Ion microprobe determination of rare earth elements in perovskite from kimberlites and alnöites

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Abstract

Ion microprobe analysis of perovskite from kimberlites and alnöites permits the accurate determination of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Yb at the part per million level. Other rare earth elements (*REE*) are subject to interferences in the mass spectrum caused by matrix-derived molecular ions and cannot easily be determined with comparable precision. Chondrite-normalized plots of the ion probe *REE* data are smooth curves, confirming the superiority of this technique over electron microprobe methods at the levels of *REE* abundance found in these perovskites. The perovskites analysed contain between 2.8 and 7.1 wt. % *REE* oxides and are highly enriched in the light *REE*, having La/Yb ratios of 577–3229. These La/Yb ratios are not representative of the parental magmas but result from *REE* fractionation during crystallization of the perovskite. Parental magma La/Yb ratios are estimated to be of the order of 120–650. The lower La/Yb ratios (80–200) found for whole-rock kimberlites are considered to result from contamination by relatively heavy *REE*-enriched crustal material.

KEYWORDS: ion microprobe, rare earth elements, perovskite, kimberlite, alnöite.

Introduction and previous studies

PEROVSKITE ($CaTiO_3$) is a ubiquitous accessory phase in kimberlites and alnöites and is the principal host for incompatible elements such as the rare earths, Nb, Ta, Sr, Th and U (Mitchell, 1986). Previous studies (Ilupin *et al.*, 1971; Blagulkina and Tarnovskaya, 1975; Boctor and Boyd, 1979, 1980, 1981, 1982; Jones and Wyllie, 1984) have demonstrated that kimberlite perovskite may contain 2–16 wt. % total rare earth element (*REE*) oxides. Unlike perovskites found in carbonatites, kimberlite perovskites do not exhibit extensive solid solution towards lueshite ($NaNbO_3$) and loparite (Na,Ce,Ca)(Ti,Nb)O_3, and typically contain less than 10 wt. % total *REE* oxides (Mitchell, 1986).

Although existing studies confirm that kimberlite perovskites are enriched in the light *REE* (La–Gd), there is no agreement as to the abundances of the individual *REE* and of the heavy *REE* (Tb–Lu) in particular. Knowledge of the distribution of *REE* in perovskite is important in that Jones and Wyllie (1984) and Mitchell (1986) have suggested that kimberlite whole-rock *REE* distribution patterns are controlled by the amount and composition of the perovskite present. Knowing the *REE* content of perovskite is particularly important with respect to the controls that this phase has upon the *REE* geochemistry of kimberlite magmas during their differentiation.

No data are available regarding the distribution of *REE* in alnöite perovskites. Studies of their major element composition (Platt and Mitchell, 1982) and of alnöite whole rock *REE* geochemistry (Nixon *et al.*, 1980) suggest that the abundances and distributions of *REE* are similar to those of kimberlite perovskites.

Perovskites in kimberlites and alnöites form small (< 0.1 mm) crystals in the groundmass and commonly occur as complex intergrowths with

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rutile, spinel and ilmenite. Because of these characteristics it is commonly impractical or inordinately time consuming to obtain a pure separate of perovskite suitable for analysis by bulk methods. Although separates, obtained with some difficulty, have been analysed by Soviet geochemists (Ilupin *et al.*, 1971; Blagulkina and Tarnovskaya, 1974; Kozlov *et al.*, 1984) the majority of the existing data have been obtained by microbeam methods.

Electron microprobe analysis of perovskite is clearly advantageous in that mineral separates are not required; however, the technique suffers from having rather high detection limits. This is a consequence of the fact that the X-ray spectrum is crowded with lines and interferences are common, so that determination of the true backgrounds is uncertain. Consequently, Reed (1986) considered that the practical limit of detection for *REE* by wavelength-dispersive methods to be of the order of 200 ppm. Jones and Wyllie (1984), using methods devised by Exley and Smith (1982), suggest detection limits of 65–200 ppm. None of the electron microprobe methods are thus suitable for determination of the heavy *REE* at the relatively low concentrations found in kimberlite perovskites.

Jones and Wyllie (1984) have argued that the electron microprobe data of Boctor and Boyd (1979, 1980, 1981, 1982) contain serious analytical errors arising from a combination of a poor choice of analytical lines and backgrounds, inadequate assessment of interferences, and less than optimum sensitivity for the *REE* with the beam current and operating voltages employed. This assertion is based upon the observation that chondrite-normalized *REE* distribution patterns of Boctor and Boyd's data do not give smooth curves similar to the *REE* distribution patterns obtained by neutron activation analysis of whole-rock kimberlites. Jones and Wyllie (1984) thus believe that the Boctor–Boyd analytical method leads to overestimation of the heavy *REE* and underestimation of Sm. Exley and Smith's (1982) method in contrast results in data that plots as smooth curves on chondrite normalized distribution diagrams. Fig. 1 illustrates clearly the different distribution patterns produced by the two methods.

Fig. 1 also depicts data obtained by Blagulkina and Tarnovskaya (1975) using X-ray fluorescence analysis of bulk separates. The irregular distribution pattern suggests that serious analytical errors with respect to Pr and Dy abundances are present in the data.

The above discussion indicates in particular that electron microprobe methods are not satisfactory and that the Boctor–Boyd technique does not produce accurate data. Although Jones and Wyllie's (1984) data are satisfactory for light *REE*, the poor detection limits do not allow determination of the heavy *REE* and thus the complete *REE* distribution pattern. A particular drawback is the inability to obtain data for Eu abundances.

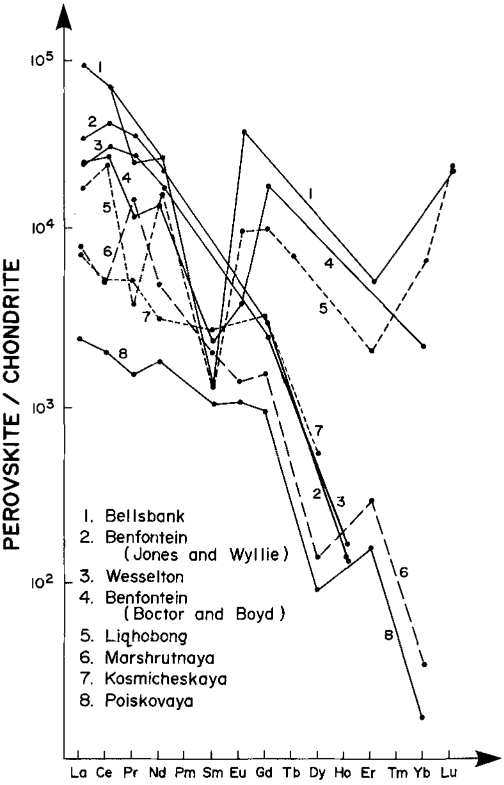

FIG. 1. Rare earth element distribution patterns for kimberlite perovskite: 1, Boctor and Boyd (1982); 2–3, Jones and Wyllie (1984); 4, Boctor and Boyd (1981); 5, Boctor and Boyd (1980); 6–8, Blagulkina and Tarnovskaya (1975).

These problems may be resolved by the use of ion microprobe analysis. This technique offers much lower detection limits for the *REE* as the secondary ion mass spectrum is almost free of background. Reed (1986) has applied the method successfully to a wide variety of accessory minerals and shown that smooth chondrite-normalized distribution patterns can be obtained with detection limits of 1–10 ppm for the heavy *REE*.

A drawback to the method is the presence of matrix effects which result in isobaric interferences on the analytical peaks. Despite this difficulty, ion microprobe analysis is shown in this study to provide data that are superior to those obtained by electron microprobe methods.

Ion microprobe methods

The ion microprobe used in the present study was an A.E.I. IM-20 as described by Banner and Stimpson (1974). The primary beam consisted of mass filtered ^{16}O-ions with an energy of 30keV relative to the specimen, to which a secondary ion accelerating potential of + 10 kV was applied. The primary beam diameter was 15-20 μm and the current approximately 20 nA. Specimens were polished and carbon-coated as for electron microprobe analysis.

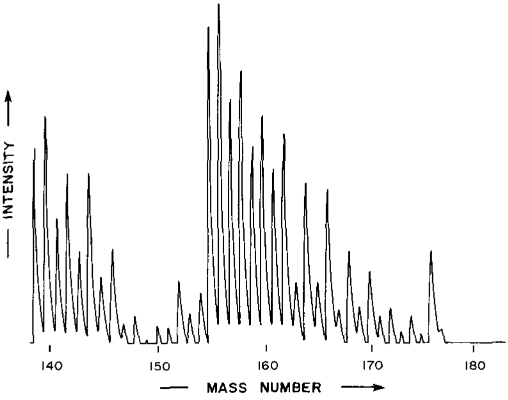

FIG. 2. Secondary ion mass spectrum of perovskite (logarithmic intensity scale).

Secondary ion intensities were recorded with an electron multiplier, the mass spectrometer being step-scanned through the peaks and the spectrum accumulated in the on-line computer memory. Fig. 2 illustrates a complete secondary ion mass spectrum covering the mass range 139-180. This includes all the significant atomic *REE* peaks and their monoxides. A major feature of this spectrum is the fact that the oxide peaks are more intense than the corresponding atomic peaks e.g. ^{156}CeO versus ^{140}Ce. Consequently the spectrum above mass 155 (LaO) is dominated by monoxide peaks, the heavy *REE* atomic peaks being comparatively insignificant. The perovskite spectrum is similar to that given by monazite (Reed, 1986).

Complete spectra were not accumulated during analysis. Peaks chosen for *REE* determination were sampled by computer-controlled step-scanning. Analytical peaks (Table 1) lying in the mass range 139 to 192, together with ^{44}Ca and ^{156}CeO, were collected at low mass resolution (*c*.300) to maximize detection limits for the heavy *REE*. Five to ten *REE* spectra were collected and averaged for each perovskite sample.

For the light *REE* (La, Ce, Pr, Nd, Sm, Eu), atomic peaks were utilized for abundance determination. For the heavy *REE* (Gd, Dy, Er, Yb), monoxide peaks were employed. The monoxides were chosen as the light *REE* monoxides seriously interfere with the atomic peaks of the heavy *REE*. Reed (1986) has demonstrated that interferences from the light *REE* dioxides are not significant. Perovskites do not contain volatiles and interferences from hydrides, hydroxides and fluorides are not present. The barium content of the perovskites studied is low (< 200 ppm) and isobaric interferences on ^{151}Eu from ^{151}BaO are negligible.

Table 1. Analytical peaks, REE concentrations and ion yields for the standard perovskite (GM 55205)

Peak	Standard concentration (ppm*)	Ion Yields	Interference Correction Factor
^{139}La	8000	0.43	1.0
^{140}Ce	16000	1.00	1.0
^{141}Pr	1700	0.14	1.0
^{146}Nd	7000	0.32	1.0
^{147}Sm	1000	0.23	1.0
^{151}Eu	250	0.038	1.0
^{174}GdO	500	0.42	0.8
^{179}DyO	320	0.20	0.8
^{182}ErO	100	0.29	0.5
^{190}YbO	45	0.31	0.2

*Standard REE contents determined by INAA. Major element composition is CaO (38.5 wt.%), TiO_2 (50.4 wt.%), FeO (1.2 wt.%), SrO (0.56 wt.%), Na_2O (0.35 wt.%). Analyst F. Wall (BMNH).

Standards

As matrix effects in ion microprobe analyses are poorly understood it is necessary to employ as a standard a perovskite whose composition does not significantly differ from that of the samples. A perovskite (Table 1) from the Gardiner melilitoid complex, Greenland (GM 55205), previously analysed by electron microprobe and instrumental neutron activation, that met these requirements was obtained from the British Museum (Natural History) courtesy of Dr P. Henderson.

Matrix-derived interferences

Interferences on the analytical peaks arising from matrix-derived molecular species can be a major problem in ion microprobe analysis. To assess the extent of such interferences, secondary ion mass spectra of the standard perovskite and several of the samples were examined at high resolution (7500). Interferences were not found to be significant for the light *REE*, and minor for Gd and Dy. Significant interferences were encountered for the heavy *REE*. Interferences at the analytical peaks of HoO, TbO and LuO were so large as to preclude use of these peaks for the determination of these elements. Empirical correction factors (Table 1) for *REE*/Ce and (*REE*)O/CeO were applied to the low-resolution intensity data for Gd, Dy, Er and Yb.

Although it is not possible to identify the exact interfering molecular species with any certainty, due to the large number of possible combinations of matrix isotopes, it is highly probable that they consist of diverse combinations of Ca, Ti and O. High-resolution spectra of a Sr-bearing (*c*. 2.8 wt. % SrO) and a Nb-bearing (*c*. 2.0 wt. % Nb_2O_5) perovskite (Table 3, samples 3 and 4) indicated increased interferences on the heavy *REE* peaks due to Sr-Ti-O and Nb-Ti-O molecular species e.g. $^{182}(^{86}Sr^{48}Ti^{16}O_3)$ on $^{182}(ErO)$. With the exception of these two samples all the other perovskites studied contained lower Sr and Nb contents and matrix-derived interferences from these elements were considered to be negligible.

Secondary ion yields

Secondary ion yields have been shown to be different for each *REE*, and may vary with the nature of the matrix. Consequently the standard was used to determine empirically ion yields for the *REE*. These are expressed as sensitivity factors for *REE*/Ce or (*REE*)O/CaO ratios normalized to Ce (Table 1) and were applied as correction factors to the low-resolution spectral data.

Determination of *REE* abundances

For quantitative analysis it is only necessary to measure the intensities of the *REE* peaks relative to an internal standard. In this study ^{140}Ce and ^{156}CeO were utilized. The Ce content of the samples was then determined by comparison with the standard. Knowing the Ce content of the sample, the abundances of the other *REE* relative to this value may then be calculated.

Using the standard perovskite, an instrument calibration factor relating the true Ce/Ca ratio to the measured Ce/Ca ratio was determined. This calibration factor was then applied to all measured Ce/Ca ratios to convert apparent Ce/Ca ratios to true Ce/Ca ratios. The Ce content of the sample was then calculated relative to the standard e.g.

$$\mathrm{Ce}_{\mathrm{sample}} = (^{140}\mathrm{Ce}/^{44}\mathrm{Ca})_{\mathrm{measured}} \div \text{calibration factor} \times \mathrm{Ca}_{\mathrm{standard}}. \qquad (1)$$

The calcium content of all of the samples was assumed to be 27.5 wt. % i.e. the Ca content of standard. This assumption does not introduce significant errors as the Ca content of the perovskites studied is unlikely to vary by more than 10% (relative) from that of the standard. For example, the Ca contents, as determined by electron microprobe of the Frank Smith cumulate, Oka, Wolgidite and Monticellitovaya perovskites are 25.7, 26.0, 26.2 and 27.8 wt. % respectively. Variation in the Ca content relative to the standard is thus within the specified limits for these samples and unlikely to exceed them in the other perovskites analysed for *REE*. Use of the actual Ca content in equation 1 results in a change in calculated *REE* abundance of less than 10% e.g. for the Oka sample, 6.5%. This error is acceptable given that the precision of many methods of trace element deter-

Table 2. Rare earth element abundances (ppm) in perovskites from kimberlites.

	1	2	3	4	5	6	7	8
La	8077	10753	6123	10449	13840	10658	8149	7851
Ce	23247	28288	15444	26499	30889	29263	26174	7445
Pr	2616	2981	1636	2672	3026	3197	3152	5528
Nd	10653	12103	6524	10099	11219	13119	13125	5018
Sm	1246	1353	874	1091	1336	1649	1517	2519
Eu	209	231	123	168	197	279	233	1400
Gd	344	342	187	303	291	443	405	617
Dy	138	145	81.6	144	138	211	163	272
Er	26.6	24.2	17.9	28.8	24.2	36.9	28.1	90.5
Yb	3.75	3.33	3.35	3.61	4.4	5.26	3.89	13.6
La/Yb	2153	3229	1828	2894	3145	2026	2095	577

1 Frank Smith, South Africa cumulate perovskite; 2 Frank Smith, South Africa, groundmass perovskite; 3 Elwin Bay, Canada; 4 Peuyuk, Canada; 5 Sydney-on-Vaal, South Africa; 6 Ngopoetsu, Lesotho; 7 Dutoitspan, South Africa; 8 Chomur, Yakutia, USSR.

mination is no better than 5–10%. Measuring the Ca content of all of the samples and using these data in equation (1) would slightly change the actual *REE* abundances but *will not change their relative distribution.* It is knowledge of the latter that is the least known and most important aspect of perovskite geochemistry.

Individual *REE* abundances were calculated relative to Ce from the *REE*/Ce or (*REE*)O/CeO ratio making appropriate corrections for ion yield and matrix-derived interferences, e.g. for La:

$$\text{La (ppm)} = (\text{La/Ce})_{\text{measured}} \times \text{sensitivity factor} \times \text{interference correction} \times \text{Ce (ppm)}.$$

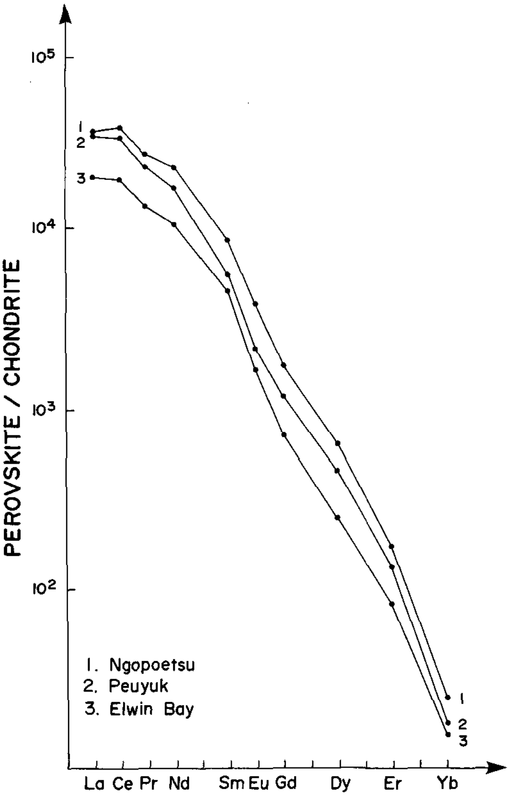

FIG. 3. Rare earth element distribution patterns for perovskites from the Ngopoetsu, Peuyuk and Elwin Bay kimberlites.

The *REE* abundances of the perovskites studied are given in Tables 2 and 3 and their chondrite-normalized distribution patterns are illustrated in figs. 3-6. Chondritic *REE* values used in the normalization of the *REE* data are from Boynton (1984).

REE abundances and distribution patterns

Total *REE* abundances expressed as oxides, in the kimberlite and alnöite perovskites range from 3.6 to 7.1 wt. % and 2.8 to 5.6 wt. % respectively. These abundances are in agreement with Jones and Wyllie's (1984) electron microprobe estimates of the total *REE* content of perovskite. All of these data are higher than the *REE* abundances obtained by X-ray spectrometric (Ilupin *et al.*, 1971; Blagulkina and Tarnovskaya, 1975) or instrumental neutron activation (Kozlov *et al.*, 1984) methods. These differences may reflect real differences between the compositions of Yakutian and other perovskites or be related to the analytical techniques employed. The low *REE* contents found by Kozlov *et al.* (1984) in particular may be related to the analysis of impure samples.

All of the kimberlite perovskites studied, with the exception of Elwin Bay, Peuyuk and Chomur, are from hypabyssal phlogopite kimberlites. The variations in *REE* content undoubtedly simply reflect the abundance of *REE* in the parental magmas. The Elwin Bay perovskites are from a hypabyssal monticellite kimberlite, and have the lowest *REE* contents. Samples from Peuyuk, a phlogopite-poor highly evolved segregation-textured hypabyssal serpentine calcite kimberlite have *REE* contents similar to perovskites from the phlogopite kimber- lites. This suggests that perovskites from isotopic group II kimberlites (Smith *et al.*, 1985) are not necessarily richer in *REE* than perovskites from isotopic group I kimberlites. Samples from Chomur are from a pelletal lapillus in a diatreme facies tuffisitic kimberlite breccia. This perovskite differs from all the others analyzed in that La is more abundant than Ce and all the heavy *REE* are present at relatively high concentrations.

Table 3 demonstrates that the *REE* abundances of alnöite perovskite are similar to those of kimberlite perovskite.

Figs. 3 to 6 demonstrate that ion microprobe analysis provides abundance data which plot as smooth curves on chondrite-normalized distribution diagrams. The only exceptions are the data for the Oka alnöite and the Wolgidee Hills lamproite which show irregular plots for the heavy *REE*. This scatter is related to the significant molecular interferences on these analytical peaks as discussed above.

The *REE* distributions are similar to those obtained by Jones and Wyllie (1984). The absence of Sm anomalies and erratic high heavy *REE* abundances clearly support Jones and Wyllie's (1984) contention that the data obtained by Boctor and Boyd (1979, 1980, 1981, 1982) are substantially in error.

Table 3. Rare earth element abundances (ppm) in perovskites from alnöites and lamproite.

	1	2	3	4
La	4697	8353	13710	10150
Ce	11872	16095	24045	14306
Pr	1274	1572	2207	1166
Nd	5205	6036	7187	3333
Sm	710	700	736	460
Eu	117	119	106	130
Gd	183	189	275	120
Dy	87	75	33.5*	108
Er	19.1	18.7	27.0*	6.2*
Yb	3.31	3.49	9.2*	2.2*
La/Yb	1419	2393	-	-

*denotes data subject to unresolved molecular interferences
1 Monticellitovaya, Yakutia USSR; 2 Haystack Butte Montana, U.S.A.; 3 Oka, Quebec, Canada; 4 Walgidee Hills, Australia.

The chondrite-normalized *REE* distribution patterns (figs. 3-6) show extreme light *REE* enrichment. Perovskites from kimberlites have similar La_N and Ce_N with either $La_N < Ce_N$ or $La_N > Ce_N$. Only the perovskite from Dutoitspan is substantially depleted in La_N relative to Ce_N. This perovskite therefore exhibits a *REE* distribution identical to that found by Jones and Wyllie (1984) for perovskite from the Benfontein and Premier kimberlites. The present data suggest that *REE* distributions in kimberlite perovskite are more varied than previously thought.

Perovskites from alnöites and the lamproite also show extreme light *REE* enrichment. They differ from the kimberlite perovskites in that they are notably enriched in La_N relative to CE_N.

None of the distribution patterns show the presence of any type of Eu anomaly. Jones and Wyllie (1984) have noted that positive Eu anomalies in the Boctor-Boyd data are probably due to unresolved interference on the weak Eu analytical peaks. The absence of any negative Eu anomalies is important in that the majority of kimberlites analysed by reliable methods do not exhibit such anomalies in their whole-rock *REE* distribution patterns (Mitchell, 1986). Although minor to significant negative Eu anomalies are found in some kimberlites (Fesq *et al.*, 1975) it would appear on the basis of the present data unlikely that these are related to the presence of perovskite.

The *REE* distribution patterns of the perovskites are steeper than those typically found for whole-rock kimberlites. This greater degree of light *REE* enrichment is reflected in the higher La/Yb ratios (577-3229) of perovskite relative to those of only 80-200 as found in the majority of kimberlites (Mitchell, 1986). This observation implies that the whole-rock *REE* geochemistry of kimberlites is controlled by factors other than the mere presence of perovskite. These factors must act to increase the levels of heavy *REE* in order that whole-rock La/Yb ratios be reduced.

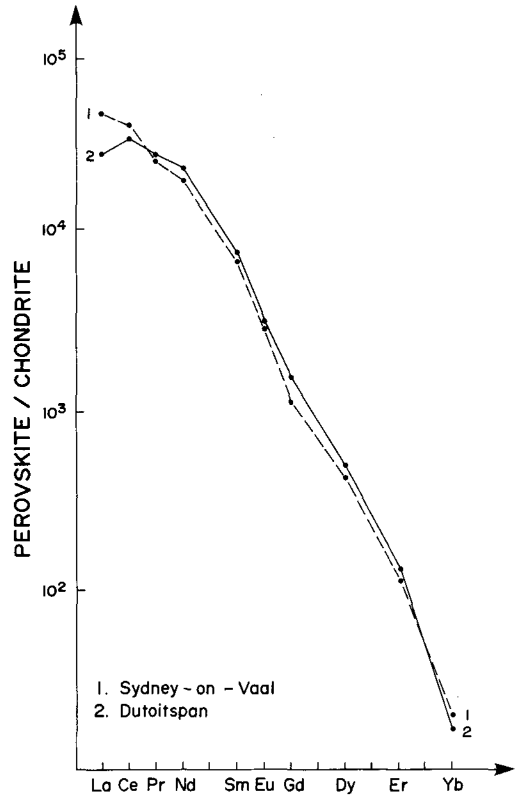

FIG. 4. Rare earth element distribution patterns for perovskites from the Sydney-on-Vaal and Dutoitspan kimberlites.

One process that can result in a significant increase in the abundance of the heavy *REE* is contamination with crustal material. The effects of this process are to decrease the slope of the distribution pattern from Tb to Lu and hence to reduce La/Yb ratios. Fesq *et al.* (1975) and Cullers *et al.* (1982) have provided data for the Premier and Bala kimberlites which clearly demonstrate such effects. Perovskites from the Chomur diatreme analysed in this work, are unlike all of those from hypabyssal kimberlites studied, in that their La/Yb ratios are low and their heavy *REE* abundances are relatively high. The diatreme environment provides an excellent site for contamination of kimberlite

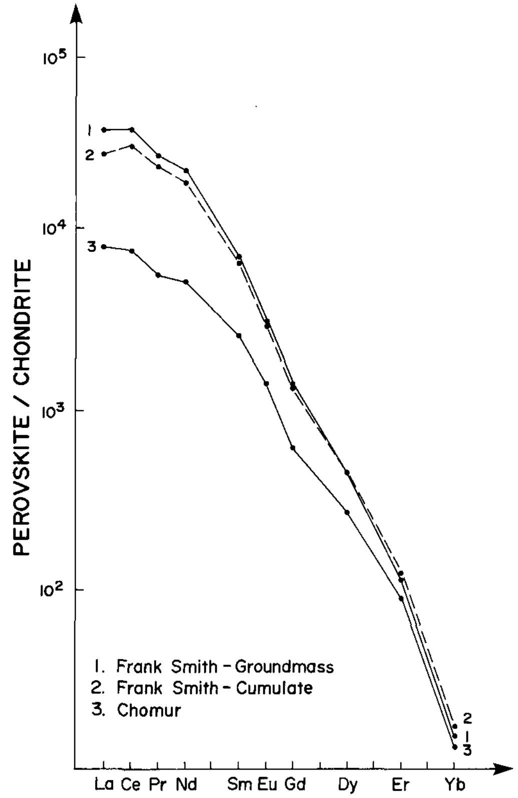

FIG. 5. Rare earth element distribution patterns for perovskites from the Frank Smith and Chomur kimberlites.

magma with *REE* derived from a wide variety of crustal xenoliths. Accordingly we believe that the *REE* abundances in the Chomur perovskite reflect such contamination of the magma prior to the crystallization of the perovskite.

The possibility that whole-rock La/Yb ratios of kimberlite have been modified by contamination with crustal material has important ramifications with respect to the La/Yb ratios of the source regions of these magmas. Although the distribution coefficients for *REE* between perovskite and kimberlite magma are unknown, experimental studies of other perovskite–silicate systems (Nagasawa *et al.*, 1980; Onuma *et al.*, 1981) suggest that they are likely to vary by a factor of 3–6 from La to Lu. Hence, separation of perovskite from kimberlite magma will be expected to result in some enrichment of La relative to Yb. Thus the high La/Yb ratios (> 1500) of perovskite are in accord with separation from a parental magma having a La/Yb ratio of approximately 120–650.

The above conclusion requires that the source regions of kimberlites have slightly higher La/Yb ratios than previously believed, and certainly precludes their formation by small degrees of partial melting from cryptically metasomatized phlogopite garnet lherzolite. Derivation from a metasomatized source containing light *REE*-enriched phases such as $Ca_3(PO_4)_2$ (Murayama *et al.*, 1986) or *REE*-bearing hollandites and crichtonites (Haggerty, 1983) would seem to provide a plausible alternative.

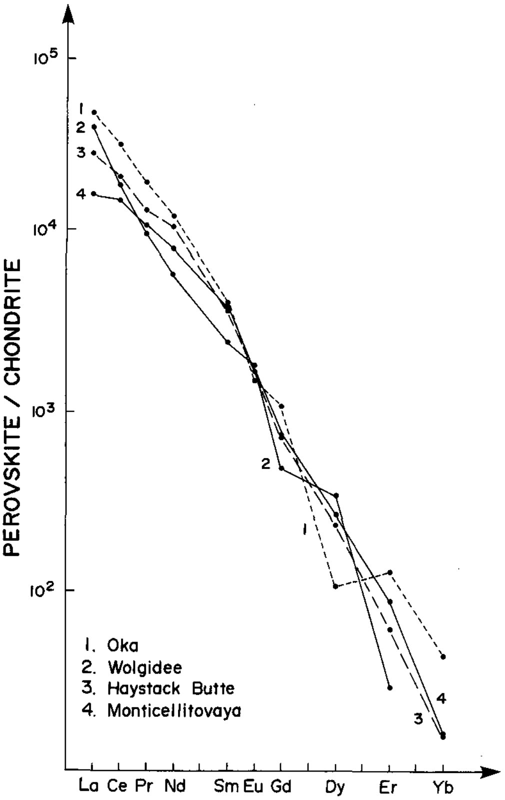

FIG. 6. Rare earth element distribution patterns for perovskites from the Oka, Haystack Butte and Monticellitovaya alnöites and the Wolgidee Hills lamproite.

Comparative electron microprobe data

Abundances of La, Ce, Pr, Nd and Sm in the Frank Smith (cumulate), Monticellitovaya and Oka perovskites were determined at the British Museum (Natural History) using a Cambridge Instruments Microscan 9 wavelength dispersive microprobe and methods described by Platt *et al.* (1987). These comparative data are given in Table 4.

The Frank Smith (cumulate) perovskite has higher La, Nd and Sm and lower Pr and Ce relative to the ion probe data. Distribution patterns (not shown) are irregular and subhorizontal. The Monticellitovaya perovskite has lower Ce, Pr and higher La, Nd and Sm relative to the ion probe abundances and a subhorizontal distribution pattern. For the Oka sample, all of the electron probe data, except Pr, are higher than the ion probe data. Distribution patterns are again irregular and subhorizontal.

Table 4. Compositions (wt.%) of some perovskites as determined by electron microprobe.

	1	2	3
La	0.94	0.61	2.03
Ce	2.06	0.86	2.63
Pr	0.15	n.d.	0.13
Nd	1.6	0.91	1.22
Sm	0.20	0.22	0.15

n.d. = not detected
1 Frank Smith (cumulate); 2 Monticellitovaya; 3 Oka.

This electron microprobe technique has been shown to provide accurate data and smooth distribution patterns for *REE* occurring at higher levels of concentration in *REE*-bearing silicates such as chevkinite (Platt *et al.*, 1987). The perovskite data however suggest that the method is unsuitable for perovskites and definitely overestimates Nd and Sm abundances. The most probable explanation for the differences between the ion probe and microprobe data is inadequate background determinations and that the spectrometer positions used by Platt *et al.* (1987) are unsuitable for perovskites of low *REE*-content.

Conclusions

It has been shown that ion microprobe analysis of *REE* in perovskite permits the accurate (±5-10%) determination of Eu and some of the heavy *REE*. The method is thus superior to existing electron microprobe methods for the determination of *REE* in perovskite. Data obtained in this work support Jones and Wyllie's (1984) contention that much of the published electron microprobe data for Sm, Eu and the heavy *REE* are erroneous. It is suggested that there is more variety in the distribution of *REE* in kimberlite perovskites than previously thought and that the La/Yb of ratio of whole-rock kimberlites has been modified by crustal contamination. The study provides the first *REE* distribution patterns for alnöite perovskite and shows them to differ from those of kimberlite perovskites in that they are richer in La.

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