutions and other technologies thus making the product cost-efficient.

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