

WHAT GARNET, CLINOPYROXENE AND DIAMOND POTENTIAL CAN TELL US ABOUT THE EVOLUTION OF SUB-CRATONIC MANTLE SECTIONS: A CASE STUDY OF THE ZAGADOCHNAYA KIMBERLITE (YAKUTIA)

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INTRODUCTION

Mantle xenoliths and xenocrysts included in alkaline volcanic rocks such as kimberlites and lamproites are the only direct samples of the sub-cratonic lithospheric mantle. The petrological studies of such samples are fundamental to understand *i*) the mineralogical and geochemical composition of the lithospheric mantle, *ii*) its thermal state, *iii*) the petrochemical processes, such as melting and fluid- or melt-driven metasomatism, which affected the sampled mantle section before the eruption of the xenolith-bearing volcanics, and *iv*) the factors that affect the diamond potential of kimberlites. The above issues can be tackled only using a multidisciplinary approach, which includes petrography, major and trace element geochemistry, geothermobarometry, and phase equilibria calculations. In peridotitic assemblages, garnet and clinopyroxene are the major hosts of trace elements and therefore have a fundamental bearing on the interpretation of petrochemical process in the mantle. Moreover, in many kimberlites, they are the only available mantle fragments suitable for geochemical and thermobarometric studies.

In this PhD thesis I focused on the petrogenesis of garnet and clinopyroxenes by integrating the following main lines of research: 1) evaluation of the single-clinopyroxene geobarometer of Nimis & Taylor (2000) for garnet peridotites, 2) thermodynamic modelling of natural peridotitic systems, focusing on the effect of pressure (P), temperature (T), and bulk compositional variations on the stability of Cr-bearing phases, and 3) a case study of mantle xenocrysts (garnets and clinopyroxenes) from the diamond-free Zagadochnaya kimberlite (Yakutia, Russia), building in part on results derived from the first two lines of research.

PART 1: EVALUATION OF SINGLE-CLINOPYROXENE GEOBAROMETRY

The single-clinopyroxene geobarometer of Nimis & Taylor (2000) represents the best alternative to the orthopyroxene-garnet barometer for garnet-bearing ultramafic rocks and the only viable method for isolated chromian diopside grains included in diamonds or recovered during mineral exploration programs. However, it suffers from two major drawbacks. First, evaluations against experiments have shown progressive underestimation of the equilibrium pressures above *ca.* 4.5 GPa (Nimis, 2002). The systematic bias at high P evidently is a consequence of the simplified, single-mineral formulation of the Cr-in-Cpx barometer and requires more detailed thermodynamic evaluations (*cf.* Part 2 below). Second, the deviations from results of orthopyroxene-garnet barometry can be very large for clinopyroxenes characterized by low values of a_{Cr} (*i.e.*, $Cr - 0.81 \cdot Na \cdot Cr\#$, $Cr\# = Cr/[Cr+Al]$, atoms per formula unit, apfu), with discrepancies up to 3.0 GPa for $a_{Cr} < 0.002$ apfu.

The reasons for the apparent low precision of the Cr-in-Cpx barometer for some compositions are still unknown. To evaluate the possible effects of analytical errors on P uncertainties, we performed multiple electron microprobe analyses on compositionally diverse clinopyroxenes, using different analytical conditions. The results demonstrated that such discrepancies are mostly related to propagation of analytical errors on the calculated Cr-in-Cpx pressures. The results of the analytical tests were then used to calculate model analytical errors and propagated P uncertainties for a large set of published analyses of mantle-derived, xenolith-borne clinopyroxenes (database of Nimis & Grütter, 2010). The estimated P uncertainties are negatively correlated with the a_{Cr} parameter and positively correlated with the $Cr\#$ ratio. The $a_{Cr}/Cr\#$ parameter can thus be used to discriminate clinopyroxenes for which analytical errors alone will propagate unacceptable P uncertainties (*i.e.*,

greater than ± 0.25 GPa, in terms of standard deviations) for several combinations of analytical conditions. Using appropriate analytical conditions, the barometer can be applied to at least 90% of clinopyroxene-bearing garnet peridotites and pyroxenites (database of Nimis & Grütter, 2010), 80% of clinopyroxene inclusions in lherzolitic diamonds, and 23% of clinopyroxene inclusions in websteritic diamonds (database of Stachel & Harris, 2008).

The xenolith database of Nimis & Grütter (2010) has been refined excluding those analyses for which the model P uncertainties were above the limit of ± 0.25 GPa. Fig. 1 shows that the discrepancies between Cr-in-Cpx and orthopyroxene-garnet pressures are greatly reduced for the refined database, especially at pressures above 3 GPa. Significant deviations are still observed only for a few samples with $Cr\# < 0.1$ (Fig. 1b), which suggests poor reliability of the Cr-in-Cpx barometer for low- $Cr\#$ compositions. Moreover, a progressive negative deviation of Cr-in-Cpx P estimates relative to orthopyroxene-garnet P estimates emerged at $P > 4.5$ GPa. This confirms the tendency of the Cr-in-Cpx barometer to underestimate at high P, which was previously observed against experimental data (Nimis, 2002). Owing to this systematic deviation, mantle palaeogeotherms calculated on the basis of single-Cpx thermobarometry will tend to show slightly different shapes than those based on orthopyroxene-garnet barometry. As discussed by Nimis (2002), this drawback will not hamper recognition of samples coming from the diamond window.

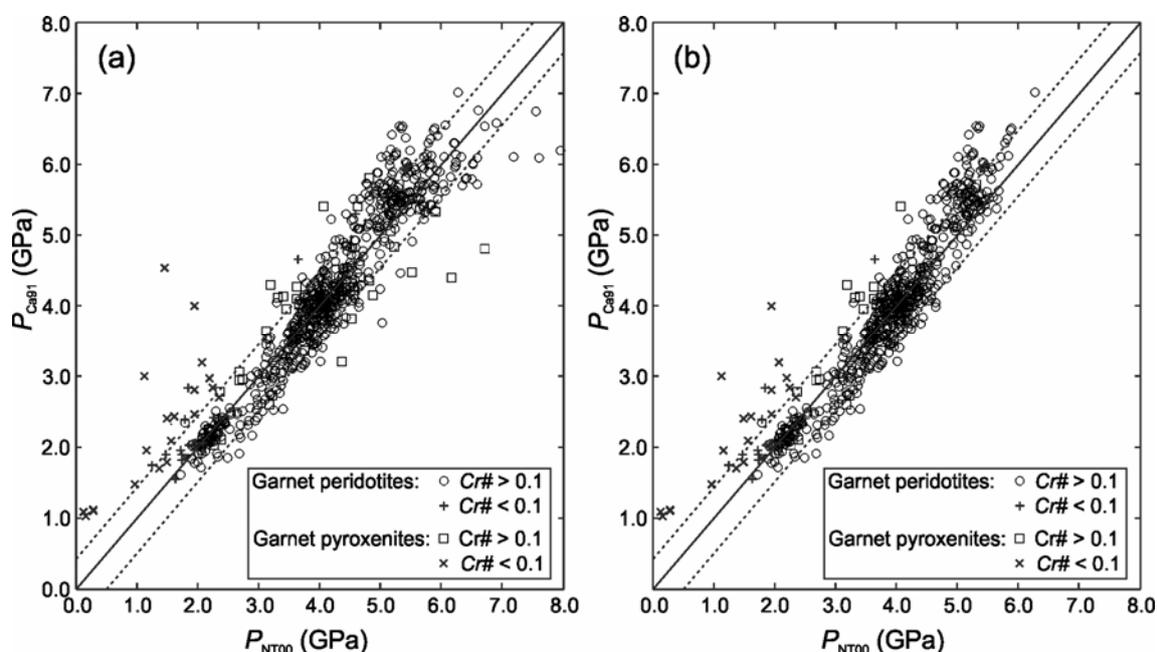


Fig. 1 - P estimates using the Cr-in-Cpx barometer (P_{NT00}) plotted *versus* P estimates using the orthopyroxene-garnet barometer of Nickel & Green (1985; as modified by Carswell, 1991; P_{Ca91}) for (a) the entire dataset of well equilibrated garnet peridotites and pyroxenites of Nimis & Grütter (2010), and (b) the same dataset cleaned from samples with calculated pressure uncertainties greater than ± 0.25 GPa. After Ziberna *et al.* (2014).

PART 2: THERMODYNAMIC MODELLING OF Cr-BEARING PERIDOTITIC SYSTEMS

As an attempt to refine thermobarometric methods based on Cr exchange between clinopyroxene and garnet, phase equilibria calculations for different peridotitic bulk compositions were carried out using well-established free energy minimization techniques using the ‘Perple_X’ set of computer programs (Connolly & Petrinì, 2002). We employed the internally consistent thermodynamic database of Holland & Powell (1998), as modified by Klemme *et al.* (2009). Some end-member data for Cr-bearing pyroxenes and mixing properties of Cr-bearing garnets were modified, so as to improve agreement with available experimental data in complex fertile and depleted, Cr-bearing peridotitic compositions. The refined model reproduces well the phase equilibria

and the compositional variations in orthopyroxene, garnet, and spinel in experiments at 2.0 - 10.0 GPa and 900-1500 °C. However, despite several attempts to further optimize the thermodynamic properties of the minerals, the model does not reproduce satisfactorily the compositional variations of clinopyroxene. This indicates the need for new, internally consistent thermodynamic data for Cr- and Na-bearing clinopyroxenes to be experimentally determined. At present, improvement of the single-clinopyroxene barometer based on a robust thermodynamic approach appears not to be possible.

As the lack of consistent thermodynamic data for Cr- and Na-bearing clinopyroxenes does not significantly affect phase relations and compositional variations in orthopyroxene, garnet, and spinel, the model has been used to predict the effect of P, T and bulk compositional variations on garnet-spinel relations in fertile and depleted mantle compositions (Zibera *et al.*, 2013a). Calculations show that the garnet + spinel stability field extends to 120-180 km in regions with cold geotherms (*i.e.*, cratonic lithosphere), in agreement with seismic observations (Lebedev *et al.*, 2009). In the garnet + spinel stability field the calculated modes of spinel are very low (0.1 - 2.8 %), suggesting that spinel grains may be easily overlooked in mantle xenoliths, especially if the xenoliths are small and not sufficiently representative of the original rock. Moreover, the thermodynamic model shows that garnet becomes increasingly enriched in Cr with increasing P and T as long as spinel is also stable. In the garnet-only field the composition of the garnet remains virtually constant. This provides a quantitative explanation of the empirically-determined compositional variations in peridotitic garnets coexisting with spinel (Ryan *et al.*, 1996; Grütter, 2006). Finally, formation of Cr-spinel inclusion in diamonds is restricted to pressures between 4.0 and 6.0 GPa and their very Cr-rich nature does not necessarily imply ultra-depleted bulk compositions.

PART 3: GEOCHEMISTRY OF GARNET XENOCRYSTS FROM THE ZAGADOCHNAYA KIMBERLITE

The diamond-free Zagadochnaya kimberlite is located in the Daldyn kimberlitic field (Yakutia, Russia) and is very close (*ca.* 30 km) to the highly diamondiferous Udachnaya kimberlite. The garnet and clinopyroxene xenocrysts included in the Zagadochnaya kimberlite show a wide range of textures and major and trace element compositions (Nimis *et al.*, 2009; Zibera *et al.*, 2013b), providing a great opportunity to investigate the petrochemical processes in this sector of the Siberian Craton and their relationships with diamond potential. Here we studied 28 representative garnet xenocrysts, performing a detailed petrographic study on back-scattered electron images, combined with in-situ major and trace element analyses (Zibera *et al.*, 2013b). The results allowed to interpret the garnets as fragments of depleted to fertile lherzolite and to distinguish three main compositional groups (Fig. 2).

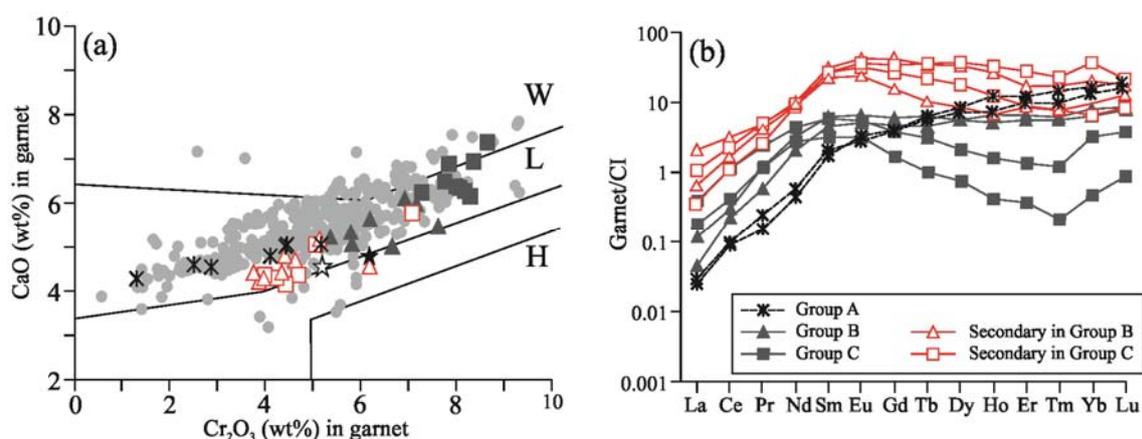


Fig. 2 - Main compositional features of Zagadochnaya garnets. (a) CaO vs. Cr₂O₃ discrimination diagram (Sobolev, 1971); the grey circles represent garnets from Zagadochnaya kimberlite concentrate (Sobolev, pers. comm.); H, harzburgite; L, lherzolite; W, wehrlite. (b) Representative CI-normalized (Anders & Grevesse, 1989) REE patterns for Zagadochnaya garnets. Modified after Zibera *et al.* (2013b).

Group A garnets ($\text{Cr}_2\text{O}_3 = 1.3\text{-}5.2$ wt.%) are often associated with chromian diopsides and are characterized by progressively increasing, CI-normalized Rare Earth Elements (REE) abundances from La to Lu; Group B garnets ($\text{Cr}_2\text{O}_3 = 5.4\text{-}8.6$ wt.%) are less depleted in Light REE (LREE) and show nearly flat patterns from Sm to Lu; Group C garnets ($\text{Cr}_2\text{O}_3 = 7.3\text{-}8.4$ wt.%) are characterized by humped to strongly sinusoidal REE patterns, with Yb between 0.5 and 3.0 x CI. The low Ni-in-garnet temperatures (≤ 860 °C; Ryan *et al.*, 1996), and the low Cr-in-Cpx pressures (Nimis & Taylor, 2000) for the associated clinopyroxenes (3.0-4.0 GPa; this work and Nimis *et al.*, 2009) suggest derivation of Zagadochnaya xenocrystic material from a relatively shallow mantle section (*ca.* 100-130 km).

The above estimates are reliable, because the composition of the Zagadochnaya diopsides is well within the limits for optimum thermobarometry, and P estimates are not affected by systematic deviations in the estimated pressure range (*cf.* Part 1 of this work). Therefore only a minor portion, if any, of the mantle sampled by the Zagadochnaya kimberlite may have been seated within the diamond stability field, thus providing a simple explanation for the absence of diamond at Zagadochnaya.

Another important part of this work concerns the interpretation of the REE compositional variations in the garnets and their relationships with the metasomatic history of the host rocks. Although the results of Part 2 (Zibera *et al.*, 2013a) may suggest a potential relationship between Cr_2O_3 variations in garnets and P-T conditions, the concurrent trace element variations, the apparent absence of primary spinel, and the restricted range of estimated P-T conditions rather suggest a major role of metasomatic processes on garnet geochemistry. Compositional variations such as those observed in Zagadochnaya garnets are often reported in garnet peridotites from other localities (*e.g.*, Burgess & Harte, 2004). As yet, however, no quantitative modelling of these variations has been provided, which takes into account the combined effects of fractional crystallization and of chromatographic and assimilation processes during percolation of metasomatic melts through the mantle column. In this work, numerical simulations of melt-rock interactions (Plate Model; Vernières *et al.*, 1997) were performed, which allowed to assess the relative contributions of the different mantle-melt processes. The results show that the wide spectrum of REE compositions observed from Group A to Group B to Group C can be produced by a unique episode of melt injection and percolation through a refractory mantle column, whereby the melt progressively changes its composition due to chromatographic ion exchange, fractional crystallization of garnet and clinopyroxene, and assimilation of peridotitic minerals, under decreasing melt/rock ratios (Zibera *et al.*, 2013b). The trace element composition of the melt appears to be distinct from that of the host kimberlite.

CONCLUDING REMARKS

The results obtained in this work provide new valuable constraints for thermobarometric and geochemical studies on peridotitic garnets and clinopyroxenes from kimberlites. Thanks to a detailed evaluation, and a new optimized analytical procedure, single-clinopyroxene geobarometry can now be applied with reasonable confidence to a wider variety of clinopyroxene compositions, thus allowing better definition of mantle thermal state and diamond potential. High-quality analyses will not eliminate recognized underestimation of pressure at $P > 4.5$ GPa, but a recalibration of the geobarometer is not possible at present, due to the lack of accurate thermodynamic data for Cr- and Na-bearing clinopyroxenes. New constraints and modelling hints were also provided for the quantitative petrochemical characterization of peridotitic garnets and clinopyroxenes from cratonic settings. They allow *i*) more reliable assessment of relationships between mineral chemistry, phase relations, and P-T conditions of equilibration in mantle harzburgitic and lherzolitic assemblages, and *ii*) better interpretation of the effects of melt/peridotite reactions on REE contents in garnets. In particular, Plate Model numerical simulations demonstrated that the coexistence of (Cr, Ca)-rich garnets with sinusoidal CI-normalized REE patterns and (Cr, Ca)-poor garnets with normal REE patterns, which is often observed in kimberlites, can be the result of a unique melt percolation event through the mantle column and does not necessarily imply involvement of genetically unrelated metasomatic melts.

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