# Clinopyroxene–garnet partition coefficients for *REE*, Sr and Y, and their relationship to major-minor element composition

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## Introduction

Concentrations of *REE*, Ba, Sr, and Y have been measured by ion microprobe (SIMS) for garnet and clinopyroxene in a suite of eclogite xenoliths from the Roberts Victor kimberlite pipe in South Africa. The xenoliths span a wide range of compositions: garnets have $Ca/(Ca + Mg + Fe)$ ratios ranging from 0.08 to 0.50, and in clinoproxenes the associated substitution $Ca(Mg,Fe)_{-1}$ is accompanied by a substantial increase in jadeite end-member with the substitution $NaAlCa_{-1}Mg_{-1}$. Temperature estimates for the eclogites based on cpx/gnt Fe/Mg ratios are largely in the range 1000 to 1200°C, and there is no correlation of trace element partition coefficients with temperature estimates. The analyses show marked correlations of the cpx/gnt partition coefficients $(D_i)$ for *REE*, Sr and Y with major-minor element composition, and these correlations form the subject of this paper.

## Results

In general, decreasing cpx/gnt $D_i$ for traces were found to correlate particularly well with atomic $Ca/(Ca + Mg)$ or $Ca(R^{2+})$, with the strongest correlation being for garnet rather than clinopyroxene. The changes in $D_i$ across the whole range of compositions are exceptionally large, and for the *LREE* amount to approximately three orders of magnitude. Evidence for large changes in partition coefficients is also seen in other data for mantle eclogites. Fig. 1 illustrates the relationships for Nd and Tb, with our data shown in solid symbols, and data from Caporuscio and Smyth (1990) and Jerde *et al.* (1993) labelled 'C. & S.' and 'J. *et al.*' respectively.

In order to determine the relationship between the variation in trace element partition coefficients and changes in major-minor element composition, we have examined the variations in cpx/gnt trace element partition coefficients as a function of variations in major-minor element partition coefficients. Fig. 2 shows a plot of trace element $\ln D_i^{cpx/gnt}$ against $\ln D_{Ca}^{cpx/gnt}$ for the traces Sr, Nd, Eu and Y; where the asterisks indicate molar partition coefficients (symbolism after Beattie *et al.*, 1993). Good linear correlations between $\ln D_i^{cpx/gnt}$ and $\ln D_{Ca}^{cpx/gnt}$ are seen in Fig. 2, irrespective of trace element valency and concentrations. Similar excellent correlations have been obtained for most *REE*, and the correlation shown for Y is matched by that found for the heavy rare-earth Ho, of similar ionic radius to Y. Graphs of trace element $\ln D_i^{cpx/gnt}$ plotted against the cpx/gnt partition coeficients for: Mg*, Mg(*M2*)*, Fe*, Al(6)*, and Na* show much weaker correlations than those shown in Fig. 2.

The relationships between $\ln D_i^{cpx/gnt}$ for *REE*, Sr and Y with $\ln D_{Ca}^{cpx/gnt}$ have been examined by linear regression analysis. With the exception of La and Lu (which both have large analytical errors), the correlation coefficients ($R^2$) are $> 0.8$ and usually $> 0.9$. The data generally show straight line relationships of the form:

$$\ln D_{Nd}^{cpx/gnt} = (\ln D_{Ca}^{cpx/gnt})C_\gamma - C_G \qquad (1)$$

where Nd represents a trace element and $C$ and $C_G$ are empirical constants.

## Discussion

The foregoing data indicate the importance of considering substitution relationships, and consideration must also be given to the meaning of empirical constants in equation (1). Given the dominantly trivalent nature of the *REE* and Y, and the divalent nature of Ca, substitutions between these trace elements and Ca must involve vacancies or coupled substitutions in order to maintain charge balance. In the following we illustrate our approach using vacancy substitution as shown by the following equation:
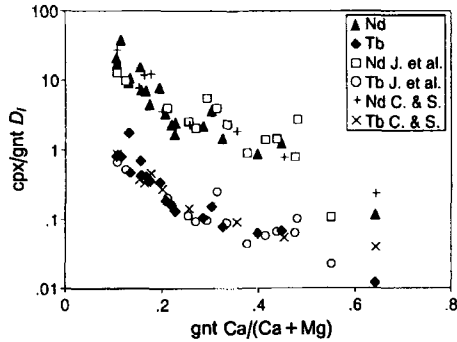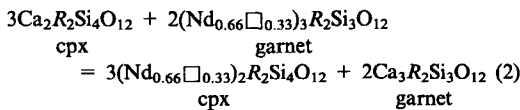
FIG. 1. Cpx/gnt partition coefficients (ppm in clinopyroxene/ppm in garnet) for Nd and Tb are shown for data from the present paper (solid symbols) in conjunction with data (labelled C&S) for Roberts Victor and Bobbejaan eclogites from Caporuscio and Smyth (1990), and data (labelled J et al.) for Siberian eclogites from Jerde et al., (1993).

$$3Ca_2R_2Si_4O_{12} + 2(Nd_{0.66}\square_{0.33})_3R_2Si_3O_{12}$$

cpx              garnet

$$= 3(Nd_{0.66}\square_{0.33})_2R_2Si_4O_{12} + 2Ca_3R_2Si_3O_{12} \quad (2)$$

cpx              garnet

In these equations (written for 12 oxygen formula units for both cpx and gnt), the contents of each type of site are enclosed in brackets and $\square$ indicates vacancies; Nd is used to exemplify a trivalent cation (REE or Y), whilst R refers to cations in [6]-fold coordination.

For (2), the equilibrium constant (K) expression may be formulated as:

$$K = \frac{(x_{Nd}^{cpx[8]} \cdot \gamma_{Nd}^{cpx[8]})^6 \cdot (x_{Ca}^{gnt[8]} \cdot \gamma_{Ca}^{gnt[8]})^6}{(x_{Ca}^{cpx[8]} \cdot \gamma_{Ca}^{cpx[8]})^6 \cdot (x_{Nd}^{gnt[8]} \cdot \gamma_{Nd}^{gnt[8]})^6} \quad (3)$$

where the X (cation or mole fraction) and $\gamma$ (activity coefficient) terms together give the activities of each species (Nd or Ca) in the Ca-bearing sites of each phase (cpx or gnt). The vacancy ($\square$) concentrations should be included in the K expression, but they have been omitted because we have no direct determinations of their relative abundances.

Rearranging the terms in equation (3) we have:

$$K = \left[ \left(\frac{x_{Nd}^{cpx}}{x_{Nd}^{gnt}}\right) \cdot \left(\frac{x_{Ca}^{gnt}}{x_{Ca}^{cpx}}\right) \cdot \left(\frac{\gamma_{Nd}^{cpx}}{\gamma_{Nd}^{gnt}}\right) \cdot \left(\frac{\gamma_{Ca}^{gnt}}{\gamma_{Ca}^{cpx}}\right) \right]^6 \quad (4)$$

and the ratios of the X terms correspond to Beattie et al.'s (1993) molar partition coefficients. Thus

$$K = \left[ (D_{Nd^{\bullet}}^{cpx/gnt}) \cdot (1/D_{Ca^{\bullet}}^{cpx/gnt}) \cdot (\gamma_{Nd}^{cpx/gnt}) \cdot (1/\gamma_{Ca}^{cpx/gnt}) \right]^6 \quad (5)$$
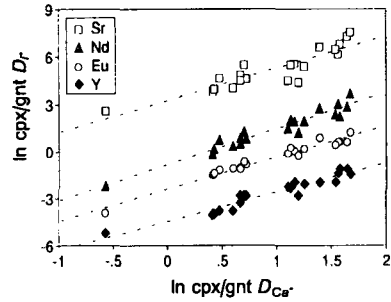


FIG. 2. Molar cpx/gnt partition coefficients, $\ln D_{i^\bullet}$, for Sr, Nd, Eu, and Y plotted against molar partition coefficients for $\ln D_{Ca^\bullet}^{cpx/gnt}$.

where $\gamma_{Nd}^{cpx/gnt}$ represents the ratio of the activity coefficients for Nd in clinopyroxene and garnet.

At equilibrium: $\Delta G^\circ = -RT\ln K$; and substituting into equation (5) we have:

$$\Delta G^\circ = -6RT[(\ln D_{Nd^\bullet}^{cpx/gnt}) - (\ln D_{Ca^\bullet}^{cpx/gnt})$$
$$+ (\ln \gamma_{Nd}^{cpx/gnt}) - (\ln \gamma_{Ca}^{cpx/gnt})] \quad (6)$$

$$\ln D_{Nd^\bullet}^{cpx/gnt} = \ln D_{Ca^\bullet}^{cpx/gnt} - \ln \gamma_{Nd}^{cpx/gnt}$$
$$+ \ln \gamma_{Ca}^{cpx/gnt} - \Delta G^\circ/6RT \quad (7)$$

The $\Delta G^\circ/6RT$ term in equation (7) will obviously vary as a function of temperature, but for samples from a limited range of temperatures such as those considered here, and assuming insignificant pressure variation, this term should effectively be a constant and may be regarded as the thermodynamic term equivalent to the empirical constant $C_G$ in equation (1).

Following Henry's Law, the activity coefficient term ($\gamma_{Nd}^{cpx/gnt}$) in equation (7) may be expected to be constant as a function of changing trace element concentration. However, in the present case we are dealing with large changes in major element composition, principally associated with the substitutions $CaMg_{-1}$ and $CaMgNa_{-1}Al_{-1}$, which apply regularly across the whole series of eclogites. Such considerations also apply to the term $\gamma_{Ca}^{cpx/gnt}$ (equation 7). Therefore, the variations in both $\gamma^{cpx/gnt}$ terms may be expected to be a regular function of $\ln D_{Ca}^{cpx/gnt}$ and thus become represented by the constant $C_\gamma$ in equation (1).

### References

Beattie, P. and many others. (1993) Geochim. Cosmochim. Acta, 57, 1605−6.

Caporuscio, F.A. and Smyth, J.R. (1990) Contrib. Mineral. Petrol., 105, 550−61.

Jerde, E.A., Taylor, L.A., Crozaz, G., Sobolev, N.V. and Sobolev, V.N. (1993) Contrib. Mineral.