

Mineral equilibria at high PT-parameters

Kuzyura A.V., Litivn Yu.A. Rare elements of diamond-forming melt chambers formed in the mantle peridotite (as estimated with the use of experimental KDRE mineral-melt at 7.0-8.5 GPa)

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Abstract. Content of rare elements within diamond-forming carbonatite melt chambers were counted based on real concentration of rare elements in minerals of peridotite and eclogite parageneses in inclusions in diamonds and diamondiferous xenoliths as well as on experimental K_D^{RE} mineral-melt. Probably, the main contribution of RE in the parental melts is made by the mantle components. High Sr concentration can be concerned with the influence of "the metasomatic agent". The diamond-and-inclusions parental melts are depleted by the medium (Sm, Eu, Gd) and heavy RE (Tb, Dy, Ho, Er, Yb, Lu, Hf) and enriched in light (Sc, Rb, Sr, Ba, La, Ce, Pr, Nd) RE and Nb, in contrast to the primitive mantle peridotite.

Key words: primitive mantle, carbonate-silicate diamond-forming melts, rare elements participation, metasomatic agent.

Citation: Kuzyura A.V., Yu.A Litivn (2013). Rare elements of diamond-forming melt chambers formed in the mantle peridotite (as estimated with the use of experimental K_D^{RE} mineral-melt at 7.0-8.5 GPa).

A formation of growth media for the bulk of natural diamonds and minerals included in them syngenetically is a part of a common process of magmatic evolution of the mantle substance and integrated to it by physico-chemical way and spatially. It is obvious, that hermetic inclusions in natural diamonds are sampled fragments of heterogeneous

diamondiferous media, but not minerals of the host mantle. It means that parental media for diamonds and inclusions, based on completely miscible carbonate-silicate melts are independent magmatic bodies within the host mantle rocks. Supposedly, the upper mantle substance produces carbonate-silicate diamond-forming melts as affected "metasomatic agent" [Dalton, Presnall, 1998]. That is, chambers of silicate-carbonatite diamond-forming media were formed within the host garnet-lherztholite mantle as a result of its primary carbonatization [Litvin, 2011, 2012]. According to existing conceptions, carbonate melts play an important role in processes of the mantle metasomatism [Green, Wallace, 1988, Yaxley et al., 1998]. A significant goal is an estimation of a geochemical background of diamond forming melts in the Earth mantle. Identification of rare elements (RE) involving into the diamond-and-inclusions parental medium together with the mantle components, on the one hand, and the "metasomatic agent", on the other, is of interest.

Due to a development of a mantle-carbonatite theory of diamond genesis [Litvin, 2011] a new approach to determination of RE concentrations in diamond forming media has appeared. It is based on a combination of results of experimental researches on rare elements participation between minerals and melts of diamond forming systems and data of analytical mineralogy of syngenetic inclusions in diamonds and deep xenoliths of a number of diamondiferous kimberlite pipes.

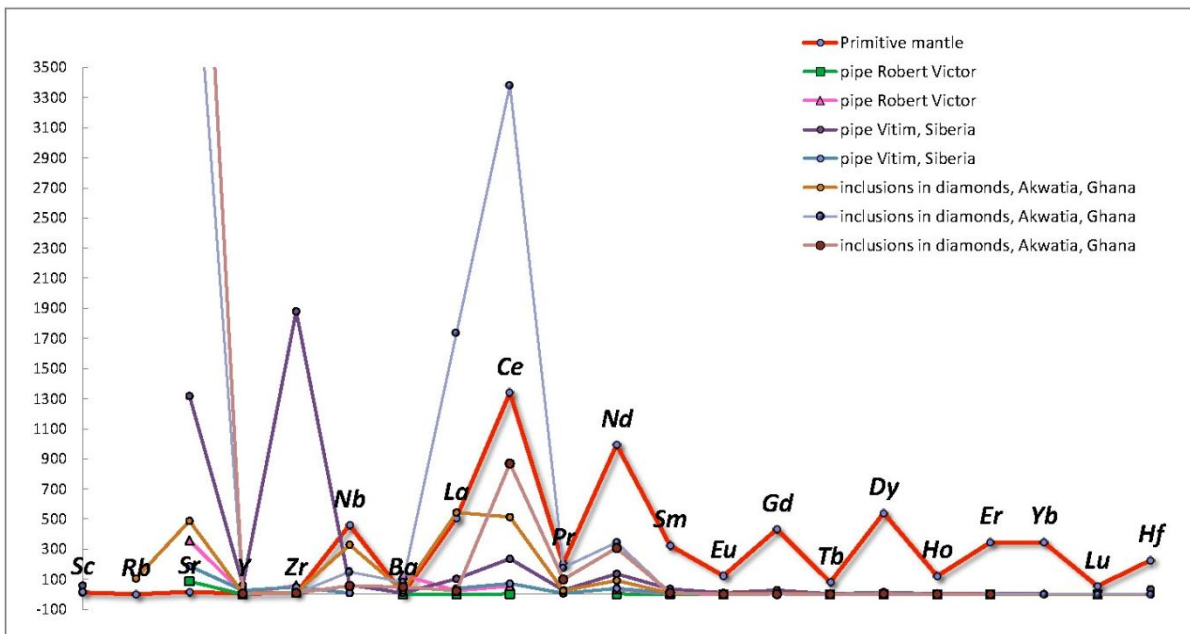


Fig.1. Model concentrations of RE in melts of parental media of xenoliths from kimberlite pipes, inclusions in diamonds for comparison to the primitive mantle [Lubetskaya, Korenaga, 2007]

RE included in a parental media for natural diamonds and primary inclusions together with the mantle component, on the one hand, and with "metasomatic agent" with another, can be identified from the RE geochemistry of mineral phases involved into the diamond-forming process. This became possible with the use of new experimental data on determination of the

interphase partition coefficients (K_D^{RE}) of 21 representative rare elements in partially melted peridotite-eclogite-carbonatite diamond-forming system at 7.0 - 8.5 GPa [Kuzyura, 2011, 2012]. The authors obtained experimentally partitioning coefficients for a number of RE (Rb, Cs, Ba, Th, U, Ta, Nb, La, Ce, Pb, Pr, Sr, Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu и Sc). It

was revealed that rare elements in peridotite-carbonatite and eclogite-carbonatite diamond forming mantle systems are characterized with similar partitioning coefficients K_D^{RE} mineral-melt. These values are also closely comparable with those for the silicate and carbonatite melts in equilibrium with mantle silicate minerals [Litvin, 2011].

The contents of RE in the minerals of peridotite and eclogite parageneses included into diamonds as well as of diamond-bearing xenoliths of several kimberlite pipes were reported in [Harte & Kirkley, 1997; Ionov, 2004; Stachel & Harris, 1997]. Based on the mineralogical data and experimentally determined K_D^{RE} mineral-melt, the plausible concentrations of the RE in natural diamond-forming carbonatite melts of the mantle chambers were calculated and presented as a spidergram in Fig. 1.

So, the model RE contents in parental diamond forming carbonate-silicate melts, from which diamonds and primary silicate inclusions in them of Akwatia pipe, Ghana, as well as deep diamondiferous xenoliths of Robert Victor and Vitim pipes. It was found that the main contribution of RE in the parental melts is made by the mantle components. The diamond-and-inclusions parental melts are depleted by the medium (Sm, Eu, Gd) and heavy RE (Tb, Dy, Ho, Er, Yb, Lu, Hf), that in contrast to the primitive peridotite case. Meanwhile, they are enriched in light (Sc, Rb, Sr, Ba, La, Ce, Pr, Nd) RE and Nb, but their content by 1-2 orders of magnitude is lower than for the primitive mantle peridotite. Most likely, the main contribution is made by the mantle components. High Sr content in the calculated parental melts makes a conspicuous. This effect can be related to a participation of a "metasomatic agent".

Support: Grants of the President ## MK-1386.2013.5, the Ministry of education and science of RF (agreements 8317, 8378) и RFBR 11-05-00401, 12-05-33044, 13-05-00835

References:

1. Harte B. & M. B. Kirkley (1997). Partitioning of trace elements between clinopyroxene and garnet: data from mantle eclogites. *Chemical Geology*, 136, 1–24.
2. Ionov D. (2004). Chemical Variations in Peridotite Xenoliths from Vitim, Siberia: Inferences for REE and Hf Behaviour in the Garnet-Facies Upper Mantle. *Journal of Petrology*, V. 45(2), pp. 343–367.
3. Kuzyura A.V., F. Wall, T. Jeffries and Yu. A. Litvin (2010). Trace elements partitioning between garnet, clinopyroxene, and diamond-forming carbonate-silicate melt at 7 GPa. *Mineralogical Magazine*, V. 74(2), p. 227–239.
4. Kuzyura A.V., Yu. A. Litvin, T. Jeffries, P. G. Vasiliev, and F Wall (2012). Experimental evidence on partitioning of trace elements in diamond-forming carbonatite, eclogite-carbonatite and peridotite-carbonatite systems at 7–8.5 GPa. *Abstracts of 1 EMC*.
5. Litvin Yu.A. (2011). Mantle origin of diamond-parent carbonatite megma: experimental approaches. *Geophysical Research Abstracts*, Vol. 13, EGU2011-3627, EGU General Assembly 2011, Vienna, Austria, 2–7 April 2011, CD.
6. Lubetskaya T., J. Korenaga (2007). Chemical composition of Earth's primitive mantle and its

variance: Implications for global geodynamics, *J. Geophys. Res.*, 112, Art. No. B03212.

7. Stachel T. & J. Harris (1997). Diamond precipitation and mantle metasomatism – evidence from the trace element chemistry of silicate inclusions in diamonds from Akwatia, Ghana. *Contributions to Mineralogy and Petrology*, V. 129, № 2-3, pp 143–154.

Sirotkina ¹E.A., Bobrov ¹A.V., Bindi ²L., Irifune ³T. Experimental study of the system $Mg_4Si_4O_{12}$ – $Mg_3Cr_2Si_3O_{12}$ at 12–25 GPa and 1600°C

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Abstract: The first results of experimental study of phase relations in the system MgO – SiO_2 – Cr_2O_3 at 12–25 GPa are summarized. Garnets were obtained at a pressure range from 12 to 20 GPa. In the whole pressure range they coexist with eskolaite (at high-Cr starting compositions) and at 20 GPa with Cr-bearing $MgSiO_3$ perovskite. Three crystals of majorite–knorringite garnets of fair diffraction quality demonstrating a wide compositional range were selected for the structural study. All garnets have cubic symmetry with a space group $Ia\bar{3}d$. We observed gradual decrease of the unit cell parameters with increase of majoritic component in garnet.

Key words: experiment at high temperatures and pressures, knorringite, majorite.

Citation: Sirotkina, E. A., A. V. Bobrov, (2013), Experimental study of the system MgO – SiO_2 – Cr_2O_3 at 12–25 GPa and 1200–1800°C.

Numerous results of investigations of crystalline inclusions in diamonds provide evidence for the formation of most of them within the pressure range of 4–7 GPa, which corresponds to depths of 150–250 km [Taylor, Anand, 2004 and others].

Garnets are widely abundant as inclusions in diamonds and those of the ultrabasic paragenesis are characterized by significant chromium admixture in the composition of knorringite ($Mg_3Cr_2Si_3O_{12}$, *Knr*) end-member [Sobolev, 1974]. It was established that incorporation of knorringite in garnet occurred from 3 GPa (beyond the diamond depth facies), and the concentration of chromium reached significant values (5–10 wt % Cr_2O_3 and more) in the pressure range of stability of most of natural diamonds (4–7 GPa) [Malinovskii et al., 1975], which is an indicative feature of diamondiferous dunite–harzburgite paragenesis of the lithospheric mantle [Sobolev, 1974].

Incorporation of majoritic component is another important peculiarity of mantle garnets. The concentration of aluminum and chromium in garnets decreases with pressure [Akaogi, Akimoto, 1977; Irifune, 1987], whereas the content of silicon in the octahedral site, as well as the concentration of divalent cations (Ca, Mg, Fe) and sodium regularly increases [Ono, Yasuda, 1996], which results in the formation of garnet with the silicon content of >3 p.f.u. This is controlled by the beginning of dissolution of pyroxene (mainly $(Mg,Fe)SiO_3$) components in garnet already from 5 GPa [Akaogi, Akimoto, 1979]. The solubility of pyroxene in garnet increases with pressure reaching significant values at 10–15 GPa, which

corresponds to the lowermost upper mantle and transition zone.

The relationship of majorite and knorringite with pressure providing evidence for similarity in their behavior, but, at the same time, for possible concurring reaction on pressure increase arose our interest to the experimental investigation of the knorringite–majorite (in chemical expression, $MgO-SiO_2-Cr_2O_3$) system in a wide range of *PT*-parameters. Here we report the first results of performed experiments.

High-pressure and high-temperature phase relations in the system $Mg_3Cr_2Si_3O_{12}-Mg_4Si_4O_{12}$ have been studied at pressures from 12 GPa to 25 GPa and temperature of 1600°C using 10/4 and 8/2.5 cell assembly on a 2000-ton split-sphere multi-anvil press at the Geodynamics Research Center, Ehime University. Tungsten carbide cubic anvils with 4.0 and 2.5 mm truncation edge length (TEL= 4.0 mm, 2.5 mm) were used as the second-stage anvils of the high-pressure apparatus. The pressure medium was a semi-sintered (Mg,Co)O octahedron of 10

and 8 mm in edge length, in which a cylindrical LaCrO₃ heater was inserted. The temperature was measured using a $W_{97}Re_3-W_{75}Re_{25}$ thermocouple with an accuracy of ± 10 °C.

We investigated the full range of starting compositions with steps of 10–20 mol% and 2–3 GPa in multi-anvil experiments, which allowed us to plot the preliminary phase diagram for the system $MgSiO_3-Mg_3Cr_2Si_3O_{12}$ and synthesize garnets of a wide compositional range.

The relative position of phases obtained in experiments is shown in Fig. 1. Among these phases are knorringitic garnet $Mg_3Cr_2Si_3O_{12}$ (*Knr*), majorite $MgSiO_3$ (*Maj*), perovskite $MgSiO_3$ (*Pv*), and eskolaite Cr_2O_3 (*Esk*). It is important that the maximal chromium contents in these phases are different. The ranges of chromium oxide are shown on the diagram as well.

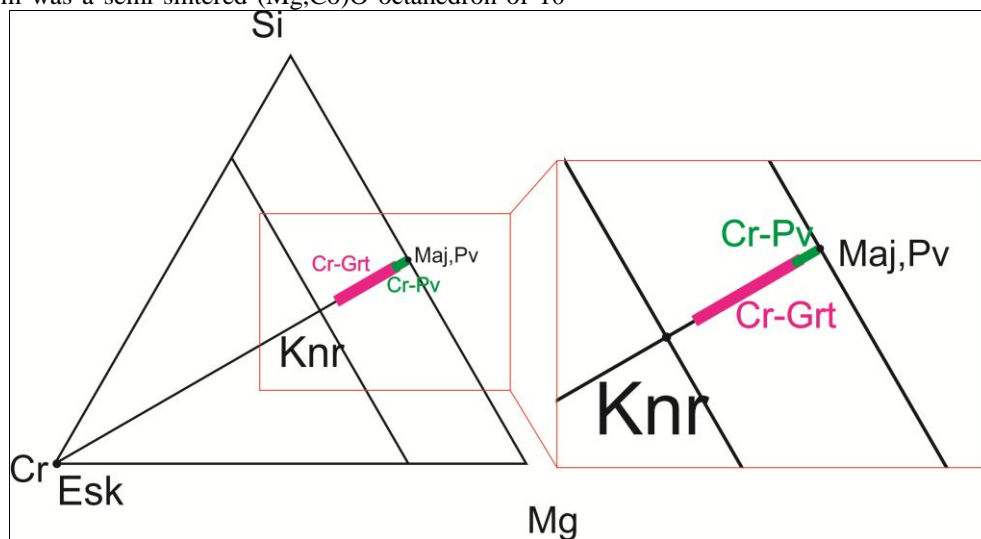


Fig.1. The relative position of phases obtained in experiments

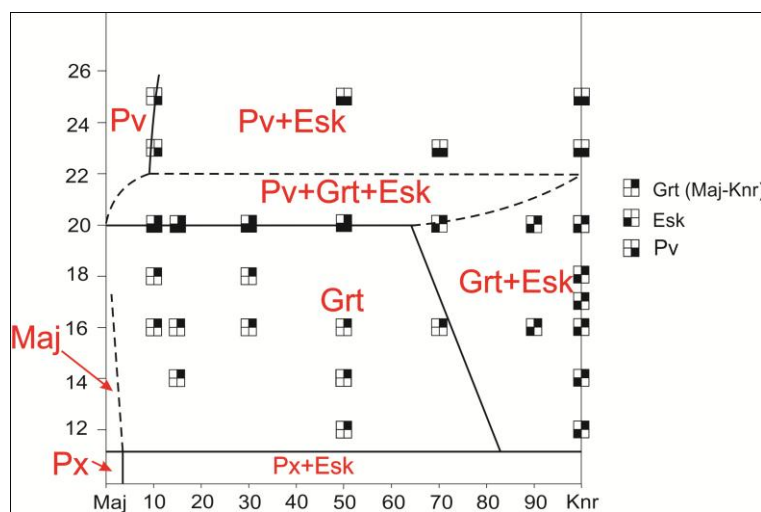


Fig. 2. Schematic P–X phase diagram of the majorite–knorringite system at 1600°C.

The preliminary phase *P–X* diagram of the majorite–knorringite system at 1600°C is demonstrated in Fig. 2. The phase assemblages for majorite-rich starting materials (<30 mol % knorringite) include garnet. With the increase

of knorringite content in the starting composition, garnet + eskolaite association is formed. Typically synthetic garnets contain significant portion of majorite (>15 mol %) even for pure $Mg_3Cr_2Si_3O_{12}$ starting composition. Garnets were

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obtained at a pressure range from 12 to 20 GPa. In the whole pressure range they coexist with eskolaite (at high-Cr starting compositions) and at 20 GPa Cr-bearing MgSiO_3 perovskite.

Garnets are characterized by wide compositional variations depending on the starting composition (Fig. 3A). The composition of garnets changes from almost pure majorite to ~85 mol % knorringite component. It is

important to note that pure knorringite cannot be produced even from $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ starting material. Garnets synthesized from the same starting materials become progressively depleted in Cr (knorringite component) and enriched in Si (majorite component) with pressure (Fig. 3B).

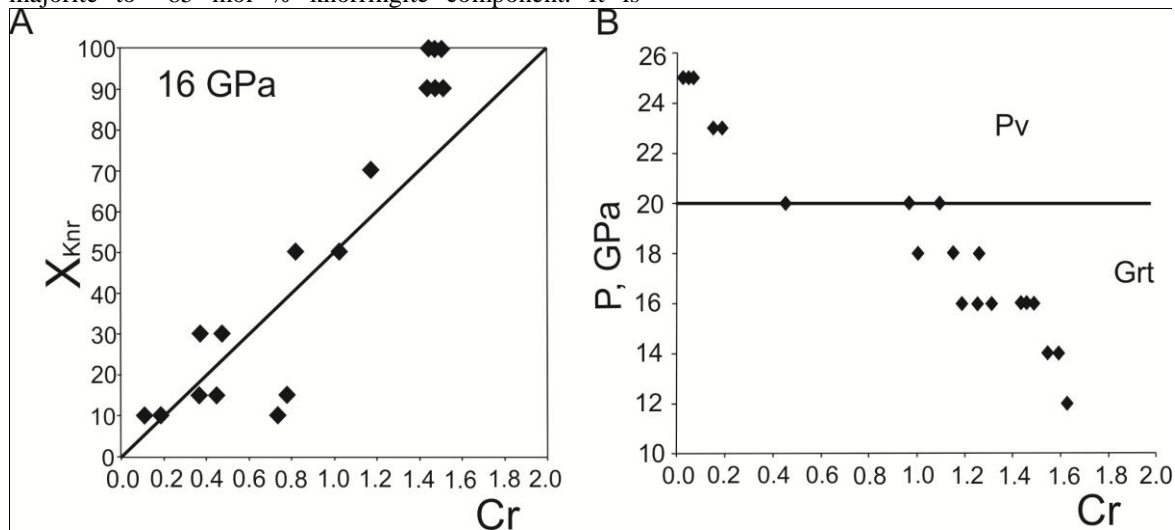


Fig. 3. A- Dependence of the composition of garnet (Cr content, pfu) on the concentration of knorringite component (mol %) in the starting material at 16 GPa

B- Dependence of Cr contents in the phases (Grt, Pv) on pressure for the starting composition of pure knorringite ($\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$).

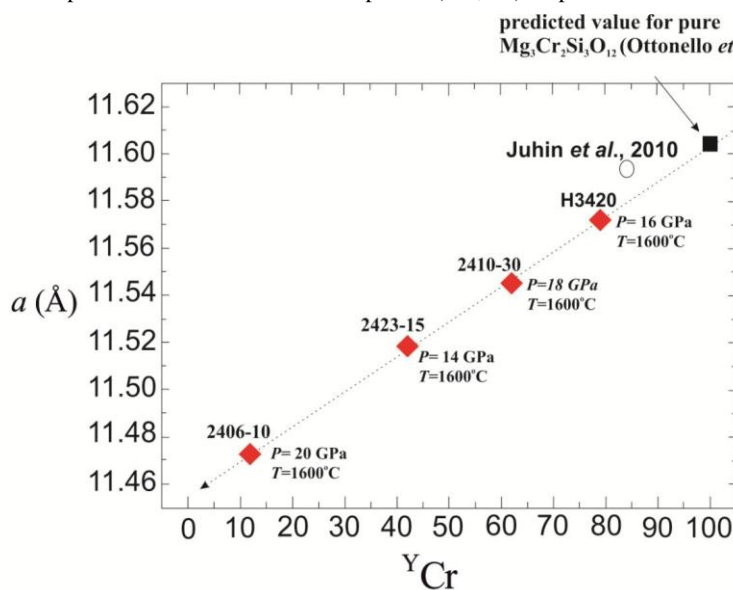


Fig. 4. Variations of unit cell parameters as a function of composition for a series of phases along the knorringite ($\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$)-Majorite ($\text{Mg}_4\text{Si}_4\text{O}_{17}$) garnet join.

Three crystals of majorite–knorringite garnets of fair diffraction quality demonstrating a wide compositional range were selected for the structural study. They were mounted on an Bruker-P4 single-crystal diffractometer and examined with graphite-monochromatized Mo- $\text{K}\alpha$ X-radiation. All garnets have cubic symmetry. The results are shown in Fig. 4. Our three garnets perfectly plot on a linear trend together with the previously synthesized Cr-rich garnet (H3420) and predicted value for pure knorringite [Ottonello et al., 1996]. Note that the X-ray powder diffraction data for Cr-rich garnet [Juhin et al., 2010] differs from our trend.

References:

1. Malinovskii, I.Yu., A.M. Doroshev, E.N.Ran (1975). The stability of chromium-bearing garnets pyrope - knorringite series, *Experimental studies on the mineralogy (1974-1976)*, Institute of Geology and Geophysics of the Siberian Branch of AS USSR, Novosibirsk, 110-115.
2. Sobolev, N.V., (1974). Deep-seated inclusions in kimberlites and the problem of upper mantle composition, *Novosibirsk. Nauka*. 264 p. (in Russian)
3. Akaogi, M., A. Akimoto (1979). High pressure phase equilibria in a garnet lherzolite, with special reference to Mg^{2+} - Fe^{2+} partitioning among constituent minerals. *Phys. Earth. Planet. Inter.*, V. 19. P. 31-51.

4. Akaogi, M., A. Akimoto, (1977). Pyroxene-garnet solid-solution equilibria in the system $Mg_4Si_4O_{12}$ - $Mg_3Al_2Si_2O_{12}$ and $Fe_4Si_4O_{12}$ - $Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures, *Phys. Earth. Planet. Inter.*, V. 111. P. 90-106.
5. Irifune, T., (1987). An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle. *Physics of the Earth and Planetary Interiors*, V. 45. P. 324-336.
6. Juhin, A., G. Morin, E. Elkaim, D.J. Frost, M. Fialin, F. Juillot, G. Calas, (2010). Structure refinement of a synthetic khorringite, $Mg_3(Cr_{0.8}Mg_{0.1}Si_{0.1})_2(SiO_4)_3$. *American Mineralogist*, V. 95. P. 59-63.
7. Klemme, S., (2004). The influence of Cr on the garnet-spinel transition in the Earth's mantle: experiments in the system MgO - Cr_2O_3 - SiO_2 and thermodynamic modeling. *Lithos*. 77, 639- 646.
8. Ono, S., A. Yasuda (1996). Compositional change of majoritic garnet in a MORB composition from 7 to 17GPa and 1400 to 1600 °C. *Physics of the Earth and Planetary Interiors*, V. 96. P. 171- 179.
9. Ottonello, G., M. Bokreta, P.F. Sciuto, (1996) Parameterization of energy and interactions in garnets: End-member properties. *American Mineralogist*. 81.
10. Stachel, T., (2001). Diamonds from the asthenosphere and the transition zone. *Eur. J. Mineral.* V. 13. P. 883-892.
11. Taylor, L.A., M. Anand, (2004). Diamonds: time capsules from the Siberian Mantle. *Chemie der Erde*, V. 64. P. 1-74.

Spivak¹A.V., Solopova¹N.A.², Dubrovinsky²L.S., Litvin¹Yu.A. Experimental study of the behavior of carbonates at conditions of the lower mantle: application to superdeep diamonds origin

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Abstract. PT-condition of melting of $CaCO_3$, $MgCO_3$ and Na_2CO_3 , phase fields for the carbonates stable melts and high temperature boundaries of the melts decomposition were studied at 11-46 GPa and up to 4000 K using diamond anvil cell with laser heating. Experimental studies demonstrate that melts of simple Ca-, Mg- and Na-carbonates which are known as primary inclusions on superdeep diamonds are stable at PT – conditions of the transition zone and lower mantle. This allows to consider them as the main components of multicomponent growth medium of sublithospheric diamonds.

Key words: Lower mantle, origin of super-deep diamonds, parental media, physico-chemical experiment, syngeneses of diamonds and mineral inclusions, diamond anvil cell, laser heating

Citation: A.V. Spivak, N.A. Solopova, L.S. Dubrovinsky, Yu.A. Litvin Experimental study of the behavior of carbonates at conditions of the lower mantle: application to superdeep diamonds origin

Mineralogical data of primary inclusions in super-deep diamonds [Kaminsky, 2011, 2012] demonstrate that processes of natural diamond formation are not limited by the upper mantle but also take place in the Earth's transition zone (TZ) and lower mantle (LM). In this connection, studying of chemical and phases composition

of parental media for sublithospheric diamonds and inclusions are started using physico-chemical experiment at high pressure [Spivak et.al., 2011, 2012]. Syngenetic inclusions in diamonds present fragments of parental media and evidenced of their heterogeneity, chemical and paragenetic variability [Kaminsky, 2011, 2012]. Primary carbonate inclusions in superdeep diamonds [Brenker et al., 2007, Kaminsky, 2012, Kaminsky et al., 2009, Wirth et al., 2009] may be the key components of carbonate-silicate and carbonate-oxide-silicate melts with dissolved carbon under the TZ and LM conditions, similarly to the case of the upper mantle [Litvin et al., 2012, Litvin, 2007].

The main goal of this work is experimental study of phase relations of $CaCO_3$, $MgCO_3$ and Na_2CO_3 at static pressure up to 46 GPa and temperature up to 4000 K using diamond anvil cell with laser heating (details see [Spivak et al., 2012]).

Experimental studies of phase relations of the carbonates, their melting and conditions of the melts decomposition with formation of oxides, CO_2 , and solid carbon (diamond and graphite) were carried out at 8.5-46.0 GPa and up to 3900 K. Results of the experiments were used to determine the phase boundaries of congruent melting and melt decomposition by reaction $X^{13}CO_3 = XO + ^{13}CO_2$, where X = Ca, Mg, Na. Conditions of diamond and graphite formation by two-stage reaction: (1) $X^{13}CO_3 = XO + ^{13}CO_2$, where X=Ca, Mg, Na; (2) $^{13}CO_2 = ^{13}C + O_2$, were also studied.

It was found that melting of calcium carbonate $Ca^{13}CO_3$ is congruent at 11-43 GPa above 2000 – 2600 K. Experimental data show that field of congruent melting is wide and within 20-43 GPa from 2100-2600 K to 3300-3400 K. Experimental results permits to specify a preliminary phase diagram of $CaCO_3$ reported by [Ivanov et al., 2002]. It was confirmed the existence of high temperature boundary of melting field of $CaCO_3$. $CaCO_3$ melts decompose to CaO и CO_2 on this boundary. At the same time, highly compressed fluid CO_2 also decomposes with formation of diamond or/and graphite at 11-43 GPa and temperature above 3300-3400 K. Raman-spectra of experimental samples heated above 3400 K contain diamond peak 1280 cm^{-1} , which is typical for diamond with carbon ^{13}C . Obviously, diamonds were formed by two-stage reaction when calcium carbonate decomposes to $CaO + ^{13}CO_2$, and then $^{13}CO_2$ decomposes to diamond ^{13}C and oxygen [Tschauner et al., 2001]. PT-conditions of described experiments are related with two-phase field $CaO + CO_2$ on phase diagram of calcium carbonate. This suggests that decomposition of $Ca^{13}CO_3$ occurs in melting state.

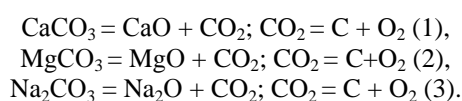
Experimental study of determination of stable melting field of Mg-carbonate was performed. It was found that in case of $MgCO_3$, similarly to $CaCO_3$, a wide field of congruent melting exists. At high temperature melt of Mg-carbonate decomposes to MgO and CO_2 (according to preliminary experimental data at 3300-3600 K and 20-30 GPa). Highly compressed fluid CO_2 decomposes with formation of solid carbon phase (diamond and/or graptite) and O_2 . Thermodynamic modeling of phase diagram of $MgCO_3$ [Fiquet et al., 2002] is in agreement with our experimental results.

Position of Na_2CO_3 congruent melting curve was determined using multianvil apparatus at high pressure of

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14 and 20 GPa and temperature 1200-1400 K by high-pressure quenching. Experimental study of stability of Na₂CO₃ melt were carried out at 14-46 GPa range and 2100-3000 K range using diamond anvil cell and laser heating. It was found that the phase field of Na-carbonate melt is limited by high temperature boundary of its decomposition to Na₂O and highly compressed CO₂ fluid. Indeed, graphite and diamond based on isotope ¹³C were found in experimental samples at 21-46 GPa and above 2100 K. Raman-spectra of the samples contain peak with maximum at 1294 cm⁻¹, which is typical for ¹³C-diamond. Similarly, Raman-spectra of the samples contain ¹³C-graphite peaks: wide G band with maximum 1546 - 1551 cm⁻¹ and D band with maximum 1305 - 1325 cm⁻¹. Experimental conditions are in agreement with PT-parameters of decomposition of CO₂ fluid by [Tschauer et al., 2001]. Similarly to the cases of CaCO₃ and MgCO₃, CO₂ decomposes to oxygen and elementary carbon with formation of diamond or/and graphite in dependence on thermodynamic and kinetic conditions of reaction.

Thus, PT conditions of CaCO₃, MgCO₃, and Na₂CO₃ melting, stability of the melts, and their decomposition were investigated at static pressures up to 46 GPa and temperatures up to 4000 K with the use of diamond anvil cell and laser heating. PT phase diagrams were plotted for CaCO₃, MgCO₃ and Na₂CO₃ systems. Evidence of congruent melting of Ca-, Mg-carbonates was obtained above 2000 K and at 11-43 GPa. Meanwhile, Na-carbonate melts congruently above 1200 K and up to 46 GPa. It was specified that the carbonate melts are stable within widely ranges of temperatures and pressures. High temperature boundaries of melting fields were determined with using of static high pressure and high temperatures experiments. It was found, that the high-temperature boundaries of Ca-, Mg-, and Na-carbonates decompose with formation of corresponding oxides and CO₂ (probably fluid). Then, CO₂ decomposes with formation of solid carbon – diamond or graphite, depending on the thermodynamic and kinetic conditions of nucleation. These processes may be explained by a two-stage decomposition reactions:



It was found that melts of CaCO₃ - C, MgCO₃ - C and Na₂CO₃ - C systems are effective diamond forming melt-solution media at low temperature side of melting fields at 18-25 GPa and 1700-2300 K.

These results are applicable to modeling the multicomponent compositions of carbonate-oxide-silicate parental media of superdeep diamonds and their primary mineral inclusions.

The study was supported by The Ministry of education and science of Russian Federation, projects 8317 and 16.740.11.0621 and RFBR grants 13-05-00835, 12-05-33044 и 11-05-00401.

References:

1. Brenker F.E., C. Vollmer, L. Vincze, B. Vekemans, A. Szymanski, K. Jansses, I. Szaloki, L. Nasdala, F. Kaminsky (2007). Carbonates from the lower part of

transition zone or even the lower mantle. *Earth and Planetary Science Letters*, 260, 1-2, 1-9.

2. Fiquet G., F. Guyot, M. Kunz, J. Matas, D. Andrault, M. Hanfland (2002). Structural refinements of magnesite at very high pressure. *American Mineralogist*, 2002, 87, 1261-1265.
3. Frost D.J., B.T. Poe, R.G. Tronnes, C. Libsike, F. Duba, D.C. (2004). Rubie A new large-volume multianvil system. *Physics of the Earth and Planetary Interiors*, 143, 507-514.
4. Ivanov A.B., A. Deutsch (2002). The phase diagram of CaCO₃ in relation to shock compression and decomposition. *Phys. Earth and Planet. Inter.*, 129, 131-143.
5. Kaminsky F. (2012). Mineralogy of the lower mantle: A review of 'super-deep' mineral inclusions in diamond. *Earth-Science Reviews*, 2012, 110, 127-147.
6. Kaminsky F., R. Wirth, S. Matsyuk, A. Schreiber, R. Thomas (2009). Nyerereite and nahcolite inclusions in diamond: Evidence for lower-mantle carbonatitic magmas. *Mineralogical Magazine*, 73, 5, 797-816.
7. Litvin Yu.A. (2007). High-pressure mineralogy of diamond genesis. In Ohtani E., ed., *Advances in High-Pressure Mineralogy*, *Geological Society of America Special Paper*, 421, 83-103.
8. Litvin Yu.A., P.G. Vasiliev, A.V. Bobrov, V.Yu. Okoemova, A.V. Kuzyura (2012). Parental media of natural diamonds and primary mineral inclusions in them: evidence from physicochemical experiment. *Geochemistry International*, 50, №9, 726-759.
9. Spivak A.V., Yu.A. Litvin, S.V. Ovsyannikov, N.A. Dubrovinskaya, L.S. Dubrovinsky (2012). Stability and breakdown of Ca¹³CO₃ melt associated with formation of ¹³C-diamond in static high pressure experiments up to 43 GPa and 3900 K. *Journal of Solid State Chemistry*, 191, 102-106.
10. Spivak A.V., L.S. Dubrovinskii, Yu.A. Litvin (2011). Congruent melting of calcium carbonate in a static experiment at 3500 K and 10-22 GPa: its role in the genesis of ultra-deep diamonds. *Doklady Earth Sciences*, 439, Part 2, 1171-1174.
11. Spivak A.V., Litvin Yu.A. (2004). Diamond syntheses in multicomponent carbonate-carbon melts of natural chemistry: elementary processes and properties. *Diamond and Related Materials*, 13, 482-487
12. Tschauer O., H.-K. Mao, R.J. Hemley (2001). New transformation of CO₂ at high pressures and temperatures. *Phys. Rev. Lett.*, 87, 7, 075701-1-4.
13. Wirth R., F.Kaminsky, S.Matsyuk, A. Schreiber (2009). Unusual micro- and nano-inclusions in diamonds from the Juina Area, Brasil. *Earth Planet. Sci. Lett.*, 286, 292-303.

Kogarko L.N. Experimental study of high-temperature differentiation of larnite-normative kimberlite melts. Clinopyroxene composition

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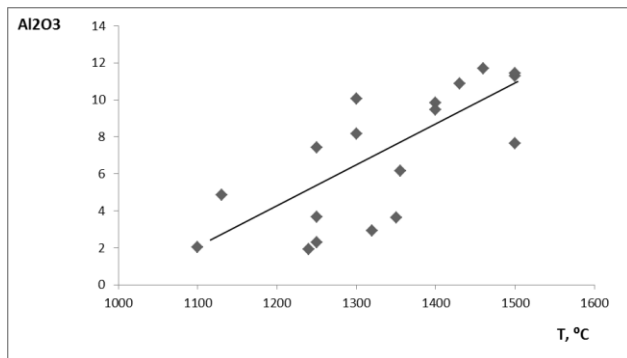
Abstract. Experiments were carried out on the investigation of phase equilibria in the course of crystallization kimberlitic larnite-normative high-calcium melt. In the course of crystallization the clinopyroxene composition was changed. With the increasing temperature the atomic contents of alumina and sodium were

increased while concentration of silica, magnesium and iron were decreased. Deep-seated high temperature differentiation of high-calcium melts would lead to the fast depletion of residual melt in alumina and generation of peralkaline magmas.

Key words: phase equilibria, kimberlitic melt, peralkaline magmas.

Citation: L.N. Kogarko, Experimental study of high-temperature differentiation of larnite-normative kimberlite melts. Clinopyroxene composition.

Experiments were carried out on the investigation of phase equilibria in the course of crystallization kimberlitic larnite-normative high-calcium melt. Main minerals during crystallization are olivine, clinopyroxene, melilite, spinel. Under higher pressure garnet became liquidus mineral. In the course of crystallization the clinopyroxene composition was changed. With the increasing temperature the atomic contents of alumina and sodium were increased while concentration of silica, magnesium and iron were decreased. Because of the atomic content of alumina in clinopyroxene increased much more actively than sodium with the temperature increase the differentiation under higher temperature lead to the appearance of agpaitic melts. Collectively, deep-seated high temperature differentiation of high-calcium melts would lead to the fast depletion of residual melt in alumina and generation of peralkaline magmas.



Reference:

1. Kogarko L.N., D. Green (1998). Phase equilibrium in the course of melting of melilite nephelinite up to 60 kb. *Dokl AN*, vol. 4, P. 522-525 (in Russian).

Kuryaeva R.G. Influence of magnesium on the compressibility of silicate glasses

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Abstract. The refractive index and the compressibility of $\text{Na}_2\text{MgSi}_4\text{O}_{10}$ and $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glasses in the pressure range to 6.0 GPa were determined using a diamond anvil cell and polarization-interference microscope within the framework of the theory of photoelasticity. For the studied glasses the degree of depolymerization was found to be $NBO/T = 0.28$ and 0.20 for $\text{Na}_2\text{MgSi}_4\text{O}_{10}$ and $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glasses, respectively. It is shown that the replacement of aluminum by magnesium in silicate glasses does not lead to a considerable decrease in compressibility, which suggests the predominant role of magnesium ions as network formers. The calculated values of the degree of depolymerization of studied glasses agree well with their compressibility.

Key words: magnesium-silicate glasses, high pressures, compressibility of glasses and melts, structure of glasses and melts.

Citation: Kuryaeva R.G. (2013). Influence of magnesium on the compressibility of silicate glasses, *Vestn. Otd. nauk Zemle*

Introduction. Glasses are models of magmatic liquids. Investigation of the properties of various compositions of glasses at high pressures is important for understanding the role of deep melts in magmatic and volcanic processes [e.g., Agee and Walker, 1988]. A change in the composition of silicate glasses and melts affects the properties that depend on the degree of polymerization, such as viscosity [e.g. Toplis et al., 1997] and compressibility [e.g., Webb and Courtial, 1996]. Recently, some papers have been published in which Mg^{2+} is suggested to play a particular part in the structure of silicate glasses and melts [e.g., Neuville et al., 2008]. Comparison of the properties of silicate glasses containing aluminum and the glasses in which Al is replaced by Mg show that the difference in the properties of Al- and Mg-bearing glasses is not so significant as should be expected from the replacement of network-forming ions by modifier ions. The properties and structure of some Mg-bearing glasses and melts have been studied with application of experimental and calculation techniques such as vibrational spectroscopy and X-ray methods, NMR spectroscopy and molecular dynamics (MD) simulations both in normal conditions and using temperature and pressure [Trcera et al., 2009; Cormier et al., 2010; Lin et al., 2007].

To have the right idea about the role of magnesium in complex silicate systems and about the degree of depolymerization of their structure, it is necessary to accumulate more experimental data on the compressibility of magnesium silicate glasses of various composition (i.e., with the different content of SiO_2 and oxides of alkali metals). In this paper we present results of measurements of refractive indices of $\text{Na}_2\text{MgSi}_4\text{O}_{10}$ and $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glasses in the pressure range to 6.0 GPa and comparison of their compressibility and the degree of depolymerization.

Experimental technique and results. $\text{Na}_2\text{MgSi}_4\text{O}_{10}$ and $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glasses were synthesized by melting the corresponding oxides and carbonates of special-purity grade at a temperature of 1650–1700 °C for 1 hour in a platinum crucible. Then, the glass was ground in a mortar made from a hard alloy, melted once more, and quenched in water. No annealing of the glass was carried out.

In the experiments polished glass plates 40–50 μm in length and width and 20–30 μm in thickness were used. The samples were polished with diamond pastes on a cardboard.

The refractive index at high hydrostatic pressures was measured by the technique described in detail in our previous works [Kuryaeva and Kirkinskii, 1994; 1997], with the use of the polarizing interference microscope MPI-5 and the apparatus with the diamond anvils. The measuring method of the refractive indices of sample n_x under pressure is based on the pressure-induced change in the optical path difference Φ caused by the sample under study. The optical path difference Φ and the refractive indices of sample n_x and the medium n , in our case a methanol-ethanol 4:1 alcohol mixture, are related by the expression $\Phi = (n_x - n)t$ (1). Expression (1) shows that a decrease in Φ results from the change in the ratio between the refractive indices of sample n_x and the medium n

Mineral equilibria at high PT-parameters

(under pressure, the refractive index of the liquid increases much more rapidly than the refractive index of the glass).

Changes in the relative densities of glass has been calculated from the experimental values of the refractive indices with the use of Mueller photoelasticity theory [Mueller, 1935] according to the following equation: $\Delta d/d = \delta n \Delta n / (n^2 - 1)(n^2 + 2)(1 - A)$, where $A = -(\Delta R/R_0)/(\Delta d/d)$ is Mueller strain–polarizability constant. The value of the strain–polarizability constant for magnesium silicate glasses is obtained to be $A=0.2$ [Kuryaeva and Surkov, 2012]. The Fig.1 demonstrates the values of relative density of the studied glasses within the pressure range up to 6.0 GPa together with the data for aluminosilicate glasses.

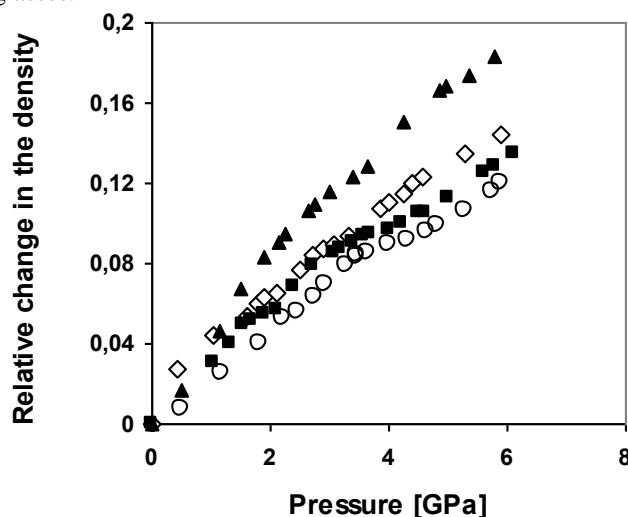


Fig. 1. Pressure dependence of the relative change in the density ($d-d_0/d$) (compressibility) of glasses: triangles – $\text{NaAlSi}_3\text{O}_8$ [Kuryaeva and Surkov, 2010], diamonds – $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ [this paper], squares – $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ [Kuryaeva and Surkov, 2013 (in press)], circles – $\text{Na}_2\text{MgSi}_4\text{O}_{10}$ [this paper]

Discussion. Fig.1 shows that aluminosilicate glasses have a higher compressibility than magnesium-silicate glasses the same compositions. The compressibility of glasses reflects the degree of depolymerization of structural network. The structural-chemical parameter NBO/T (NBO – non-bridging oxygen), characterizing the ratio between the number of gram-ions of non-bridging oxygen atoms and the total number of gram-ions of network formers [Mysen, 1988] will be used for the quantitative determination of the degree of depolymerization. The values of degree of depolymerization of aluminosilicate glasses $NBO/T = 0.08$ and 0.25 were calculated in previously works [Kuryaeva, 2004; Kuryaeva and Surkov, 2013] for $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ and $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ glasses respectively. To see a correlation between the values of compressibility and degree of depolymerization of magnesium silicate and aluminosilicate glasses, it is necessary to calculate the value NBO/T for magnesium silicate glasses.

As the coordination number is one of the main parameters determining the role of magnesium in the structure, many authors studied the local surrounding of magnesium in magnesium silicate glasses and melts. There is no general agreement among the authors. Some authors [Kubicki et al., 1992; Hanada et al., 1988] have concluded that Mg^{2+} ions in these glasses have mainly a fourfold coordination (average coordination number of magnesium

to oxygen 4.1–4.5), while others [Ildefonso et al., 1995; Shimoda et al., 2007] report that magnesium is five- or six-coordinated. Shimoda et al. [2007] interpreted the discrepancy as a result of the incorporation of magnesium in glasses in distorted MgO_6 polyhedra, with different lengths of Mg-O bonds. Yin et al [1983], using analysis of radial distribution function, showed that in MgSiO_3 glass Mg^{2+} ions are, on the average, surrounded by six oxygen atoms. Four oxygen atoms form Mg-O pairs with an average distance of 2.08 \AA , whereas the other two oxygen atoms form Mg-O pairs with an average distance of 2.50 \AA . On the basis of the known rule (the shorter the Mg-O distance, the higher degree of bond covalence), $2/3$ of magnesium ions are assumed to form quite strong bonds with oxygen, which have a greater degree of covalence and are network formers, whereas $1/3$ of Mg ions are modifiers. These data evidence that at normal pressure magnesium silicate glasses contain $\sim 67\%$ magnesium with coordination number four and $\sim 33\%$ magnesium with coordination number five or six.

Study of glasses and melts of the system $\text{M}_2\text{O} - \text{MgO} - \text{SiO}_2$ (where M are alkali elements) by different spectroscopic techniques [Shimoda et al., 2007; Cormier et al., 2010] showed that most Mg^{2+} ions have a coordination number to oxygen close to four and the cations of alkali metals are not modifiers but compensate the charge in magnesium-oxygen tetrahedral.

Raman spectroscopy of silicate glasses and melts of the system $\text{Na}_2\text{O}-\text{MgO}-\text{SiO}_2$ was used by Lin et al. [2007] for obtaining data on the polymerization of structure. The Raman spectra of silicate glasses and melts show a number of bands in the high-frequency spectral region from 800 to 1200 cm^{-1} , which correspond to the silicon – oxygen stretching vibrations in silicate tetrahedral units containing four (850 cm^{-1}), three (900 cm^{-1}), two ($1000-950 \text{ cm}^{-1}$) and one ($1100-1050 \text{ cm}^{-1}$) non-bridging oxygen atoms [e.g., McMillan, 1984]. To determine the proportional quantity of structural units in glass, it is necessary to know the integral intensities of corresponding bands. For solving this problem the total contour is deconvoluted into individual bands. The shape of curves is described using the Gaussian function. Data obtained from the Raman spectra allowed the authors to observe quantitative changes of various structural units depending on the compositions and, as a rough approximation, to estimate the degree of depolymerization of studied glasses. For the glasses of the $\text{Na}_2\text{O}-\text{MgO}-\text{SiO}_2$ system the degree of depolymerization NBO/T differs from the calculated value (for the case when Mg^{2+} and Na^+ are modifiers), at least by 0.5 .

The value NBO/T can be obtained from the dependence of the compressibility of silicate glasses on the degree of depolymerization. Such dependencies are reported in [Kuryaeva, 2009] for $P = 3.0, 4.0$ and 5.0 GPa . The pressure-induced changes in the structure of highly polymerized aluminosilicate glasses in the range of $0 - 6.0 \text{ GPa}$ are of topological character [e.g., Kelsey et al., 2007]. Such changes have a minor influence on the degree of depolymerization, which allowed construction of $(d-d_0)/d - NBO/T$ dependencies at various pressures with invariable values of NBO/T . Owing to the similarity of the structure of silicate glasses, all of them, irrespective of the presence of any components in them, should obey these

dependencies in case of the correct calculation of the degree of depolymerization.

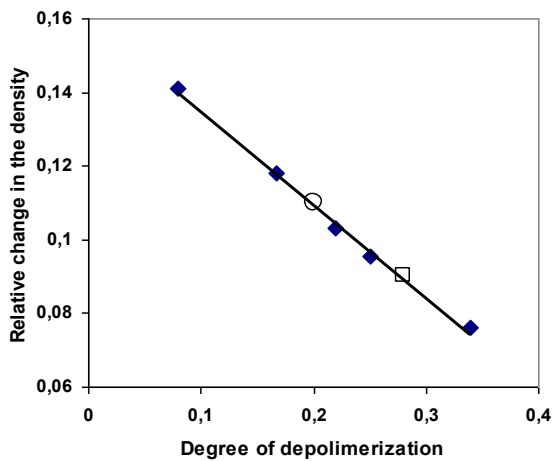


Fig. 2. Correlation between the degree of depolymerization NBO/T and the relative change in the density $(d-d_0)/d$ (compressibility) for glasses at pressure $P = 4.0$ GPa: diamonds – $Ca(Na_2O) - Al_2O_3 - xSiO_2$ [Kuryaeva, 2009; Kuryaeva and Surkov, 2010; Kuryaeva and Surkov, 2013 (in press)], circle – $Na_2MgSi_6O_{14}$ [this paper], square – $Na_2MgSi_4O_{10}$ [this paper]

Figure 2 shows the linear dependence $(d-d_0)/d - NBO/T$ for pressure $P = 4.0$ GPa, corresponding to equation $y = -0.252x + 0.16$ ($x = NBO/T$, $y = (d-d_0)/d$) (2). Coefficient of determination for the equation (2) is $R^2 = 0.9973$. Fig. 2 also shows the dots denoting the compressibility values $(d-d_0)/d = 0.09$ and 0.11 at $P = 4.0$ GPa obtained in this work vs. the independently calculated values $NBO/T = 0.28$ and 0.2 for $Na_2MgSi_4O_{10}$ and $Na_2MgSi_6O_{14}$ glasses, respectively.

The structure of magnesium-silicate glasses studied in [Kubicki et al., 1992; Sanchez-Valle and Bass, 2010] does not change significantly under the pressure to 6.0 GPa either. The only change is a change in the volume related to the decrease in bond angles T—O—T at an invariable coordination state of ions, implying that no significant change in the degree of polymerization can be expected in the studied pressure range.

The position of the dots in Fig. 2 for $Na_2MgSi_4O_{10}$ and $Na_2MgSi_6O_{14}$ glasses evidences agreement between the compressibility of glass and its degree of depolymerization, which makes it reasonable at this stage of investigations to use a common scheme (67% magnesium ions are network formers and 33% magnesium ions are modifiers) for calculating the degree of depolymerization of alkali magnesium-silicate glasses and provides a means for estimation of the compressibility (without the experiment) from the known equations.

References:

1. Agee C.B., D. Walker (1988). Static compression and olivine flotation in ultrabasic silicate liquid. *J. Geophys. Res.*, v. 93, pp. 3437-3449.
2. Cormier, L., G. Calas, G.J. Cuello (2010). Structural study of Ca–Mg and K–Mg mixing in silicate glasses by neutron diffraction. *J. Non-Cryst. Sol.*, v. 356, pp. 2327-2331.
3. Hanada, T., N. Soda, T. Tachibana (1988). Coordination state of magnesium ions in rf-sputtered amorphous films in the system MgO–SiO₂. *J. Non-Cryst. Sol.*, v. 105, pp. 39-44.

4. Ildefonse, Ph., G. Calas, A.M. Flank, P. Lagarde (1995). Low Z elements (Mg, Al, and Si) K-edge X-ray absorption spectroscopy in minerals and disordered systems. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* v. 97, pp. 172-175.
5. Kelsey, K.E., J.F. Stebbins, L.-S. Du, B. Hankins (2007). Constraining ¹⁷O and ²⁷Al NMR spectra of high-pressure crystals and glasses: New data for jadeite, pyrope, grossular and mullite. *Am. Min.*, v. 92, pp. 210-216.
6. Kubicki, J.D., R.J. Hemley, A.M. Hofmeister (1992). Raman and infrared study of pressure-induced structural changes in MgSiO₃, CaMgSi₂O₆ and CaSiO₃ glasses. *Am. Min.*, v. 77, pp. 258-269.
7. Kuryaeva R.G. (2004). Degree of polymerization of aluminosilicate glasses and melts. *Glass Phys. Chem.*, (Engl. Transl.) v. 30, pp. 157-166.
8. Kuryaeva, R.G. (2009). The state of magnesium in silicate glasses and melts. *Glass Phys. Chem.*, (Engl. Transl.) v. 35, pp. 378-383.
9. Kuryaeva R.G., V.A Kirkinskii (1994). Measuring a refractive index at high pressure in a diamond anvil cell. *Instrum. Exp. Tech.*, (Engl. Transl.) v. 37, pp. 774-778.
10. Kuryaeva R.G., V.A. Kirkinskii (1997). Influence of high pressure on the refractive index and density of tholeiite basalt glass. *Phys. Chem. Minerals*, v. 25, pp. 48-54.
11. Kuryaeva R.G., N.V. Surkov (2010). Behavior of the refractive index and compressibility of albite glass at pressures up to 6.0 GPa. *Geochim. Int.*, (Engl. Transl.) v. 48, No. 8. pp. 835-841, doi: 10.1134/S0016702910080100.
12. Kuryaeva, R.G., N.V. Surkov (2012). Refractive index and the compressibility of Di₆₄An₃₆ glass at pressures up to 5.0 GPa. *Geochem. Int.* (Engl. Transl.) v. 50, pp. 1026-1031.
13. Kuryaeva R.G., N.V. Surkov (2013). Effect of the replacement of aluminum by magnesium on the compressibility and degree of polymerization of silicate glasses. *J. Mater. Sci.*, v.48, pp.4416-4426.
14. Lin, C.-C., S.-F. Chen, L.-G. Liu, C.-C. Li (2007). Anionic structure and elasticity of Na₂O–MgO–SiO₂ glasses. *J. Non-Cryst. Sol.*, v. 353, pp. 412-425.
15. McMillan, P. (1984). A Raman spectroscopic study of glasses in the system CaO–MgO–SiO₂. *Am. Min.*, v. 69, pp. 645-659.
16. Mueller H. (1935). Theory of photoelasticity in amorphous solids. *Physics*, v. 6, pp. 179-182.
17. Mysen, B.O. (1988). Structure and properties of silicate melts. *Elsevier, Amsterdam*.
18. Neuville, D.R., L.Cormier, V. Montouillout, P. Florian, F. Millot, J.-C. Rifflet, D. Massiot (2008). Structure of Mg- and Mg/Ca aluminosilicate glasses: ²⁷Al NMR and Raman spectroscopy investigations. *Am. Min.*, v. 93, pp. 1721-1731.
19. Sanchez-Valle, C., J.D. Bass (2010). Elasticity and pressure-induced structural changes in vitreous MgSiO₃ – enstatite to lower mantle pressures. *Earth Plan. Sci. Lett.*, v. 295, pp. 523-530.
20. Toplis M.J., D.B. Dingwell, T. Lenci (1997). Peraluminous viscosity maxima in Na₂O–Al₂O₃–SiO₂ liquids: The role of triclusters in tectosilicate melts. *Geochim. Cosmochim. Acta*, v. 61, pp. 2605-2612.
21. Trcera, N., D. Cabaret, S. Rossano, F. Farges, A.-M. Flank, P. Lagarde (2009). Experimental and theoretical study of the structural environment of magnesium in minerals and silicate glasses using X-ray absorption near-edge structure. *Phys. Chem. Min.*, v. 36, pp. 241-257.
22. Webb S., P. Courtial (1996). Compressibility of melts in the CaO–Al₂O₃–SiO₂ system. *Geochim. Cosmochim. Acta*, v. 60, pp. 75-86.
23. Yin, C.D., M. Okuno, H. Morikawa, F. Marumo (1983). Structure analysis of MgSiO₃ glass. *J. Non-Cryst. Sol.*, v. 55, pp. 131-141.