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Cycle: XXV

Abstract

Interpreting the evolution of lithospheric mantle from the study of peridotitic garnets and clinopyroxenes requires a good understanding of relationships between pressures and temperatures of formation, upper mantle phase relations and trace element signatures of petrochemical processes. This PhD tackles these issues by integrating three lines of research. i) Evaluation of single-clinopyroxene geobarometry for garnet peridotites: it can be extremely sensitive to analytical uncertainties for particular clinopyroxene compositions, but a new optimized analytical procedure allows a better definition of clinopyroxene-based geotherms. ii) Thermodynamic modeling of chromium-bearing peridotitic systems: it provides a quantitative explanation of compositional variations in peridotitic garnets coexisting with spinel. iii) The case study of garnet xenocrysts from the diamond-free Zagadochnaya kimberlite (Yakutia): a detailed thermobarometric and major and trace element study provides new insights into petrochemical processes during ascent of kimberlitic melts through the lithospheric mantle, and their bearing on diamond potential of kimberlites.

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 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 modeling 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•Na•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, I 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 new optimized analytical procedure was successively tested on a new clinopyroxene xenocryst suite (\( N = 120 \)) from the Novinka kimberlite pipe (Upper Muna field, Siberia), which contained a large fraction of samples with low \( a_{Cr}/Cr# \) ratios. With respect to the results based on analyses acquired using standard conditions, the scatter of P–T estimates was significantly reduced, allowing a much better definition of the thermal state beneath Novinka.

Based on a refined version of the dataset of Nimis & Grütter (2010), in which only xenoliths containing clinopyroxenes with “safe” compositions were considered, 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 (cf. 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.

**Part 2: Thermodynamic modeling 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 and Petrini 2002). I employed the internally consistent thermodynamic database of Holland and 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 phase equilibria and 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. 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 (cf. 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, and this work), providing a great opportunity to investigate the petrochemical processes in this sector of the Siberian Craton and their relationships with diamond potential. Here I studied 28 representative garnet xenocrysts, performing a detailed petrographic study on back-scattered electron images, combined with in-situ major and trace element analyses. The results allowed to interpret the garnets as fragments of depleted to fertile lherzolite and to distinguish three main compositional groups. Group A garnets (Cr$_2$O$_3$ = 1.3–5.2 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 (Cr$_2$O$_3$ = 5.4–8.6 wt%) are less depleted in Light REE (LREE) and show nearly flat patterns from Sm to Lu; Group C garnets (Cr$_2$O$_3$ = 7.3–8.4 wt%) are characterized by humped to strongly sinusoidal REE patterns, with Yb between 0.5 and 3.0 xCl. 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 may suggest a potential relationship between Cr$_2$O$_3$ 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. The composition of the melt appears to be distinct from that of the host kimberlite.

Most of Group B and C garnets show evidence of replacement by a secondary mineral assemblage made of (Ca, Cr)-poor garnet, chromian diopside, and chromite (± phlogopite ± amphibole). The (Ca, Cr)-poor garnets are enriched in almost all incompatible trace elements, and often show humped CI-normalized REE patterns. The textures and mineralogy of these secondary mineral assemblages, the calculated compositions of the melts in equilibrium with the secondary garnets and clinopyroxenes, and...
Ca concentration profiles across garnet zoning, indicate deep-seated (90–130 km) pervasive reaction with melts strictly related to the host kimberlite.

The lack of mantle materials from depth greater than 130 km, the absence of diamond, the abundance of secondary mineral assemblages, and the high-Mg composition of the kimberlite are consistent with a relatively slow ascent of the melts to shallow lithospheric levels and extensive melt–mantle interactions before eruption. This scenario might also apply to other, geochemically similar, diamond-free kimberlites from the same kimberlitic field.

Conclusions

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.

References


SUMMARY OF PhD'S ACTIVITIES

Courses:
SALMASO, L., CORAIN, L.: "Statistica applicata alla sperimentazione scientifica", Centro Studi per l'Ambiente Alpino, S. Vito di Cadore, Università degli Studi di Padova.
CAMARA, F.: "Risoluzione strutturale di sostanze inorganiche a struttura cristallina ignota", Dipartimento di Geoscienze, Università degli Studi di Padova.
NESTOLA, F.: “Metodologie analitiche”, Dipartimento di Geoscienze, Università degli Studi di Padova.
CESARE, B.: “Corso Breve di Inclusioni Fluide”, Dipartimento di Geoscienze, Università degli Studi di Padova.
PUTNIS, A.: “Mineralogische Prozesse”, Westfälische Wilhelms-Universität Muenster (Germany).
ANGEL, R. J.: “Scientific Communication in English”, Dipartimento di Geoscienze, Università degli Studi di Padova.

Schools and workshops
BODNAR, R. J., DANYUSHEVSKY, L. V., WEBSTER, J. D.: "Short course on fluids in the Earth". October 25th–29th, Napoli.

BAYERISCHES GEOINSTITUT and DEUTSCHE MINERALOGISCHE GESELLSCHAFT: “High-pressure experimental techniques and applications to the earth’s Interior”. February 13th–17th 2012, Bayreuth.

Oral communications:

Posters:

**Publications:**


**Teaching activities:**


**Experimental activities:**

Major elements analysis of garnet and clinopyroxene grains with CAMECA "CAMEBAX" electron microprobe at the IGG-CNR, Unit of Padua.

In-situ trace element analyses of garnet and clinopyroxene grains by laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) at IGG-CNR, Unit of Pavia.

SEM analysis on garnet grains and associated inclusions at the Dipartimento di Geoscienze, Università degli Studi di Padova.

**Other:**

Visit of Bayerisches Geoinstitut (Bayreuth, Germany) in May 2010, to learn the analytical technique for the determination of ferric iron by electron microprobe (Flank method) on garnets.

Co-organiser for the school: “Diamonds, the mantle petrologist’s best friends”, hosted in Bressanone by the University of Padova joint with University College London, February 21st to 26th 2011.

Attending the “10th International Kimberlite Conference”, February 6th-11th, Bangalore.

Pre-Conference Field Trip to South Indian Kimberlites (10th International Kimberlite Conference). February 1st-5th, India.

Visit of the Institute of Mineralogy at the University of Münster (Germany) in April 2011, December 2011, and from April to June 2012, to learn the thermodynamic modeling of peridotitic systems using advanced modelling program “perple_x” (in collaboration with Prof. Stephan Klemme).