

Comment on “Trace-element crystal chemistry of mantle eclogites” by F.A. Caporuscio and J.R. Smyth

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Received November 28, 1990/Accepted July 18, 1992

Abstract. Caporuscio and Smyth have presented crystal chemical study on eleven mantle-derived eclogites from the Bellsbank (8) and Roberts Victor (3) kimberlites, South Africa. They combine these results with experimental partition coefficients and geochemical modelling to argue for a high pressure igneous cumulate origin from a MORB-like melt for these eclogites. In particular, they highlight the kyanite-bearing eclogites (grosopydites), especially the presence of a “middle rare-earth-element (MREE) enrichment”, which may also be considered in terms of LREE and HREE depletions. Caporuscio and Smyth, as well as Smyth et al., cite this phenomenon as evidence for an origin by igneous accumulation of hyperaluminous clinopyroxene at high pressure. However, this type of REE pattern has also been interpreted as depicting a positive Eu anomaly inherited from a subducted, plagioclase-rich oceanic crustal protolith (Shervais et al., Taylor and Neal, Neal et al.).

This manuscript presents an alternative interpretation of the data presented by Caporuscio and Smyth. The results presented here demonstrate that high-pressure igneous accumulation of hyperaluminous pyroxene from a MORB-like liquid, followed by exsolution of major amounts of garnet and kyanite, is unlikely to account for all chemical signatures exhibited by grosopydites. Our approach is to undertake quantitative geochemical modelling of these processes using the actual samples and literature values quoted by Caporuscio and Smyth.

Previous work

In order to thoroughly evaluate the petrogenesis of any rock, the largest number of chemical parameters must be gathered and synthesized. On the basis of modal analyses, mineral and whole-rock major- and trace-element chemistry, as well as Sr, Nd, and O isotopes, we previously defined three groups of eclogites from the Bellsbank kimberlite (Neal and Taylor 1989, 1990a, b; Neal et al. 1989a, b, 1990; Pyle et al. 1987; Shervais et al. 1985, 1986, 1988; Taylor and Neal, 1989; Taylor et al. 1989, 1990). Group A eclogites

exhibit chemical signatures consistent with products of igneous accumulation from a Group II kimberlite magma, and this process can be modelled using both isotopic and trace element compositions. Groups B and C eclogites are considered to be the remnants of ancient subducted oceanic crust; Group B eclogites exhibit chemical signatures consistent with the basaltic portion, and Group C the plagioclase-rich cumulate portion. Evidence for this comes from the low $\delta^{18}\text{O}$ (+2.9 to +4.7‰) for these eclogite types relative to “typical” mantle values (~5.5‰). The light oxygen isotope values of the B and C eclogites are consistent with a crustal origin and could not have been directly generated within the mantle. The range in Sr and Nd isotopes ($\epsilon_{\text{Nd}} = +40$ to +219; $^{87}\text{Sr}/^{86}\text{Sr} = 0.70832$ to 0.71006—Neal et al. 1990) are consistent with an origin as seawater-altered oceanic crust. Similar results have been reported for Roberts Victor eclogites (Jagoutz et al. 1984, 1985; MacGregor and Manton 1986).

Rare-earth element concentrations

Shervais et al. (1988), Taylor and Neal (1989), Taylor et al. (1990), and Neal et al. (1989, 1990) concluded that the presence of a **positive Eu anomaly** in the Group C eclogites (grosopydites) from the Bellsbank kimberlite supports the role of plagioclase in the petrogenesis of these eclogites. It is this geochemical signature which Smyth et al. (1989) and Caporuscio and Smyth (1990) consider is simply MREE enrichment originating in the mantle through hyperaluminous clinopyroxene accumulation.

In order to further examine the shape of the REE profiles, we have recently performed ion microprobe analyses on several of the clinopyroxenes and garnets from the Bellsbank eclogite suite, both with and without garnet exsolution from clinopyroxene. We have effectively duplicated, but in far more detail, the profiles we had previously determined by INAA (Taylor and Neal 1989) and isotope dilution (Neal et al. 1990) and concluded that the terminology of “positive Eu anomaly” rather than “MREE enrichment” is properly applied to these eclogites/grosopydites. In fact, Fig. 3 of Caporuscio and Smyth (1990) depicts REE profiles analyzed by the ion microprobe for garnet in eclogite SBB-3H. This exhibits a positive Eu anomaly rather than a MREE enrichment,

and the composition quoted in the figure caption ($\text{Gr}_{50}\text{Alm}_{22}\text{Py}_{28}$) is consistent with a Group C classification.

Geochemical modelling

Parameters

Caporuscio and Smyth (1990) stated that grospyditic (Group C) eclogites resulted from the accumulation of hyperaluminous clinopyroxene, and we present quantitative modelling of this scenario. Hyperaluminous clinopyroxene is fractionated from a "typical MORB" liquid and then exsolved garnet and residual clinopyroxene REE compositions are calculated from this initial cumulate. The parental liquid used in this study is KD-11 of Kay et al. (1970) (Fig. 1a) and the hyperaluminous clinopyroxene/liquid partition coefficients of Shimizu (1980) (sample D-A-30-73; Fig. 1b), both as quoted by Caporuscio and Smyth (1990) (Table 1). In order to calculate the REE composition of exsolved garnet and residual clinopyroxene from this initial hyperaluminous cumulate, the garnet/cpx and cpx/garnet REE ratios (Fig. 1a and Table 1) have been calculated from the two grospydites described by Caporuscio and Smyth (1990) (SRV-1 and SBB-2H) (Fig. 1b and Table 2). It is possible that a third grospydite was reported by Caporuscio and Smyth (1990, Fig. 3), but this has been ambiguously labelled throughout their manuscript and will not be included here.

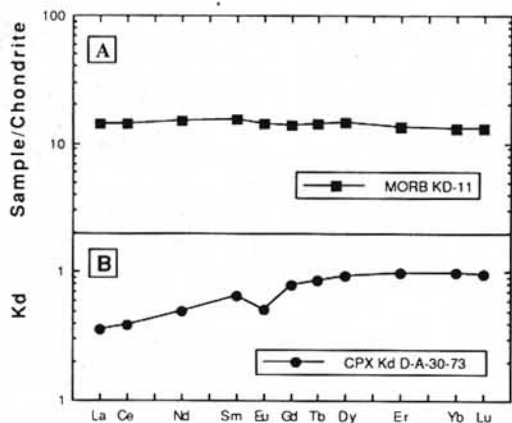


Fig. 1A, B. Modelling components, as quoted by Caporuscio and Smyth (1990). A the "typical MORB" KD-11 of Kay et al. (1970); B the hyperaluminous clinopyroxene crystal/liquid partition coefficients of Shimizu (1980)

Table 1. Modelling parameters. Where possible, profiles have been extrapolated to include other REE

	MORB ^a KD-11	CPX Kd ^b D-A-30-73	SRV-1 ^c Cpx/Gt	SRV-1 ^c Gt/Cpx	SBB-2H ^c Cpx/Gt	SBB-2H ^c Gt/Cpx
La	4.66	0.355	1.46	0.683	3.73	0.268
Ce	12.33	0.387	0.746	1.34	2.36	0.424
Nd	9.49	0.497	0.235	4.26	1.47	0.678
Sm	3.10	0.641	0.063	15.9	0.246	4.07
Eu	1.11	0.512	0.056	18.0	0.203	4.93
Gd	3.80	0.795	0.044	22.8		
Tb	0.82	0.867	0.040	25.2	0.289	3.46
Dy	4.98	0.940	0.033	30.4	0.231	4.33
Er	3.04	0.992	0.024	41.0		
Yb	2.89	0.990	0.017	59.6	0.034	29.0
Lu	0.44	0.968	0.029	34.3	0.042	23.7

^aKay et al. (1970); ^bShimizu (1980); ^cCaporuscio and Smyth (1990)
KD-11 in ppm; all others are ratios

Table 2. Modelling results

	Hyperaluminous Clinopyroxene Cumulative		Calculated SRV-1		Analyzed SRV-1 ^a		Calculated SRB-2H		Analyzed SRB-2H ^a	
	CPX	GT	CPX	GT	CPX	GT	CPX	GT	CPX	GT
La	1.65	2.41	1.13	0.477	0.326	6.15	0.442	0.835	0.224	
Ce	4.77	3.56	6.39	1.06	1.42	11.26	2.02	1.52	0.644	
Nd	4.72	1.11	20.1	1.05	4.47	6.94	3.20	0.585	0.397	
Sm	1.99	0.125	31.6	0.165	2.63	0.49	8.10	0.044	0.179	
Eu	0.568	0.032	10.2	0.085	1.53	0.115	2.80	0.030	0.148	
Gd	3.02	0.133	68.9	0.058	1.32					
Tb	0.711	0.028	17.9	0.01	0.252	0.205	2.46	0.026	0.090	
Dy	4.68	0.150	142	0.045	1.37	1.08	20.3	0.233	1.01	
Er	3.02	0.072	124	0.020	0.820					
Yb	2.86	0.049	170	0.012	0.715	0.10	82.9	0.018	0.522	
Lu	0.426	0.012	14.6	0.003	0.103	0.018	10.1	0.003	0.071	

^aData from Caporuscio and Smyth (1990)

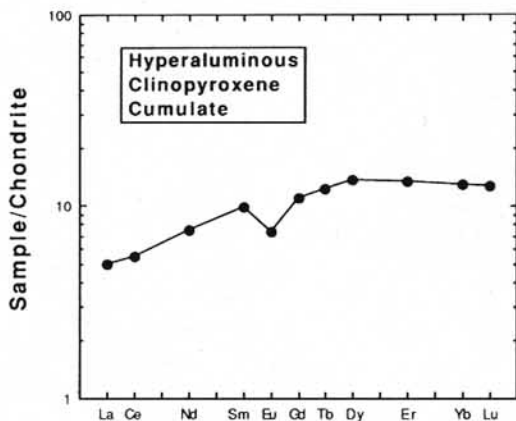


Fig. 2. The chondrite-normalized REE pattern of a hyperaluminous clinopyroxene cumulate calculated from the components in Fig. 1 and assuming 100% clinopyroxene crystallization. This is consistent with the experimental observations of Shimizu (1980) that only clinopyroxene would crystallize at depth

The most important aspect of the modelling parameters is the nature of sample D-A-30-73 of Shimizu (1980), the hyperaluminous clinopyroxene/liquid partition coefficients. Note from Fig. 1b that if these partition coefficients are correct, any hyperaluminous clinopyroxene cumulate from a MORB-like melt will be LREE-depleted and HREE-enriched with a negative Eu anomaly. Furthermore, these partition coefficients will not produce a MREE-enrichment in a hyperaluminous clinopyroxene cumulate from a MORB liquid. In fact, unless the postulated MORB liquid has a pronounced positive Eu anomaly, the cumulate will intuitively contain a negative Eu anomaly. Figures 2 and 3 of Caporuscio and Smyth (1990) reveals distinct positive Eu anomalies, as do Group C Bellsbank eclogite REE patterns shown by Taylor and Neal (1989; Fig. 4).

Results

The hyperaluminous clinopyroxene cumulate, calculated by assuming 100% clinopyroxene crystallization, is LREE-depleted and HREE-enriched with a negative Eu anomaly (i.e., no overall MREE-enrichment is produced; Fig. 2 and Table 2). The calculation of exsolved garnet and residual clinopyroxene REE profiles from this cumulate was carried out by applying the cpx/garnet and garnet/cpx partition coefficients (Table 1 and Fig. 3a) to the calculated initial hyperaluminous clinopyroxene cumulate. As we are assuming equilibrium and a closed-system process, proportions of garnet are not important and simply multiplying the cumulate composition by the cpx/garnet (to obtain the clinopyroxene REE profile) or the garnet/cpx (to obtain the garnet REE composition) partition coefficient is sufficient (Fig. 4).

SRV-1. The garnet analyzed from SRV-1 contains a REE profile which is LREE-depleted, but convex upward

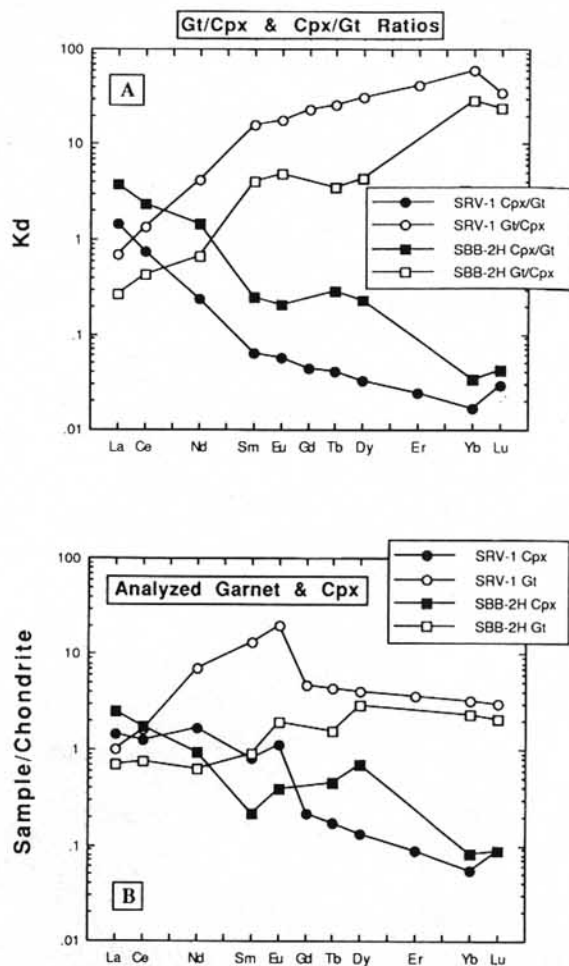


Fig. 3. A garnet/clinopyroxene and clinopyroxene/garnet partition coefficients calculated for gneissites SRV-1 and SBB-2H; B chondrite-normalized REE profiles for clinopyroxene and garnet from SRV-1 and SBB-2H. Data from Caporuscio and Smyth (1990)

(Fig. 3b) with a maximum at Eu [$\sim 19 \times$ chondrites: $(\text{Sm}/\text{Eu})_N = 0.65$]. The middle and heavy REE (Tb to Lu) are relatively flat at $4\text{--}5 \times$ chondrites. The calculated garnet REE profile (Fig. 4), using the garnet/cpx partition coefficients calculated from SRV-1, exhibits a steady increase in REE abundance from La ($\sim 3.5 \times$ chondrites) to Yb ($\sim 780 \times$ chondrites). A negative Eu anomaly is present [$(\text{Sm}/\text{Eu})_N = 1.2$]. The clinopyroxene analyzed from SRV-1 is LREE-enriched, but with a maximum at Nd ($1.7 \times$ chondrites; Fig. 3b). This may be due to the large errors associated with analyzing Nd by INA, but this is unclear from the description given by Caporuscio and Smyth (1990). The analyzed clinopyroxene contains a positive Eu anomaly [$(\text{Sm}/\text{Eu})_N = 0.74$], but no evidence of a MREE-enrichment (Fig. 3b). The calculated clinopyroxene REE profile is also LREE-enriched (Fig. 4), but like the

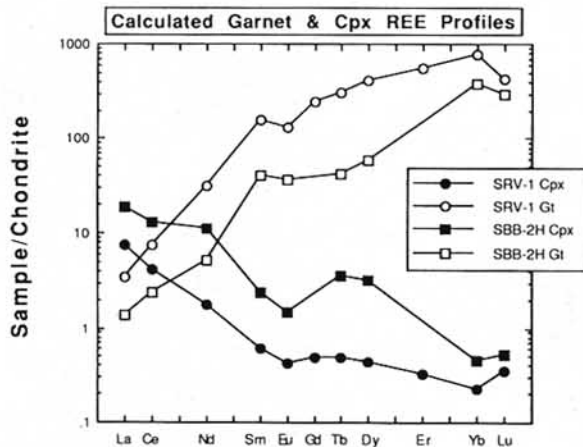


Fig. 4. Modelling results. Calculated garnet and clinopyroxene REE profiles (chondrite-normalized) after hyperaluminous clinopyroxene accumulation and garnet exsolution. Note that there is a negative rather than a positive Eu anomaly. Where possible, Gd and Er have been included by extrapolation of the REE profiles in Fig. 3

calculated garnet contains a negative Eu anomaly $[(\text{Sm}/\text{Eu})_N = 1.5]$.

SBB-2H. The garnet analyzed from SBB-2H contains a LREE-depleted profile which exhibits a general increase from La ($\sim 0.68 \times$ chondrite) to Yb ($\sim 2.3 \times$ chondrite). A positive Eu anomaly is evident (Fig. 3b) $[(\text{Sm}/\text{Eu})_N = 0.46]$. The calculated garnet REE composition is LREE-depleted with a maximum at Yb ($\sim 370 \times$ chondrites). There is a break in slope of the REE profile between Sm and Tb (Fig. 4), which may be interpreted as a negative Eu anomaly $[(\text{Sm}/\text{Eu})_N = 1.1]$. The clinopyroxene analyzed from SBB-2H contains a generally LREE-depleted, but if the values quoted by Caporuscio and Smyth (1990) are plotted, a spiked REE pattern is evident (Fig. 3b), positive Dy and negative Sm anomalies are evident $[(\text{Sm}/\text{Eu})_N = 0.56]$! The calculated clinopyroxene REE profile is LREE-enriched with a maximum at La ($\sim 1.4 \times$ chondrites; Fig. 4). Again, a negative Eu anomaly is present $[(\text{Sm}/\text{Eu})_N = 1.6]$.

Discussion

This modelling demonstrates that hyperaluminous pyroxene cumulates crystallizing from a MORB-like liquid at high-pressure cannot contain a MREE-enrichment or positive Eu anomaly. Rather, using the parameters defined by Caporuscio and Smyth (1990), they should contain a negative Eu anomaly. If exsolution of garnet (and kyanite) is a closed system process, then it is impossible for the observed garnet and clinopyroxene REE patterns from the two grosspydites (SRV-1 and SBB-2H) to be generated by the exsolution process, especially as ion microprobe analyses of kyanite in Bellsbank eclogites demonstrate that kyanite essentially contains no REE (L.A. Taylor, unpublished data). Furthermore, the oxygen

isotopes of the Group C eclogites or grosspydites do not indicate a mantle derivation ($\delta^{18}\text{O} = +3.4$ to $+4.7\text{‰}$), but are more consistent with a protolith of seawater-altered MORB.

In our recent publications (Shervais et al. 1988; Taylor and Neal 1989; Neal et al. 1990), we have concluded that the positive Eu anomaly in Group C eclogites (grosspydites) is a remnant of plagioclase accumulation in the eclogite protolith. However, Caporuscio and Smyth (1990) stated that if grosspydites were derived from plagioclase accumulation, a LREE-enrichment, strong positive Eu anomaly, and slight Sr enrichment relative to MORB would be expected. We would agree with this if, after subduction, the protolith remained a closed system. Jerde et al. (1991) indicate that a convex-upward REE profile (i.e., MREE-enrichment) can be achieved by partial melting of the eclogite after transformation has occurred. The Nd isotopes of both the Group B and C Bellsbank eclogites (Neal et al. 1989, 1990; Taylor et al. 1989; Neal and Taylor 1990), which are considered to be related in that they are both derived from oceanic crust, demonstrate that these eclogites have experienced ancient depletions after the initial formation of the protolith. This is evident both in high Sm/Nd ratio and high ϵ_{Nd} . Caporuscio and Smyth (1990) also suggested that the high- Al_2O_3 content (29.0 wt.%) and non-existent K_2O content of their corundum grosspydite (SBB-2H) negates a crustal protolith for the Group C eclogites because such compositions does not resemble any crustal rock. However, Archean anorthosites have been reported containing up to 31 wt.% Al_2O_3 (Ashwal et al. 1983). This is significant as Sleep and Windley (1982) concluded that the Archean oceanic crust contained a significant proportion of plagioclase-rich cumulates, based upon thermal and buoyancy considerations. It is the effect of depletion event(s) which is significant in dictating the chemical composition of Group B and C eclogites.

The Nd model ages of the Group B and C eclogites suggest a final equilibration close to the Archean-Proterozoic boundary. The effect of depletion event(s) upon a plagioclase dominated REE pattern of the Group C eclogites (grosspydites) is to remove the LREE, K, and Sr, especially if the transition to eclogite has already taken place, producing the observed Group C or grosspydite trace-element compositions. This would lead inevitably to a LREE-depleted signature and would reduce, but not obliterate the positive Eu anomaly because although clinopyroxene does not preferentially incorporate Eu into its structure (e.g., Irving and Frey 1984; Green and Pearson 1985; Shimizu 1980), the positive Eu anomaly would have been substantial in the protolith, and it is the remnant of this anomaly which is now seen in the Group C basalts.

Conclusions

Modelling of grosspyditic (Group C) eclogite petrogenesis by high pressure (30 kb) accumulation of hyperaluminous from a MORB-like liquid using the parameters quoted by Caporuscio and Smyth (1990), followed by garnet (+ kyanite) exsolution cannot account for the observed

REE patterns in Group C eclogites/grosopydites. In fact, such a process produces eclogites with *negative* Eu anomalies. Therefore, these results demonstrate that petrogenesis by igneous fractionation of hyperaluminous clinopyroxene is not the mechanism by which such eclogites are formed. An alternative mechanism is that of plagioclase accumulation in an ancient (Archean) oceanic eclogite protolith followed by depletion(s) either during or after transformation to eclogite.

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Editorial responsibility: T. Grove