

DIAMOND FORMATION AND MANTLE METASOMATISM: A TRACE ELEMENT PERSPECTIVE

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Until the 6th International Kimberlite Conference in 1995, trace element and in particular REE data on inclusions in diamonds, were, with few exceptions, (e.g. Shimizu and Richardson, 1987), an exotic commodity. Since then, a number of trace element studies have been completed using either SIMS (ion microprobe) or, more recently, laser ablation ICP-MS techniques. So far these data have been interpreted in the context of their specific diamond sources only. However, a combined data base of major and trace element analyses for inclusions in diamonds world-wide represents a powerful tool to assess the evolution of diamond sources in the lithospheric mantle and provides important constraints on the possible presence of fluids or melts during diamond formation.

PERIDOTITIC SUITE

The trace element chemistry of harzburgitic and lherzolitic inclusions in diamonds is assessed on the basis of analyses of 135 garnet inclusions (100 harzburgitic, 35 lherzolitic) from eight different cratons, including the works of Shimizu et al. (1997) and Wang et al. (2000), besides our own published and unpublished analyses. This data set had previously been filtered to exclude ten aberrant samples (determined by exceptionally high and low Nd and Ho). The data set covers the compositional space observed for garnet inclusions world-wide with the exception that no garnets with less than 4 wt% Cr₂O₃ were analyzed. Harzburgitic garnet inclusions are characterized almost exclusively by sinusoidal REE_N patterns whereas lherzolitic garnets show both sinusoidal patterns and flat MREE_N-HREE_N (Fig. 1).

Hoal et al. (1994) and Shimizu et al. (1997) explained sinusoidal REE_N patterns with disequilibrium models involving modification of pre-existing garnet and precipitation from a supersaturated melt. However, Van Orman et al. (2002) showed that the essential prerequisite for these two disequilibrium models – diffusion of REE in garnet decreases significantly from LREE to HREE – is inconsistent with experimental data. Normalization of REE concentrations of garnets to C1-chondrite visually implicates a more complex behavior of REE than in reality: if normalized to a garnet from a primitive mantle composition the REE pattern appear much simpler (Fig. 2). The steep positive slope within chondrite normalized LREE is just an artifact of rapidly increasing compatibility within the garnet structure due to decreasing ionic radius. Average harzburgitic and lherzolitic garnets have LREE enriched V-shaped REE-pattern, when compared to garnet from primitive mantle, and lherzolitic garnets

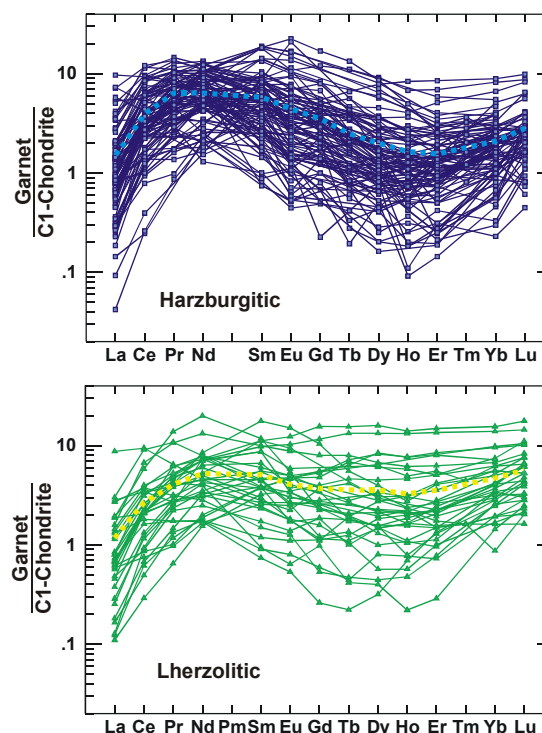


Figure 1: Chondrite normalized REE patterns of harzburgitic and lherzolitic garnet inclusions from world-wide sources. Average compositions are indicated as dotted lines.

with flat MREE_N-HREE_N (e.g. from the Birim deposits in Ghana) actually approach a primitive trace element composition. The consistency of certain characteristics, such as a fixed turning point at Er over a large compositional range from highly depleted to almost primitive compositions (Fig. 2) clearly is not in support of disequilibrium models either.

Thus only three hypotheses for the origin of peridotitic REE patterns are considered: (i) the patterns are an inherent characteristic of cratonic garnet peridotites, related to their primary formation, (ii) they are the result of a re-enrichment event that also modified the major element composition of these rocks, i.e. melt infiltration, and (iii) they were caused by fluid metasomatism involving CHO-agents enriched in incompatible trace elements, but without significant impact on major elements.

The first two hypotheses would require that discernible correlations between major and trace element compositions exist. The Cr/Al ratio (or Cr content) of garnet is a measure of the Cr/Al ratio of the source rock

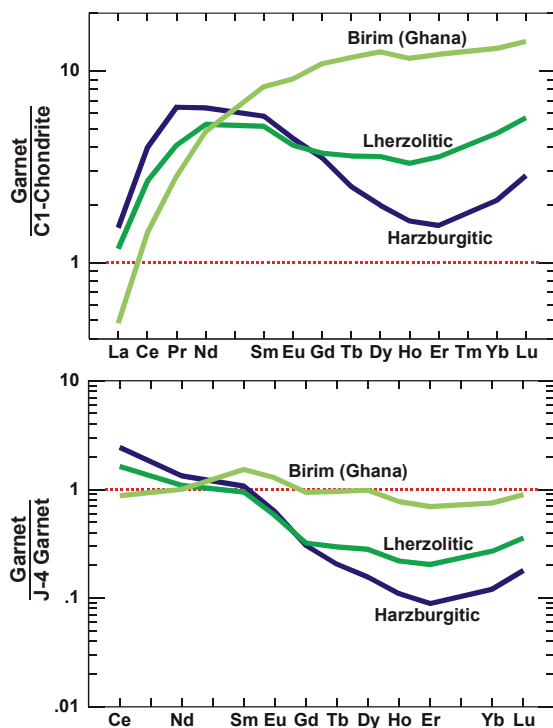


Figure 2: Average compositions of harzburgitic and lherzolitic garnet inclusions from world-wide sources and of three lherzolitic garnets with “flat” MREE-HREE from the Birim deposits in Ghana (Stachel and Harris, 1997). The data are normalized to C1-chondrite and to a garnet from a primitive mantle bulk rock composition (J-4 of Jagoutz and Spettel, see Stachel et al., 1998).

which in turn is a proxy for the degree of depletion in major elements. Griffin et al. (1999) have shown that this relationship is sufficiently strong to employ Cr in garnet to predict the major element and modal composition of cratonic garnet peridotites. Thus, the molar Cr-number ($100\text{Cr}/[\text{Cr}+\text{Al}]$) of garnet inclusions will be used to examine possible correlations between major and trace elements.

The shape of garnet REE_N patterns (Fig. 1) is determined by the existence and position of a peak within the LREE_N and by the slopes (i) within the LREE_N, (ii) from LREE_N to MREE_N and (iii) from MREE_N to HREE_N. The actual concentrations of REE are less diagnostic as they will be strongly influenced by the amount of modal garnet present. In addition, for lherzolitic garnets LREE concentrations (and consequently ratios of LREE to MREE and HREE) will be influenced by the presence of clinopyroxene.

No significant linear correlations between Cr-number and relative and absolute REE concentrations are observed for peridotitic garnets. However, for the harzburgitic garnets it is noted (i) that the highest La contents occur at Cr-number greater than 25 (Fig. 3) and (ii) that the few samples with positive LREE_N-MREE_N slopes (and high MREE and Y) or with extremely steep MREE_N-HREE_N (and high Yb and Lu) are restricted to Cr-numbers below 30 (Fig. 3). The apparent relationship between high Cr-number and high

average La content possibly reflects highly depleted rocks with low modal garnet, thus being very sensitive to metasomatic modification. Similarly, for the lherzolitic garnets positive slopes from LREE_N to MREE_N (super-chondritic Y/Nd in Fig. 3) and the highest concentrations in MREE-HREE (from Tb onwards) are restricted to Cr-numbers below 30, whereas the highest contents in Ce and also in Sr are found for the three garnets with Cr-number above 40. Sr contents above 2 ppm otherwise are only observed among harzburgitic garnets, suggesting that low modal clinopyroxene (possibly accompanied by low modal garnet) in the source of Cr-rich lherzolitic garnets may be the cause of relatively high Ce and Sr.

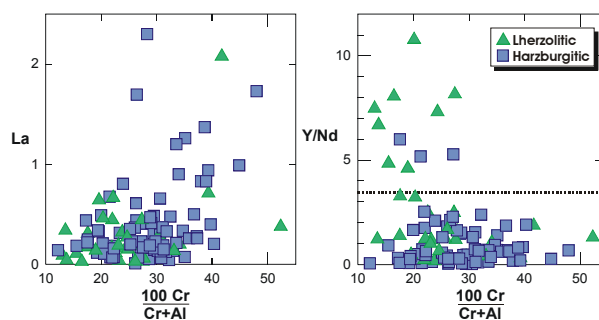


Figure 3: Covariations of REE (with Y as a replacement for MREE) and major element composition of garnet inclusions world-wide. The dotted line indicates the value of a chondritic Y/Nd ratio.

Despite the observation that a few harzburgitic samples with low Cr-number show low LREE_N/HREE_N or very low MREE_N/HREE_N, the REE_N patterns for the largest part of the harzburgitic garnets are independent from the bulk rock major element composition. For lherzolitic garnets it is evident that positive slopes from LREE_N to MREE_N-HREE_N are restricted to less Cr rich samples but this relationship does not take the form of a linear correlation and a number of samples with low Cr-number have sinusoidal patterns. The lack of a linear correlation between bulk rock major element and garnet REE composition excludes the possibility that the bulk rock trace element patterns are inherited from the primary processes, which caused the chemical depletion of the subcratonic lithospheric mantle. This reinforces the two stage model first proposed by Frey and Green (1974). However, for some lherzolitic and a very few harzburgitic garnets it appears that there is a direct relationship between MREE and/or HREE enrichment and decreasing depletion in the bulk rock major element composition. The non-linearity of this relationship may either be attributed to variations in the style of metasomatic overprint or in the degree of primary depletion of the source rock (leading to different starting compositions for metasomatic overprint), or both.

To test if there is a possible dependence of the style of metasomatic overprint on the thermal regime compositional parameters are plotted versus garnet-olivine equilibration temperatures (O'Neill and Wood, 1979; O'Neill, 1980; calculated for a fixed pressure of 5 GPa). For the data base evaluated here there is a

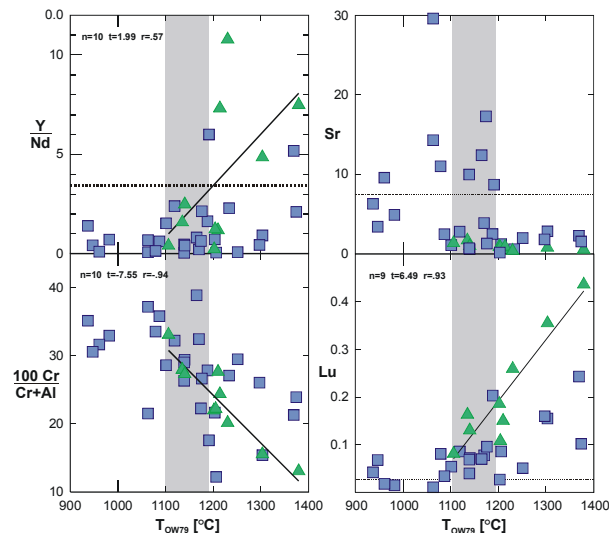


Figure 4: Covariations between compositional parameters of garnet inclusions and equilibration temperature (calculated from garnet-olivine equilibria for a fixed pressure of 5 GPa). Regression lines are based on Iherzolitic inclusions (green triangles) only. Dotted lines indicate chondritic abundance or ratio. The shaded area indicates the approximate temperature where a change in metasomatic regime appears to take place.

negative correlation between equilibration temperature and Cr-number (Fig. 4) which is particularly prominent for Iherzolitic garnets and which appears to possibly break down for harzburgitic garnets at temperatures below about 1100°C. This implies a decreasing degree of chemical depletion of the diamond source rocks with increasing temperature for all samples that formed above about 1100°C. For the ten Iherzolitic garnets where temperatures could be obtained, this increasing fertility in major elements correlates positively with the MREE-HREE from Eu onwards and with the other HFSE Ti, Y and Zr. For the harzburgitic garnets no linear relationships are observed, but high Sr (>3 ppm, see Fig. 4) and Ce (>4 ppm) are restricted to equilibration temperatures below about 1150-1200 °C, whereas high HREE (Yb >50 ppb and Lu >100 ppb, see Fig. 4) occur only in some of the samples which formed above 1150-1200 °C. Fig. 4 also shows that a similar, non-linear relationship exists for the $LREE_N$ - $MREE_N$ slope (represented by the Nd/Y ratio), where positive slopes for Iherzolitic and harzburgitic garnets only occur above 1190 °C.

These observations imply that the Iherzolitic diamond sources were affected by metasomatism, which increased in intensity with temperature and affected both major and trace elements. This coincides with the fact that formation of Iherzolitic diamonds generally takes place above the solidus temperature (about 1100-1150 °C at 5 GPa in the presence of CHO, e.g. Wyllie, 1987) facilitating percolation of silicate melts along grain boundaries. The bulk of the harzburgitic diamond sources, on the other hand, were affected by metasomatic processes that enriched incompatible trace elements but that show no relationship to equilibration temperature and major element composition. This

suggests metasomatism by CHO-fluids with highly fractionated trace element compositions (e.g. very high LREE/HREE) and is consistent with the high solidus temperature of harzburgite, which effectively prevents grain boundary percolation of dry silicate and carbonate melts (as they would freeze upon equilibration with the host rock). Metasomatism characterized by high Sr and Ce appears to be limited to relatively cool (below about 1150-1200 °C) harzburgitic sources which indicates that the most fractionated fluids appear to be absent at high temperatures. Only a few garnets, which equilibrated at temperatures above 1190°C, appear to be influenced by “Iherzolite style” metasomatism affecting the HREE and all of these samples have Cr-numbers below 30. Equilibration temperatures are still far below the harzburgitic solidus, but these samples may be derived from the vicinity of magmatic intrusions or the base of the lithosphere, where silicate melts may penetrate for some distance into a harzburgitic rock before they freeze upon equilibration. The observation that harzburgitic garnets show a (poor) linear correlation between equilibration temperature and Cr-number without accompanying trace element trends suggests operation of an additional process which cannot be constrained based on this data set.

ECLOGITIC SUITE

The, in part, very light carbon isotopic composition of eclogitic diamonds has been interpreted by numerous authors to reflect diamond formation from subducted organic matter (e.g. Frank, 1969, Kirkley et al., 1991). However, high equilibration temperatures of eclogitic inclusions are inconsistent with diamond formation within cold subducting slabs (Stachel et al., 2002) and it appears more likely that isotopic fractionation is the true cause of the observed range in $\delta^{13}C$ (Cartigny et al., 1998), which is conceivable because of the poor buffering capacity of eclogite for hydrous CO₂ fluids (Luth, 1993). Oxygen isotopic analyses (e.g. Macgregor and Manton, 1986; Jacob and Foley, 1999) nevertheless provide strong indications that eclogitic diamond sources probably have crustal protoliths. It is generally assumed that cratonic eclogites are not simply the metamorphosed equivalent of Archean seafloor, but that partial melting, probably in the eclogite stability field, lead to chemical depletion, thereby explaining the absence of a free SiO₂ phase. Based on REE analyses of 39 garnet and 22 clinopyroxene inclusions in eclogitic diamonds from six different cratons (including data from Taylor et al. (1996) and excluding four aberrant garnet and clinopyroxene analyses) it is possible to revisit the question of possible oceanic precursors.

Eclogitic garnets (Fig. 5) show REE_N pattern that are similar in shape to the most fertile Iherzolitic inclusions (see Fig. 2, Birim garnets), i.e. a steep positive slope within the LREE_N and fairly flat MREE_N-HREE_N, but at higher MREE-HREE concentrations (averaging at about 30x chondritic abundance). Eclogitic clinopyroxenes have positive slopes within the LREE_N, peaking at Nd and then slowly decrease in MREE_N and HREE_N to about chondritic abundance for Lu. This is

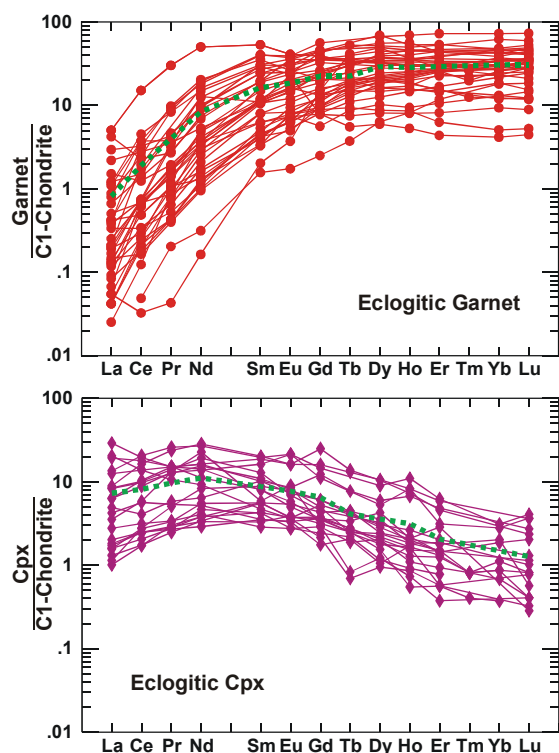


Figure 5: Chondrite normalized REE concentrations in eclogitic garnet (top) and clinopyroxene inclusions in diamonds from world-wide sources.

distinctive from the majority of peridotitic clinopyroxenes which often have negative slopes within the $LREE_N$ and sub-chondritic Lu. It has been shown that eclogitic diamond sources, after emplacement in the cratonic lithosphere, are affected by both metasomatic overprint and repetitive partial melting (e.g. Taylor et al., 1996). However, the overall consistency of the majority of analyses shown in Fig. 5 suggests that metasomatic overprint may not have completely eradicated the primary signature of the eclogitic sources and that perturbations in the bulk of the data may be limited to the most incompatible elements. Assuming that eclogite represents approximately equal proportions of garnet and clinopyroxene, an average source composition (Fig. 6) can be calculated based on the mean compositions shown in Fig. 5. This calculated mean composition compares extremely well with an N-MORB precursor that has lost about 10% of a partial melt in the eclogite stability field and that subsequently experienced some re-enrichment in LREE. Two garnet-clinopyroxene inclusion pairs in diamonds from Namibia may be used to support this interpretation: Both pairs yield similar bulk rock compositions for the MREE and HREE but differ in LREE, with Nam-203 resembling a strongly (ca 20%) melt depleted oceanic protolith and Nam-38 showing the effect of metasomatic re-enrichment in LREE. Additional support for the presence of “primary” trace element signatures comes from the observation of negative and positive Eu-anomalies in eclogitic inclusions in diamonds from Kankan (Guinea), Venetia (S.A.) and Namibia. We therefore conclude that the trace element

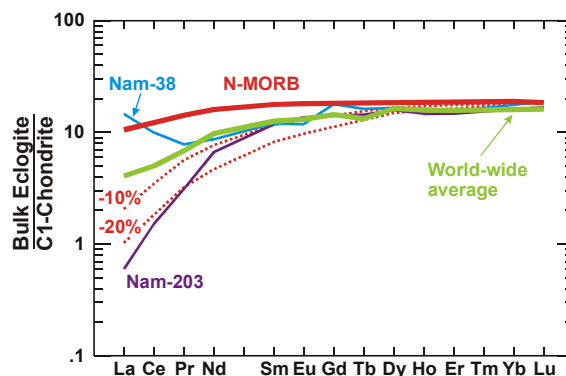


Figure 6: Based on a garnet-clinopyroxene ratio of 1:1, whole rock REE patterns are calculated (i) from the average compositions shown in Fig. 5 and (ii) for coexisting garnet-clinopyroxene pairs in two diamonds from Namibia. In addition the composition of N-MORB is shown together with residues of an original N-MORB composition after 10 and 20% of partial melt were removed in the stability field of eclogite (batch melting with a garnet-cpx residue).

signature of eclogitic inclusions in diamonds is in support of crustal protoliths. Similar to peridotitic sources, precipitation of eclogitic diamonds probably occurred in the course of infiltration by fluids/melts, as indicated by the close spatial relationship of eclogitic diamonds to metasomatic veins (Schulze et al., 1996; Taylor et al., 2000).

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