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PETROLOGICAL INFERENCES FOR THE ROLE OF EXSOLUTION IN UPPER MANTLE: EVIDENCE FROM THE YAKUTIAN KIMBERLITE XENOLITHS

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INTRODUCTION

Despite presenting only minor portions, pyroxenite-websterite xenoliths in kimberlites and alkali basalts are of great interest for they can provide valuable information on the formation of the compositionally heterogeneous cratonic lithospheric mantle. Among the population of pyroxenite xenoliths, some are observed to contain garnet and pyroxene porphyroblasts with exsolution lamellae In particular, exsolution lamellae in mantle xenolith minerals from kimberlite pipes of the Siberian Craton have been described in several publications (e.g. Sobolev, Sobolev, 1964; Taylor et al., 2003; Roden et al., 2006).

Petrographic and compositional information from garnet and pyroxene porphyroblasts in mantle-derived pyroxenite-websterite xenoliths, combined with data of their exsolution features, allows taking constraints on the composition of primary phases crystallized at magmatic temperatures, and the subsolidus processes that have modified them. This knowledge places important inferences for the origin, evolution, and P-T history of lithospheric mantle.

In this report, garnet-bearing varieties of pyroxenite-websterite xenoliths from Yakutian diamondiferous Mir and Udachnaya and barren Obnazhennaya kimberlites have been studied. All rocks have pyroxene and/or garnet porphyroblasts containing multiphase exsolution assemblages that are the focus of this work. The compositions of porphyroblasts and their associated populations of exsolved phases are used to constrain on the subsolidus chemical and P-T history of this sample suite, with important implications for the evolution of portions of Siberian lithosphere.

XENOLITH PETROGRAPHY

Pyroxenite and peridotite mantle xenoliths were collected from three Yakutian kimberlite pipes: Udachnaya-East, Mir, and Obnazhennaya. Xenoliths are generally coarse-grained, and include garnet- and spinel-garnet varieties of websterites, olivine websterites, lherzolites, orthopyroxenites and clinopyroxenites. Most of rocks are inequigranular, containing large pyroxene and garnet porphyroblasts (up to 3 cm) and finer-grained matrix of the same mineral assemblage ± olivine, phlogopite, oxides, and sulfides of various sizes. Orthopyroxene, clinopyroxene, and garnet porphyroblasts host exsolution phases.

Pyroxene exsolution textures

Pyroxene porphyroblasts have exsolved pyrope garnet, diopside/enstatite, Cr-spinel and Ti-oxides (rutile, ilmenite). Exsolved phases hosted by pyroxene occur in three morphological forms: thin lamellae up to 20 μm thick (usually 3 to 5 μm); large tabular and lenticular inclusions or platelets that are generally up to 500 μm thick; and thickened lamellae that have transformed into well-defined grains (recrystallized), and blebs within the host mineral or adjacent to the grain boundary. Exsolutions generally form parallel to {100}, {010}, and {001} planes of the host pyroxenes. Garnet exsolution is often associated with orthopyroxene lamellae (e.g. O-173, O-207, and O-332). Complex exsolution lamellae in pyroxenes are often observed. The associations of rutile and ilmenite (e.g. O-173, O-264), pyroxene and garnet, rutile and chromite (M34/01, UV345/08), chromite and pyroxenes (M4/01, O-436, UV345/08), and rutile/ilmenite together with corresponding pyroxenes (Fig. 1a) among exsolved phases are common.

Garnet exsolution textures

Garnet porphyroblasts contain exsolution lamellae of diopside (together with sodic plagioclase in garnet websterite M5/01), enstatite, rutile, ilmenite, chromite and oriented arrays of crichtonite and olivine in some samples. Compared to pyroxene porphyroblasts, large garnet crystals generally contain lower exsolution proportions (generally

<3.6 vol.%). Within garnet, exsolved phases occur as: thin needles (generally <50 µm wide, and <100 µm long); and lamellae that often parallel the {111} plane and commonly exceed 100 µm in length, with constant or variable thickness that is generally <30 µm wide. Most of the garnet porphyroblasts contain complex exsolution lamellae. For example, different exsolution phases (rutile, clinopyroxene, orthopyroxene, ilmenite) are intergrown on the intersection of lamellae forming internodal blebs (Fig. 1b). Pyroxenes + rutile, rutile + ilmenite, rutile + chromite lamellae locating on the extension of each other and/or forming one needle or platelet are also found. Complex lamellae often show cross-cutting relationships, e.g. clinopyroxene lamella in garnet from websterite O-264 contains rutile and ilmenite exsolutions.

MINERAL CHEMISTRY

Major elements

Clinopyroxene has diopside compositions ($Wo_{43\text{-}48.9}En_{44.3\text{-}51.6}Fs_{2.1\text{-}9.7}$. The range of Mg# values observed in clinopyroxene porphyroblasts varies from 84.1 to 96.0. Within individual clinopyroxene porphyroblasts, significant compositional variation is observed. The Mg# of clinopyroxene in garnet websterite O-107 generally increases from the core (86.9) to the rim (88.5). Core-rim compositional relationships show significant variations in Al_2O_3 and Na_2O contents in clinopyroxenes from websterite (e.g., O-301, O-107, UV41/03), clinopyroxenite (O-125) and olivine websterite (O-207) xenoliths. The TiO_2 content in clinopyroxene in websterite xenolith O-301 decreases from the core (0.56 wt.%) to the rim (0.31 wt.%).

Most of the clinopyroxene lamellae within orthopyroxene have compositions that are similar to those of clinopyroxene porphyroblasts. However, lamella in three samples (O-173, O-550, and UV41-03) have higher MgO and CaO contents, and lower Al_2O_3 and Na_2O abundances when compared to the clinopyroxene porphyroblasts. Other notable variations between porphyroblast and exsolved clinopyroxene compositions include TiO_2 contents that are lower in the lamellae in some websterites (e.g., O-173 and UV41/03), and Cr-rich lamellae in some olivine websterites (e.g., M4/01 and O-436).

Orthopyroxenes generally have enstatite compositions ($Wo_{0.2\text{-}1.2}En_{87.5\text{-}94.6}Fs_{5\text{-}12.2}$), however, occasional bronzites ($Wo_{0.2\text{-}0.7}En_{75.2\text{-}86}Fs_{13.7\text{-}24.4}$) have been identified (samples O-125, O-332, UV41/03). The Mg#s of orthopyroxene porphyroblasts (80.7 to 95.0) are typically lower than those of coexisting clinopyroxene porphyroblasts. Within individual orthopyroxene grains, compositional zoning is generally low; however, four xenoliths (O-107, O-207, O-301, and O-332) have variations of up to 1.0 wt% in Al_2O_3, FeO and/or MgO contents. Orthopyroxenes from websterite sample O-301 also show a significant decrease in Cr_2O_3 content from core (1.08 wt. %) to rim (0.34 wt.%).

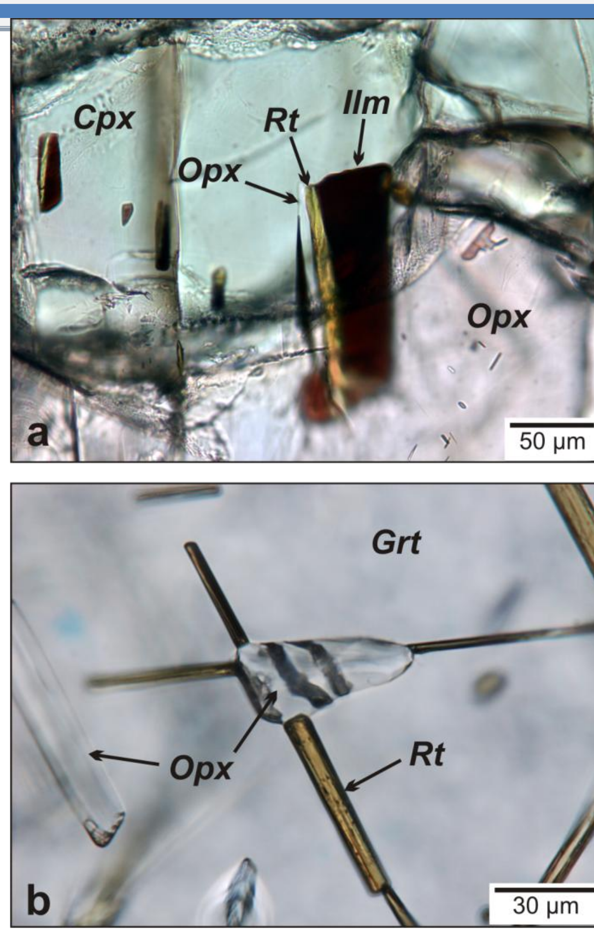

Fig. 1. Complex exsolution lamellae in clinopyroxene (a) and garnet (b). The intergrown rutile (Rt), ilmenite (Ilm) and orthopyroxene (Opx) platelets in clinopyroxene (Cpx) host (a) and the intersection of {111} oriented rutile needles and orthopyroxene bleb in garnet (Grt) porphyroblast (b) are shown.

In some websterite xenoliths, exsolved orthopyroxene in clinopyroxene porphyroblasts have compositions that can vary significantly (e.g., up to 2.0 wt.% Al_2O_3, 0.6 wt.% FeO and 1.8 wt.% MgO), whereas little variation is observed in the orthopyroxenite and clinopyroxenite xenoliths. Websterite sample O-332 contains orthopyroxene that is exsolved from garnet and this crystal has CaO contents up to 0.52 wt.%, a value that is higher than that of orthopyroxene porphyroblasts (0.31-0.33 wt.%), and the orthopyroxene lamellae (0.37 wt.%) in clinopyroxene, from the same sample.

Garnet porphyroblast major element compositions cover a range of pyrope and almandine contents ($Prp_{46.3\text{-}76.1}Alm_{11.4\text{-}44.3}$) and have low Ca-components (Grs <9.3, Uvr <12.9 mol.%, Andr 0.4-5.4 mol.%, Ti-Andr <1.4 mol.%) in all samples. The garnets have Mg# from 55.7 to 86.5. High pyrope contents are typical of samples that contain olivine (e.g., O-301, O-571, and M34/01), but are also observed in some samples containing no observable olivine (e.g., O-264, O-550, and M5/01). In nearly all samples, garnets have near-uniform intra- and inter-mineral Prp-Alm-Grs proportions. Cr_2O_3 contents vary within garnet porphyroblasts from a limited number of xenoliths (e.g., O-571 and M34/01); with Cr-rich cores (2.73 and 4.62 wt.%) and lower Cr-contents in the corresponding rim (2.3 and 4.41 wt.%). All garnets have low Na_2O (< 0.1 wt. %) and TiO_2 (< 0.51 wt. %) abundances.

Garnets exsolved from pyroxenes are generally characterized by slightly lower Cr_2O_3 contents, compared to garnet porphyroblasts from the same sample. For instance, garnet lamellae in clinopyroxene (UV201/09) and orthopyroxene (O-436) have 1.58 and 1.94 wt.% of Cr_2O_3, whereas garnet porphyroblasts in these samples contain 2.38-2.39 and 2.66-2.81 wt.%, respectively.

Trace elements

Being sensitive to the mantle processes during the formation, trace element (in particular, rare earth element) distribution in minerals allows to constrain mantle rock evolution. In this study, 13 pyroxenite/websterite and peridotite xenoliths from Udachnaya, Mir and Obnazhennaya were analyzed for concentrations of REEs in garnet and clinopyroxene. Trace-element analyses were made in-situ in polished thick sections, with LA-ICP-MS at the GEMOC National Key Centre, Macquarie University, Australia. Methods and operating conditions have been described by Norman et al. (1996).

Garnets from studied set of xenoliths show depleted chondrite-normalized REE patterns (Fig. 2). These websteritic/pyroxenitic garnets are all characterized by low concentrations of light rare earth elements (LREEs), with La_n of 0.01–0.12. Except for Obnazhennaya O-125 clinopyroxenite (where Yb_n is as low as 1.2 and $[Dy/Yb]_n$ = 1.9), the other samples are heavy rare earth element (HREE)-enriched (Fig. 2), showing positive $[Dy/Yb]_n$ ratios and relatively high Yb contents (Yb_n of 5.2–47.0). REE distribution data in the studied garnets are similar to those for garnets from Udachnaya, Mir and Obnazhennaya eclogite xenoliths (e.g. Sobolev et al., 1994; Beard et al., 1996; Taylor et al., 2003). Five garnets show slight to medium positive Eu anomalies. The Eu/Eu* ratios are 1.2 for two Mir and Udachnaya olivine websterites (M31/01, UV127/09), and Udachnaya clinopyroxenite (UV201/09), and 1.9–2.1 for Obnazhennaya clinopyroxenite and websterite (O-125 and O-107).

Clinopyroxenes exhibit both convex-upward and simple-enrichment REE patterns, and the HREEs are depleted relative to LREEs (Fig. 2). Chondrite-normalized La contents vary from 4.8 (Obnazhennaya garnet clinopyroxenite O-125) to 66.0 (Mir phlogopite-rich garnet olivine websterite M31/01). Ytterbium contents range from 0.13 to 3.57 times chondrite concentrations. $[La/Yb]_n$ are 4.7–124.3, with the maximum values in Mir olivine websterites M31/01 and M4/01. Only two clinopyroxenes (Obnazhennaya clinopyroxenite O-125 and websterite O-107) show significant positive Eu anomalies, with Eu/Eu* 1.8. The Sr contents in clinopyroxenes from the studied samples are from 140 to 774 ppm and it is 7–39 times higher than that of primitive mantle (PM) concentrations estimated (McDonough, Sun, 1995). The similar feature was revealed in clinopyroxenes from African mantle xenoliths (Macdougall, Haggerty, 1999) with garnet containing exsolution lamellae.

EQUILIBRATION CONDITIONS

Xenolith pressure-temperature conditions were calculated using the Ca-in-orthopyroxene thermometer (Brey, Kohler, 1990), in combination with the garnet-orthopyroxene barometer of Brey and Kohler (1990). P-T estimates of some samples were excluded due to large temperature discrepancies (i.e. >100 °C) between thermometers. The pyroxenites equilibrated at relatively low pressures and temperatures (2.0 to 4.5 GPa and 690 to 910 °C), which are similar to that obtained for the spinel-garnet lherzolite xenoliths from Mir (2.4 GPa and 740 °C). Xenoliths from the Paleozoic Mir kimberlite span the range of P-T conditions, whereas the younger Obnazhennaya pipe has lower P-T values, compared to the Paleozoic Udachnaya kimberlite. Olivine websterites were equilibrated at the highest temperatures.

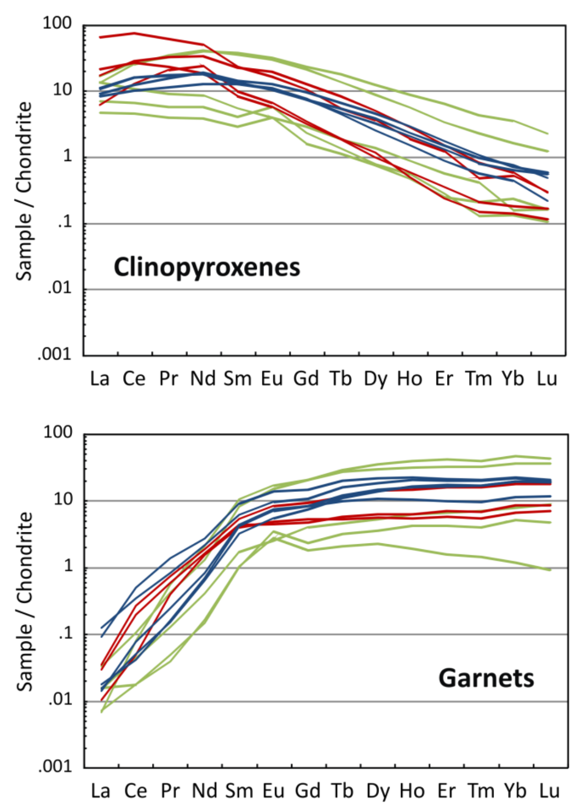

Fig. 2. REE contents in clinopyroxenes and garnets from the pyroxenite/websterite mantle xenoliths of Udachnaya (blue), Mir (red) and Obnazhennaya (green) kimberlite pipes normalized to the chondrite values of McDonough and Sun (1995).

COMPOSITION RECONSTRUCTIONS

To constrain the magmatic conditions that may have crystallized the pyroxenitic protolith, reconstructed porphyroblast major element compositions have been calculated by combining the volume proportions of the host mineral with exsolved phases of known major element compositions and assumed densities.

Reconstructed clinopyroxene compositions show $Wo_{38-48.6}En_{45-54.4}Fs_{2.4-12}$ variations for all studied xenoliths. These compositions have higher Mg and Al contents than porphyroblast clinopyroxenes of the corresponding xenoliths. Additionally, some samples also yield reconstructed clinopyroxene compositions that have relatively high TiO_2 concentrations (up to 1.51 wt.%). The highest TiO_2 values (0.95-1.51 wt.%) are in reconstructed clinopyroxenes from websterite (O-264, O-173, M5/01), olivine websterite (O-207) and lherzolite (O-571) xenoliths. Compared to measured clinopyroxene compositions, the reconstructed clinopyroxenes contain lower jadeite (up to 20.5 mol.% vs. 1.2-26.2 mol.%) and higher Ca-tschermakite (up to 10.9 mol.% vs. 0-4.9 mol.%) contents, suggesting that the aluminum cations may have redistributed in clinopyroxenes from IV to VI coordination during exsolution process. Some of olivine websterites (O-436 and M4/01) have reconstructed clinopyroxene compositions with Cr_2O_3 contents higher than corresponding matrix compositions (1.43 and 3.25 wt.% vs. 1.36 and 2.41 wt.%, respectively).

Reconstructed orthopyroxene compositions have $En_{75.7-93.8}Fs_{5.1-23.9}$ contents that are similar to orthopyroxene porphyroblast compositions, with higher wollastonite proportions (0.4-4.2 mol.%). The reconstructed compositions suggest that these pyroxenes may have been characterized by relatively high Al_2O_3 contents (up to 6.29 wt.%), with up to 12.3 mol.% tschermakite. CaO and TiO_2 contents are up to 2.13 wt.% and 0.96 wt.%, respectively. Reconstructed orthopyroxenes from olivine websterite and garnet orthopyroxenite (O-436 and UV345/08) are characterized by relatively high Cr_2O_3 contents (1.3 wt.% and 1.2 wt.%, respectively). Sodium contents increase slightly in reconstructed compositions (for example, from 0.06 wt.% in porphyroblast composition to 0.24 wt.% of Na_2O in the reconstruction for sample M5/01).

The *reconstructed garnet* major element compositions did not significantly differ from measured garnet porphyroblast compositions, and have a similar range of pyrope, almandine and uvarovite contents ($Prp_{45.7-75.4}Alm_{12-43.7}Uvr_{0.1-12}$). Grossular (<7.9 mol. %) and andradite (<4.9 mol.%) contents are slightly lower than those measured in porphyroblast garnets. Reconstructed compositions generally have higher TiO_2 (up to 1.9 wt.%), and consequently have higher Ti-andradite contents (up to 5.1 mol.%), with the highest TiO_2 values observed in garnets from olivine websterites UV223/09 and UV127/09 (TiO_2 1.58-1.9 wt.%, 4.3-5.1 mol.% of Ti-Andr). Despite the high volume portion of pyroxene lamella in most garnets (up to 1.85 vol.% in garnets from UV223/09), the corresponding reconstructed garnet compositions still maintain normal Si/O ratios (about 3 Si atoms per 12 oxygens), which likely results from a balancing of majoritic and titaniferous components within precursor garnet compositions.

DISCUSSION

The compositions of xenolith porphyroblasts, and their associated populations of exsolved phases, can be used to place constraints on the subsolidus chemical and P-T history. The abundant exsolution lamellae in garnets and pyroxenes from these pyroxenites require mantle residence at relatively low pressures and temperatures for extended periods of time. The mineral compositions of the pyroxenites xenoliths in this study are very similar to those of the lherzolites, which also equilibrated at relatively low pressures and temperatures, suggesting that regardless of the history of the pyroxenites, they last equilibrated at upper mantle conditions.

Variations in molecular Ca and Al in silicate porphyroblasts indicate significant subsolidus redistribution of cations. Brey et al. (1990) have suggested that Ti-contents in garnets may correlate positively with pressure, which is consistent with experimental work by Zhang et al. (2003). Experimental observations indicate that Ti-phases exsolve from garnet as pressure decreases. In addition, it has been suggested that Ti is more comfortable in the pyroxene structure, compared to that of garnet, over the temperature interval of 1100 to 1300 °C, while at lower temperatures Ti may prefer oxide (ilmenite and rutile) structures (Zhang et al., 2003). In addition, textural relationships among exsolution features of several studied garnets support the notion that ilmenite and rutile may have exsolved from an earlier pyroxene exsolution. Coexisting exsolution of pyroxenes and Ti-oxides (rutile and ilmenite) in garnets provides evidence that Ti is strongly coupled to Na+Si. These observations provide important evidence that some portions of the Siberian lithospheric mantle may have experienced cooling to <1100 °C prior to kimberlite-entrainment, and this cooling was potentially accompanied by a decrease in pressure.

Many authors have suggested that exsolution features in pyroxene and garnet porphyroblasts in pyroxenite mantle xenoliths can largely be accounted for by decreasing temperature and pressure conditions subsequent to magmatic crystallization (e.g. Sobolev, Sobolev, 1964; Sen, Jones, 1988), and observations from this study of Siberian xenoliths can generally be explained by a broadly analogous P-T history. Additionally, the reconstructed compositions of pyroxenes and garnets often contain significant NATAL components, and many initial garnets may have had high Si-contents consistent with majorite compositions, i.e. features which would support initial crystallization at elevated pressure conditions.

Similar to the garnet porphyroblasts reported in this study, garnets from kimberlite-hosted peridotite and pyroxenite xenoliths (e.g. Kaapvaal Craton, Sautter et al., 1991) and ultramafic portions of UHP terranes (e.g. Pandey et al., 2010) contain pyroxene lamellae, which may be accounted for by exsolution from an initial garnet of majorite composition. High pressure experiments suggest that majorite garnet is stable at pressures in excess of 6 to 10 GPa (e.g. Irifune, 1987). Si substitution increases with pressure, and results in extensive, or even complete, dissolution of pyroxene into garnet in the mantle transition zone (e.g. Irifune, 1987). Si-excesses are observed within this suite of Yakutian pyroxenites, suggesting that xenoliths containing these garnet porphyroblasts may have originated at great depth. Taken together, primary pyroxene and garnet phases in the Yakutian pyroxenite suite may be explained by magmatism occurring over a wide range of pressures, some of which may have taken place in the presence of majoritic garnet.

Some globally distributed suites of pyroxenite xenoliths that contain multiphase exsolution assemblages have trace element, radiogenic and stable isotope compositions that may indicate the involvement of recycled oceanic crust and depleted mantle in regions of melt generation (e.g. Downes, 2007). This evidence may suggest that subducted lithosphere is present in asthenospheric environments, and the geochemical and chronological characteristics suggest that compositional and isotopic heterogeneities persist over long time periods (>1 Ga) in Earth's upper mantle.

SUMMARY

Pyroxenites with garnet and pyroxene porphyroblasts containing multiphase exsolution lamellae are interpreted to be the result of complex subsolidus history of the host rocks following the magmatic crystallization.

Occurring in morphologically different forms exsolved phases are generally constant in major element composition indicative of chemical re-equilibration with hosts after exsolution process. According to mineral chemistry most of the rocks were equilibrated within upper mantle under low pressure-temperature conditions (690 to 910 ºC and 2.0 to 4.5 GPa).

Reconstructed compositions of initial pyroxene and garnet crystals suggest that several of the studied pyroxenites were formed at temperatures up to 1300 ºC and pressures that may approach the majorite stability field. Coexisting exsolution of pyroxenes and Ti-oxides (rutile and ilmenite) in garnets provides evidence that Ti is strongly coupled to Na+Si and that the mantle rocks may have cooled after pressure decrease.

The positive Eu anomalies (Eu/Eu* 1.2 for Mir and Udachnaya and 1.8–2.1 for Obnazhennaya samples) for some garnets and clinopyroxenes and relatively high Sr (140–774 ppm) contents in studied clinopyroxenes may suggest the involvement of an oceanic crustal component in the formation of these rocks.

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