

## The pyroxenite-diamond connection

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### Abstract

Pieces of the Earth's mantle occurring either as tectonic fragments or xenoliths in volcanic rocks are dominantly peridotites, assemblages of olivine, ortho- and clinopyroxene with minor garnet and/or spinel. They frequently contain pyroxene-rich inclusions which have compositions intermediate between peridotite and basalt. These pyroxenites typically contain varying amounts of more iron-rich (than peridotite) clinopyroxene, orthopyroxene, garnet and/or spinel and are commonly compositionally layered. Surprisingly, despite their subordinate abundance in mantle fragments, pyroxenitic compositions appear to be the dominant sources of majoritic garnet inclusions in diamonds, the principal window into the mineralogy of the deep upper mantle and the transition zone (Kiseeva *et al.*, 2013a). In this study we show that the pyroxenite-diamond association is a consequence of the interaction between basaltic and peridotitic compositions in the presence of carbonate melt and that layering of the pyroxenites is a natural consequence of this interaction. Reduction of carbonate to carbon at high pressures is responsible for the genetic connection between pyroxenite and diamond and the abundance of pyroxenitic inclusions reflects this connection rather than a high abundance of this rock type in the mantle.

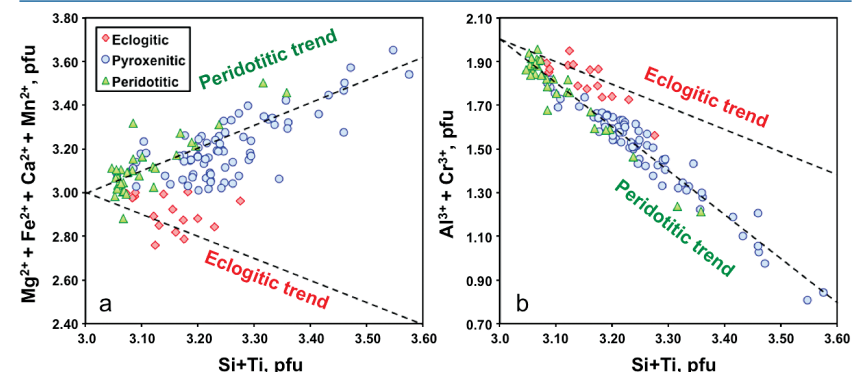
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### Letter

Between 8–15 GPa, with increasing pressure the orthopyroxene and clinopyroxene of peridotite dissolve into garnet through the peridotitic “majorite” substitution:  $2\text{Al}^{3+} = \text{Si}^{4+} + \text{M}^{2+}$ , where  $\text{M}^{2+}$  represents divalent Mg, Fe, Ca and Mn (Fig. 1). In the transition zone (410–660 km depth) “peridotite” thus becomes a biminer- alic rock composed of majorite plus a high pressure polymorph of  $(\text{Mg,Fe})_2\text{SiO}_4$  (wadsleyite or ringwoodite). Under the same conditions basalt initially transforms to eclogite (garnet plus clinopyroxene) and then with increasing pressure the clinopyroxene dissolves into the garnet through a combination of the peridotitic

substitution and a second eclogitic substitution:  $\text{M}^{2+} + \text{Al}^{3+} = \text{Na}^+ + \text{Si}^{4+}$ . In this case, the garnets become richer in Si and Na and poorer in Al and, in the deepest parts of the transition zone (pressure >18 GPa), eclogite becomes monomineralic garnetite.

Majoritic garnets are fairly common inclusions in sublithospheric diamond and, based on their compositions, are generally categorised as either “eclogitic” (high Ca, low Cr, low  $\text{Mg\#} = 100\text{Mg}/(\text{Mg}+\text{Fe})$ ) or “peridotitic” (low Ca, high Cr, high  $\text{Mg\#}$ ). Kiseeva *et al.* (2013a) showed, however, that the majority of the inclusions exhibit the peridotitic substitution, but have high Ca (up to 14.7 wt. %  $\text{CaO}$ ), low Cr (<0.53 wt. %  $\text{Cr}_2\text{O}_3$ ) and low  $\text{Mg\#}$  (~50–80) indicating source compositions intermediate between those of eclogite and peridotite (Figs. 1, 2; Hirschmann and Stolper, 1996). These intermediate compositions are broadly pyroxenitic (Kiseeva *et al.*, 2013a). The potential implication is that pyroxenite could be a major rock type in the mantle transition zone, a hypothesis explored extensively 30 years ago (Anderson and Bass, 1986). An alternative possibility is that inclusions in diamond are biased toward the pyroxenite lithology, which requires an intimate connection between the source of diamond carbon and pyroxenite generation. This connection is investigated here.

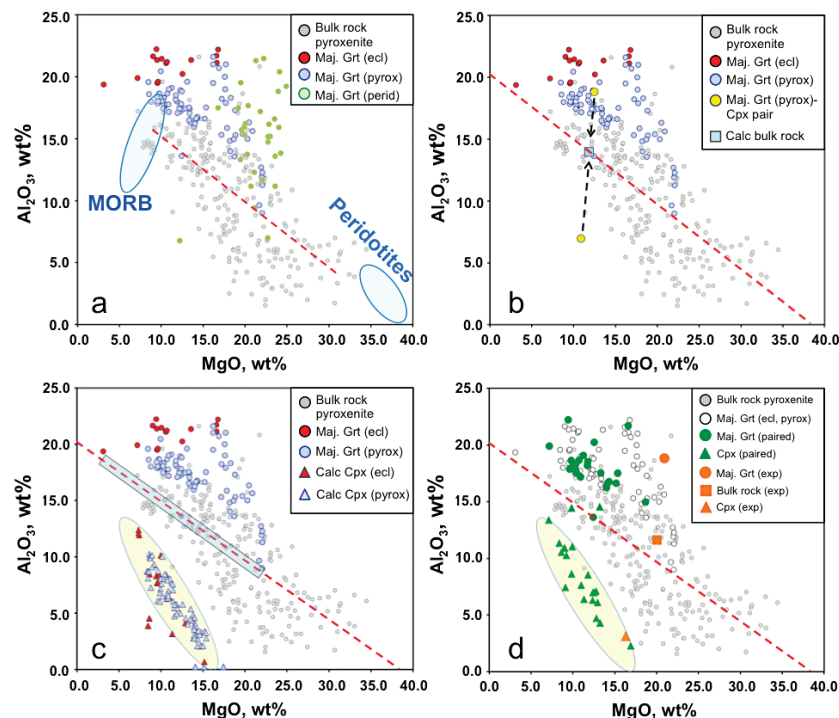


**Figure 1** Compositions of 16 eclogitic, 75 pyroxenitic and 32 peridotitic majorite inclusions in natural diamonds as functions of  $(\text{Si} + \text{Ti})$  pfu (per formula unit), showing (dashed lines) the theoretical “peridotitic” and “eclogitic” substitutions discussed in the text (after Kiseeva *et al.*, 2013a).

Figure 2a shows the compositions of majoritic inclusions, MORB, peridotites and pyroxenites. Garnets of pyroxenitic affinity are higher in  $\text{MgO}$  and lower in  $\text{Al}_2\text{O}_3$  than those of eclogitic affinity. Using geobarometers based on the Si content of majoritic garnet (Collerson *et al.*, 2010; Beyer, 2015), these inclusions were formed at pressures of 7–18 GPa with values above 15 GPa being rare. At these pressures clinopyroxene should coexist with the garnet in some, but not all, pyroxenitic compositions, an inference which is supported by general compositional differences between majorite garnet and bulk MORB and pyroxenite

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**Figure 2** Bulk compositions of natural pyroxenites (grey circles) plotted in  $\text{MgO}$ - $\text{Al}_2\text{O}_3$  compositional space. Dashed red line shows the regression line for all the pyroxenites. (a) Compositions of majoritic inclusions in diamonds of eclogitic (red), pyroxenitic (blue) and peridotitic (light green) affinities. Fields of bulk rock peridotite and MORB are shown as blue ovals. (b) Tie line between a majoritic garnet and calculated coexisting clinopyroxene (Cpx; see text for details). A possible bulk rock composition for this pair was placed on the red regression line. (c) Population of natural majoritic garnets and reconstructed clinopyroxene compositions. Field of Cpx compositions is shown with the yellow oval. Note wide range of potential bulk (pyroxenitic) source rock compositions. Placement of the latter around the regression line is meant only to be indicative. (d) Majoritic inclusions in diamonds (green circles) which coexist with clinopyroxene(s) (green triangles) within the same diamond. The range of observed natural clinopyroxene compositions occupy the area predicted by our modelling. Orange circles show the bulk composition and the majorite-clinopyroxene pair which crystallised in an experimental run at 15 GPa and 2150 °C.

(Fig. 2a and Supplementary Information). Instances of 2 phase (clinopyroxene-garnet) assemblages in the same diamond are, however, rare, which may reflect a specific connection between the diamond-forming process discussed below and garnet. Nevertheless, we began by estimating the compositions of the clinopyroxenes with which the observed majoritic garnets should coexist. We used

around 50 high-pressure experiments on garnet-clinopyroxene pairs as a basis of our estimates (Supplementary Information). These experiments give us a Na partitioning expression:

$$Na_{Cpx}^{6ox} = \frac{Na_{Grt}^{12ox}}{0.262 + 0.0241P - 0.00014T} \quad \text{Eq. 1}$$

where P is in GPa and T is in K. In Equation 1, the Na contents of clinopyroxene (Cpx) and garnet (Grt) are cation values on 6 and 12 oxygen bases, respectively. We then assumed that, at these high pressures, tetrahedral Al in clinopyroxene is low (0.01 cations per formula unit) and that octahedral Al on the M1 site is Na plus octahedral Al coupled to tetrahedral Al (*i.e.*  $\text{NaAlSi}_2\text{O}_6$  and  $\text{CaAl}_2\text{SiO}_6$  substitutions respectively). We calculated the Ca content of the M2 clinopyroxene site by assuming that Na+Ca on this site is 0.95 cations per formula unit, thus allowing 0.05 of (Mg+Fe) on the large M2 site. We then assumed that Si is 2.0 minus tetrahedral Al and that Mg+Fe fill the remaining M1 and M2 sites. The ratio  $\text{Mg}/(\text{Mg}+\text{Fe})_{\text{Cpx}}$  was obtained from the garnet composition using our experimental observations which yield:

$$K_d^{\text{Grt-Cpx}} = \frac{[\text{Fe}/\text{Mg}]_{\text{Grt}}}{[\text{Fe}/\text{Mg}]_{\text{Cpx}}} \approx 2 \quad \text{Eq. 2}$$

In this study we use a database of 16 eclogitic, 75 pyroxenitic and 32 peridotitic majorites reported in the literature (Fig. 2a) and calculate a clinopyroxene composition for each one, shown in each one, shown in Figure 2b.

Figures 2a,b,c show bulk rock compositions of natural pyroxenites (*e.g.*, Hirschmann and Stolper, 1996) together with observed compositions of garnet inclusions in diamond and those of clinopyroxenes calculated to coexist with these garnets. Tie lines between garnet and clinopyroxene cross the pyroxenite field and, for the “pyroxenitic” inclusions cover almost the entire range of compositions of pyroxenites (Fig. 2c and Supplementary Information). For simplicity we have placed a putative “bulk” composition for the source of each inclusion on the red regression line through the pyroxenite compositional data of Hirschmann and Stolper (1996). Note that the recalculated clinopyroxenes occupy a fairly narrow field highlighted in Figure 2c by a yellow oval.

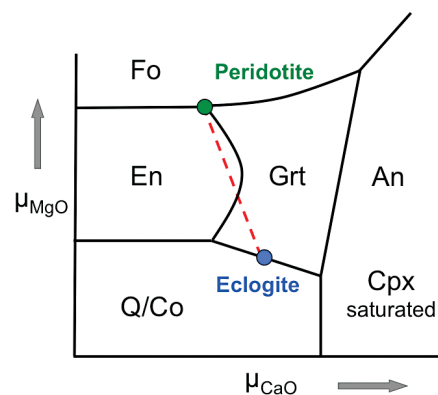
As mentioned above, inclusions of majoritic garnet and clinopyroxene in the same diamond are extremely rare, but nevertheless the few occurrences available enable us to test our calculation method (Fig. 2d). In Figure 2d we compare our field of calculated clinopyroxene compositions with the observed compositions of clinopyroxenes coexisting with garnet in the same diamond. As can be seen, the agreement is excellent. Similarly, in Figure 2d we show the results of an experiment in which a pyroxenitic bulk composition was reacted at 15 GPa and 2150 °C. Despite the extreme temperature, used to enhance reaction rates, the composition of clinopyroxene coexisting with garnet can also be seen to be in excellent agreement with our calculation approach.



The large number of pyroxenites found in ophiolitic complexes, alpine massifs, and as mantle xenoliths (Hirschmann and Stolper, 1996; Fig. 2a) suggest that there are common and widespread mechanisms for the formation of lithologies intermediate between a typical basalt (or eclogite) and peridotite. Given the wide range of compositions and mineralogies found in such “pyroxenites” it is likely that more than one mechanism applies (Downes, 2007). However, the predominance of sublithospheric garnet inclusions of pyroxenitic affinity (Kiseeva *et al.*, 2013a) strongly suggests that one important and widespread mechanism involves carbon. Since diamond is inert, the most plausible origin of the association is through interaction between eclogite and peridotite in the presence of carbonated melt or fluid.

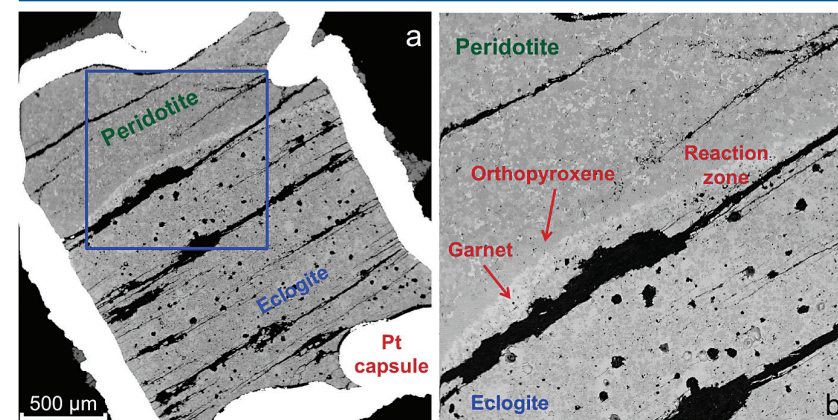
In order to investigate the possible formation of pyroxenite through the interaction of carbonated eclogite with peridotite we performed high-pressure sandwich experiments in a piston-cylinder apparatus. Model quartz-eclogite and peridotite compositions in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  (reduced in CaO content to take account of added carbonate) were mixed with ~5 % of  $\text{CaCO}_3$  and loaded on top of one another in a 3 mm Pt capsule. The capsule was welded shut and the experiments performed at 3 GPa and 1350 °C for between 1.5 and 8 hours (Supplementary Information). Under these conditions a  $\text{SiO}_2$ -poor carbonate melt develops from the  $\text{CaCO}_3$  introduced in the starting materials and enhances the rates of reaction between the two principal lithologies.

The experiments simulate a sharp compositional boundary between peridotite and basalt (coesite-eclogite at 3 GPa), analogous to the situation in subducted lithosphere having veins and lenses of basaltic composition dispersed in peridotite (Allègre and Turcotte, 1986). In such cases, according to Korzhinskii (1959), we would expect development of high variance assemblages, typically monomineralic zones, controlled by diffusion of major elements between the two components. Figure 3 shows a schematic (simplified) chemical potential diagram in  $\mu_{\text{CaO}}\text{-}\mu_{\text{MgO}}$  space which exhibits how mineralogical banding should develop between coesite-eclogite and peridotite.



**Figure 3** Chemical potential diagram (at fixed pressure and temperature) showing stabilities of phases coexisting with clinopyroxene. Curvature of garnet field boundaries is due to changing composition on passing from eclogite to peridotite (see text). Interaction between eclogite and peridotite will lead to gradients in chemical potentials of MgO and CaO (red dashed line) and layers of orthopyroxene next to peridotite and garnet next to eclogite. Fo – forsterite, En – orthopyroxene, Q/Co – quartz/coesite, Grt – garnet, An – anorthite, Cpx – clinopyroxene.

Both rocks contain clinopyroxene and garnet, but the excess  $\text{SiO}_2$  in the eclogite should react with the peridotite to form a layer of orthopyroxene ( $\pm$  clinopyroxene) next to the peridotite and a layer enriched in garnet and without coesite next to the eclogite. The garnet should become more Mg-rich as we pass from eclogite to peridotite and we have represented this predicted change with curved boundaries to the garnet field. Figure 4 shows back-scattered electron images of the products of experiment SA2-1 which generated the predicted monomineralic layers between eclogite and peridotite. As predicted, after 8 hours of reaction at 1350 °C, garnet composition changes progressively from 22.9 wt. % MgO, 8.8 wt. % CaO in the eclogite layer to 25.1 wt. % MgO, 7.0 wt. % CaO in the garnet layer to 27.0 wt. % MgO, 6.1 wt. % CaO in the peridotite. These phase compositions, in an idealised Fe-free system are consistent with those found in lherzolites and eclogites. The model sandwich experiments demonstrate, therefore, that zoned garnet pyroxenites may be formed as a result of a wall-rock reaction between silica-saturated, carbonated eclogite and silica-undersaturated peridotite.



**Figure 4** Back-scattered electron images of SA2-1 run products. The experimental conditions are 3 GPa and 1350 °C. Panel (b) shows an enlarged area from panel (a). Orthopyroxene (on the peridotite side) and garnet (on the eclogite-side) are formed within the reaction zone between carbonated eclogite and peridotite.

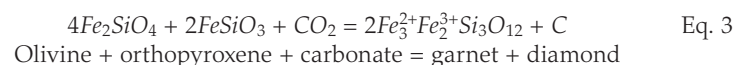
In the Beni Bousera peridotite massif of Morocco there are frequent veins and lenses of pyroxenite, with or without garnet. That these rocks have been subjected to high pressure (>4.5 GPa) is evidenced by the presence in the pyroxenites of graphite pseudomorphs after diamond (Pearson *et al.*, 1993). Boundaries between pyroxenite and peridotite are generally sharp and pyroxenite veins are often layered with margins of orthopyroxenite or websterite, consistent with Figure 3 and our experiments. The layering has previously been recognised as likely due to interaction between melts and peridotite, and the association





with carbon is consistent with our hypothesis of a connection between carbon and high pressure pyroxenite formation. In this case the carbon has  $\delta^{13}\text{C}$  of -16 to -28 per mil, consistent with subducted carbon and the pyroxenites have  $\delta^{18}\text{O}$  of +4.9 to 9.3 per mil suggesting an origin as altered oceanic crust. Trace element patterns of websteritic garnet inclusions in diamonds also suggest a mafic precursor source, most likely subducted heterogeneous oceanic crust (Aulbach *et al.*, 2002).

Estimates of the amounts of carbonate subducted into the mantle range from 2.4 to  $4.8 \times 10^{13}$  g of C per year (Dasgupta and Hirschmann, 2010) and numerous studies have indicated that most carbonate survives this process, carrying a characteristic isotopic signature into the deeper mantle (*e.g.*, Kerrick and Connolly, 2001; Yaxley and Brey, 2004). Based initially on density considerations and later on oxygen thermobarometry of garnet peridotites, however, Wood *et al.* (1990, 1996) calculated that carbonate would be unstable in the mantle at depths greater than 140–150 km and would oxidise  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ , the latter dissolving into garnet in reactions similar to:



Measurements of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios in garnets from the deeper parts of the continental lithosphere (*e.g.*, Woodland and Koch, 2003) support this hypothesis of increasing stability of diamond relative to carbonate with increasing depth. We also found direct evidence of diamond growing in carbonate in an experiment performed on carbonated eclogite at 13 GPa and 1400 °C (Kiseeva *et al.*, 2013b). Similarly, Stagno *et al.* (2013) have shown experimentally that, in normal mantle, carbonate is replaced by diamond and  $\text{Fe}^{3+}$ -bearing garnet at depths below ~160 km further confirming the validity of our model.

Our experimentally-tested model of the formation of inclusions in diamonds of pyroxenitic affinity therefore follows reaction between eclogite and peridotite in the presence of subducted carbonate to produce garnet-pyroxenite. This is followed by dissolution of pyroxene components into the garnet via the majorite substitution at pressures above ~7 GPa which shifts garnet composition into the general field of pyroxenite (Fig. 2a). The intimate association of C and garnet-bearing pyroxenite culminates with the breakdown of carbonate to diamond plus  $\text{Fe}^{3+}$ , the latter dissolving in the majoritic garnet. The preponderance of garnet inclusions over those of clinopyroxene may be explained by a combination of the shift of garnet composition into the pyroxenite field with increasing pressure (Fig. 2a) and the potential bias introduced by the diamond-garnet connection described above. The inheritance of shallow crustal signatures observed in sublithospheric pyroxenitic inclusion assemblages (*e.g.*, negative Eu anomalies at elevated MREE–HREE<sub>N</sub>; Tappert *et al.*, 2005) and elevated  $\delta^{18}\text{O}$  signatures (Ickert *et al.*, 2015) are predictable outcomes of our model. We conclude that the high relative abundance of “pyroxenitic” garnets as inclusions in diamonds

is a consequence of the genetic relationship between carbon and pyroxenite-formation rather than an indication of the high abundance of pyroxenite in the transition zone.

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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1601](http://www.geochemicalperspectivesletters.org/article1601)



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## References

- ALLÈGRE, C.J., TURCOTTE, D.L. (1986) Implications of a 2-component marble-cake mantle. *Nature* 323, 123–127.
- ANDERSON, D.L., BASS, J.D. (1986) Transition region of the Earth's upper mantle. *Nature* 320, 321–328.
- AULBACH, S., STACHEL, T., VILJOEN, K.S., BREY, G.P., HARRIS, J.W. (2002) Eclogitic and websteritic diamond sources beneath the Limpopo Belt – is slab-melting the link? *Contributions to Mineralogy and Petrology* 143, 56–70.
- BEYER, C. (2015) Geobarometry, phase relations and elasticity of eclogite under conditions of Earth's upper mantle. *PhD thesis*, University of Bayreuth, Interdisciplinary Institutions, 217pp.
- COLLERSON, K.D., WILLIAMS, Q., KAMBER, B.S., OMORI, S., ARAI, H., OHTANI, E. (2010) Majoritic garnet: a new approach to pressure estimation of shock events in meteorites and the encapsulation of sub-lithospheric inclusions in diamond. *Geochimica et Cosmochimica Acta* 74, 5939–5957.
- DASGUPTA, R., HIRSCHMANN, M.M. (2010) The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters* 298, 1–13.
- DOWNES, H. (2007) Origin and significance of spinel and garnet pyroxenites in the shallow lithospheric mantle: Ultramafic massifs in orogenic belts in Western Europe and NW Africa. *Lithos* 99, 1–24.



- HIRSCHMANN, M.M., STOLPER, E.M. (1996) A possible role for garnet pyroxenite in the origin of the "garnet signature" in MORB. *Contributions to Mineralogy and Petrology* 124, 185-208.
- ICKERT, R.B., STACHEL, T., STERN, R.A., HARRIS, J.W. (2015) Extreme  $^{18}\text{O}$ -enrichment in majorite constrains a crustal origin of transition zone diamonds. *Geochemical Perspectives Letters* 1, 65-74.
- KERRICK, D.M., CONNOLLY, J.A.D. (2001) Metamorphic devolatilization of subducted oceanic metabasalts: implications for seismicity, arc magmatism and volatile recycling. *Earth and Planetary Science Letters* 189, 19-29.
- KISEEVA, E.S., YAXLEY, G.M., STEPANOV, A.S., TKALCIC, H., LITASOV, K.D., KAMENETSKY, V.S. (2013a) Metapyroxenite in the mantle transition zone revealed from majorite inclusions in diamonds. *Geology* 41, 883-886.
- KISEEVA, E.S., LITASOV, K.D., YAXLEY, G.M., OHTANI, E., KAMENETSKY, V.S. (2013b) Melting and phase relations of carbonated eclogite at 9–21 GPa and the petrogenesis of alkali-rich melts in the deep mantle. *Journal of Petrology* 54, 1555-1583.
- KORZHINSKII, D.S. (1959) Physicochemical basis of the analysis of the paragenesis of minerals. Translated from Russian. Consultants Bureau, New York. 142pp.
- PEARSON, D.G., DAVIES, G.R., NIXON, P.H. (1993) Geochemical constraints on the petrogenesis of diamond facies pyroxenites from the Beni Bousera peridotite massif, North Morocco. *Journal of Petrology* 34, 125-172.
- STAGNO, V., OJWANG, D.O., MCCAMMON, C.A., FROST, D.J. (2013) The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature* 493, 84-90.
- TAPPERT, R., STACHEL, T., HARRIS, J.W., MUEHLENBACHS, K., LUDWIG, T., BREY, G.P. (2005) Subducting oceanic crust: the source of deep diamonds. *Geology* 33, 565-568.
- WOOD, B.J., BRYNDZIA, L.T., JOHNSON, K.E. (1990) Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* 248, 337-345.
- WOOD, B.J., PAWLEY, A., FROST, D.R. (1996) Water and carbon in the Earth's mantle. *Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences* 354, 1495-1511.
- WOODLAND, A.B., KOCH, M. (2003) Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters* 214, 295-310.
- YAXLEY, G.M., BREY, G.P. (2004) Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: implications for petrogenesis of carbonatites. *Contributions to Mineralogy and Petrology* 146, 606-619.

