

Partitioning of REE between minerals and coexisting melts during partial melting of a garnet lherzolite

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Abstract

Partition coefficients ($D_i^{a/b} = C_i^a/C_i^b$, where C_i is the concentration of element i in phases a and b) for Ce, Sm, and Tm between garnet, clinopyroxene, orthopyroxene, olivine, and melt have been determined at 35 kbar for 2.3, 8, 20, and 37.7% melting of a garnet lherzolite nodule with chondritic REE abundances. Partition coefficients increase as the degree of partial melting increases. From 2.3 to 8% melting, this increase is largely a consequence of non-Henry's law behavior of REE in minerals. At melt percentages $\geq 9\%$, changing temperature and melt composition, as well as non-Henry's law behavior, also influence the values of REE partition coefficients. The total increase in $D_{\text{REE}}^{\text{crystal/melt}}$ from 2 to 38% melt may be up to 100% for some minerals and REE, and the assumption made in petrogenetic modeling of constant partition coefficients is therefore questioned.

Experimentally determined REE abundances in the 2.3 and 8% melts can be adequately modeled with an equilibrium partial melting model and a melting reaction, determined by Mysen (1977a), in the system CaO–MgO–Al₂O₃–SiO₂:



REE abundances cannot be calculated at higher percentages of melting because the melting reaction is not known.

The LREE enrichment in the 2.3% melt is 22 times chondritic abundance, and this melt has chondrite-normalized Ce/Tm = 4.18. The generation of REE abundances typical of most alkali basalts (Ce enrichment 40–200 and Ce/Tm 2–15) is not possible even by low percentages of partial melting of a garnet lherzolite unless the material has been enriched in LREE relative to chondrites.

Introduction

The enrichment of trace elements such as light rare earth elements (LREE) in alkali basalts implies that these magmas may be generated by small percentages of partial melting of a source material with a chondritic REE pattern. Likely source materials are garnet lherzolite and spinel lherzolite. Gast (1968), Kay and Gast (1973), and Shimizu and Arculus (1975) suggested that the necessary LREE enrichment and HREE depletion in alkali basalts could be modeled by small percentages of melting of a garnet peridotite source. It has been shown by Mysen and Holloway (1977), however, that spinel lherzolite will not yield melts containing the appropriate REE con-

tents for alkali basalts unless a prior metasomatic event is invoked.

The REE concentrations in melts that may be generated from a model garnet peridotite source are largely determined by the relative abundances of garnet and clinopyroxene in the source (Kay and Gast, 1973), by the magnitude of partition coefficients for REE between these minerals and the melts, and by the stoichiometry of the melting reaction (Mysen, 1977a). In the absence of a definitive set of partition coefficients for natural garnet peridotite minerals and coexisting melts, data from other systems (*e.g.*, experimentally determined values in simple and complex synthetic systems: Shimizu and Kushiro, 1975; Irving, 1978; Mysen, 1978a) must be extrapolated to the problem at hand. It has been found that garnet/liquid partition coefficients and, to a lesser degree, clinopyroxene/liquid partition coefficients vary as a

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function of pressure, temperature, and phase composition (e.g., Wood, 1976; Harrison, 1978; 1979a,b; Irving, 1978; Irving and Frey, 1977, 1978; Mysen, 1978a,b), as well as the REE concentration in the crystals (Wood, 1976; Harrison, 1977, 1978; Mysen, 1978a). Because physical conditions and phase compositions change during a melting event (Mysen and Kushiro, 1977), it is unlikely that partition coefficients will remain constant. Thus, model calculations of REE abundances in melts that employ constant values of partition coefficients, determined from other systems, will be imprecise.

Partition coefficients for three REE between olivine, orthopyroxene, clinopyroxene, garnet, and melt have been determined for 2.3, 8, 20, and 37.7% melting of a natural garnet lherzolite to assess the magnitude of variation of partition coefficients during a melting event. Additionally, REE enrichments in the melts have been calculated to evaluate the possibility that the REE characteristics of alkali basalts may be generated by small degrees of melting of a garnet lherzolite with chondritic REE abundances.

Experimental methods

The starting material was a sheared garnet lherzolite nodule, PHN 1611, described by Nixon and Boyd (1973). This nodule was chosen because its major element composition is considered representative of undepleted upper mantle material and its REE pattern is essentially chondritic (Shimizu, 1975).

The starting material was crushed to $< 5 \mu\text{m}$ and fired at 1150°C at $f(\text{O}_2) = 10^{-9}$ atm for 18 hr to decompose secondary hydrous minerals. Three samples of the dried, powdered material were spiked with radiotracers for trace element analysis by autoradiography (Mysen and Seitz, 1975). Cerium-141, samarium-151, and thulium-171 are suitable light, intermediate, and heavy REE, respectively. These β isotopes were added in dilute acidic solutions (1.716 ppm ^{141}Ce , 1.277 ppm ^{151}Sm , and 0.0536 ppm ^{171}Tm). The spiked samples were ground thoroughly under alcohol and stored at 110°C prior to use.

Partitioning studies require selected percentages of melt coexisting with known mineral assemblages. Previous determinations of the melting relations of PHN 1611 have been made with platinum or platinum-gold capsules as sample containers, and iron loss from both minerals and melts is incurred (Mysen and Kushiro, 1977; Wendlandt and Mysen, 1978). Mysen and Kushiro (1977) reported 20% iron loss from samples at 20 kbar and 1550°C and substantially greater loss at 35 kbar. Because the sub-

stitution of Fe for Mg results in an expansion of the crystal structure in many mantle minerals, Fe-bearing minerals will probably tolerate more REE than Fe-free minerals. It was decided that an attempt to reduce Fe loss should be made to obtain more realistic partition coefficients. A redetermination of the melting relations was carried out by use of a double capsule configuration comprising an inner graphite capsule and an outer platinum capsule.

An additional sample of powdered material was spiked with 15 ppb ^{185}W in NH_4OH solution (kindly supplied by Dr. G. Cowan, Los Alamos Scientific Laboratory). The technique of determining amounts of melting in which a trace element partitions entirely into the melt phase was described originally by Mysen and Kushiro (1977) for the element ^{14}C . This element will be taken up by the inner graphite capsules, however, and thus ^{185}W was selected as an alternative (Wendlandt and Mysen, 1978).

The REE contents of minerals and melts were determined by autoradiography (Mysen and Seitz, 1975). Partition coefficients ($D_i^{a/b} = [\text{concentration of element } i \text{ in phase } a]/[\text{concentration of element } i \text{ in phase } b]$) were then calculated, in addition to a chondrite-normalized REE pattern for the melts. As discussed by Mysen and Holloway (1977), a pattern equivalent to the chondrite-normalized pattern may be obtained by dividing the radioactive REE content of the melt by the initial radioactive REE spike. The accuracy of trace element concentrations determined by autoradiography has been discussed by Mysen (1978a), and all aspects of the procedure used in this work are identical with those described by him.

The standards necessary for autoradiography were albite glasses, prepared at 20 kbar and 1600°C , containing known amounts of cerium, samarium, or thulium. A sample of PHN 1611, completely melted at 16 kbar and 1650°C (containing 15 ppb ^{185}W and 5.31 wt.% H_2O), was prepared as a standard for determination of degrees of melting.

All experiments were conducted with a solid-media, high-pressure apparatus (Boyd and England, 1960). A piston-out technique was used throughout. No corrections for pressure loss due to friction were made, and nominal pressures quoted are precise to ± 0.5 kbar (Eggler, 1977). Temperatures were measured with $\text{Pt}_{100}\text{-Pt}_{90}\text{Rh}_{10}$ thermocouples and were automatically controlled to $\pm 1^\circ\text{C}$ (Hadidiacos, 1972). No corrections were made for the effect of pressure on thermocouple electromotive force.

Samples were contained in 2-mm-diameter graphite capsules that were stored at 110°C prior to use.

These were contained in 3-mm platinum capsules, which were sealed by welding. The double capsule configuration was employed to minimize the access of H₂O to the dried samples during capsule assembly and experimental runs. Glass-sleeved furnace assemblies were used in all experiments to reduce further the access of hydrogen to the samples from H₂O released from the talc sleeve.

All runs were conducted at 35 kbar for a duration of 1 hr. The high temperatures necessary to achieve anhydrous melting preclude longer run durations. An estimation of minimum distances of REE diffusion calculated with diffusion coefficients of about 10⁻¹¹ cm² sec⁻¹ at 1600°C for REE in garnets (Harrison and Wood, 1980) indicates that a run duration of 1 hr is more than adequate to attain equilibrium in the small crystals grown in these experiments (15–25 μm diameter). Reversal experiments for REE data would require that the individual minerals be synthesized containing calculated amounts of REE and re-equilibrated with a REE-free melt. The melts undergo extensive crystallization on quenching from 35 kbar, and because of the problems inherent in electron microprobe analysis of stable phases coexisting with quenched phases (*e.g.*, Mysen and Kushiro, 1977), no attempt has been made to analyze the major element compositions of minerals and melts. Independent synthesis of phases for reversal experiments is therefore precluded.

Results

Phase relations of nodule PHN 1611

The 35 kbar anhydrous melting relations of nodule PHN 1611 as a function of the weight percentage of partial melting are shown in Figure 1. Experimental details are presented in Table 1. Also shown, for comparison, are melting relations of the same nodule determined by Mysen and Kushiro (1977), without control of iron loss.

The general features of the melting relations are comparable in both cases. The present experiments yield a lower estimated solidus temperature, 1575°C, compared with 1625°C estimated from the experiments of Mysen and Kushiro (1977). Three stable phase assemblages are observed (phase identification is based on optical microscopy): olivine + orthopyroxene + clinopyroxene + garnet + liquid, olivine + orthopyroxene + clinopyroxene + liquid, and olivine + orthopyroxene + liquid. A fourth phase assemblage, olivine + liquid, is inferred from the observations of Mysen and Kushiro (1977). These

phase fields extend over different percentages of melting and are stable at systematically lower temperatures than the same phase fields in the system where iron loss occurred.

The first phase to melt out with increasing temperature is garnet, which disappears within the initial 10% melting (1580°–1590°C), whereas in the experiments of Mysen and Kushiro (1977), garnet persists over a melting interval of about 40°C (1620°–1660°C) before it disappears at 25% melting. The much reduced stability field of garnet in these experiments may be interpreted in terms of the lower temperature stability of an iron-bearing garnet relative to a pyrope-rich garnet.

The slope of the melting interval in which garnet is a liquidus phase is very nearly independent of temperature. Mysen and Kushiro (1977) and Wendlandt and Mysen (1978) have shown that melting in natural systems, for example PHN 1611, is analogous to melting in synthetic systems such as CaO–MgO–Al₂O₃–SiO₂. In the system CMAS, with four components and five phases (olivine, orthopyroxene, clinopyroxene, garnet, and liquid) the initial melting interval is isobarically invariant. The nodule PHN 1611 approaches this behavior much more closely (*i.e.*, the melting curve is flatter) when Fe is retained in the system (Fig. 1).²

The second phase to melt out is clinopyroxene. The melting interval in which the stable phase assemblage is olivine + orthopyroxene + clinopyroxene + liquid extends from 9 to 40% melting over a temperature range of 1590° to 1635°C. As in the garnet in the lowest melting interval, the presence of Fe reduces the stability of clinopyroxene (Kushiro, 1968) so that it is no longer present at 40% melt compared with 45% melt in the experiments of Mysen and Kushiro (1977). The reduced stability of garnet

² It is likely that the reduced melting temperatures observed in the present experiments result from the retention of iron in the system. It is possible, however, that the presence of volatile species such as CO₂ and CO (formed by reaction between the graphite capsule and oxygen in the sealed platinum capsule) and perhaps H₂O or CH₄ (formed by hydrogen diffusion into the capsules) may reduce melting temperatures. Generous estimates of 0.1 wt.% of volatile species could result in the formation of a few tenths of a percent of melt, several hundred degrees below the observed solidus. Such a small amount of melt would not be detectable and would have a negligible effect on melt compositions at higher degrees of melting. Because the difference in melting temperatures in this study and that of Mysen and Kushiro (1977) increases with degree of melting, it is believed that better iron retention is the most satisfactory explanation for the lowered melting temperatures.

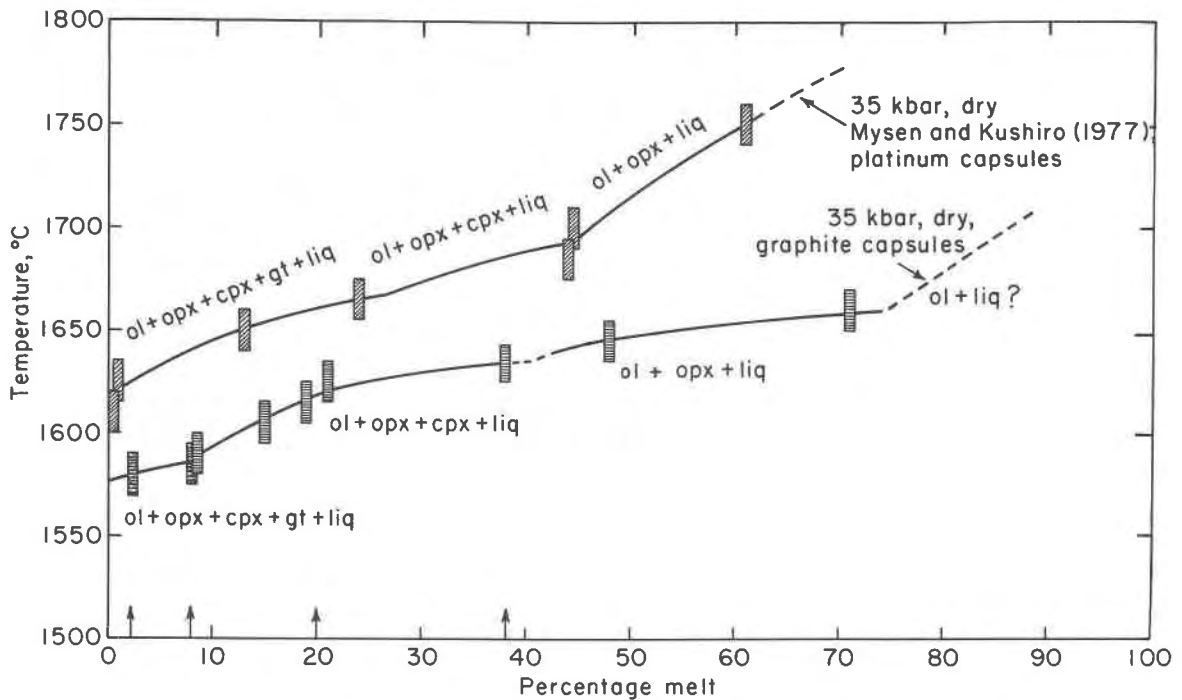


Fig. 1. Melting curves of nodule PHN 1611 at 35 kbar pressure (anhydrous). Upper curve determined by Mysen and Kushiro (1977) with no control on iron loss to noble-metal capsules. Lower curve determined in this investigation with graphite capsules. Size of symbols includes uncertainties in temperature ($\pm 10^\circ\text{C}$) and determination of percentage of liquid ($\pm 1\sigma$). Arrows indicate conditions selected for partitioning experiments.

results in an extension of the stability of the phase assemblage olivine + orthopyroxene + clinopyroxene + liquid to lower temperatures (1590°C) and lower percentages of melt (9%) than in the experiments of Mysen and Kushiro (1977).

The steeper slope of the interval olivine + orthopyroxene + clinopyroxene + liquid may indicate isobaric univariant melting behavior (four significant components and four phases, as discussed by Mysen and Kushiro, 1977). At temperatures greater than 1640°C , orthopyroxene and olivine are present in the melting interval and are stable to at least 70% melt and 1660°C . The temperature above which olivine alone remains on the liquidus is unknown. The progressively steeper slope of the melting interval reflects a further degree of freedom relative to the melting interval for olivine + orthopyroxene + clinopyroxene + liquid, as a consequence of the loss of another phase (four significant components and three phases).

On the basis of the redetermined melting relations of nodule PHN 1611, four melt percentages were selected for REE studies: 2.3% melt (1580°C), 8.0% melt (1585°C), 20% melt (1620°C), and 37.7% melt (1635°C). The first two melts coexist with the min-

eral assemblage olivine + orthopyroxene + clinopyroxene + garnet (Fig. 1). As discussed above, the melting reaction of this assemblage is essentially isobarically invariant so that, to a first approximation, partitioning behavior may be examined independently of pressure (35 kbar), temperature (1580°C – 1585°C), and melt composition; *i.e.*, as a function of the amount of melting alone.

The second two melts (20 and 37.7%) coexist with the assemblage olivine + orthopyroxene + clinopyroxene. Because this assemblage melts in an essentially isobaric, univariant fashion, partitioning of the REE may not be evaluated independently of temper-

Table 1. Melting relations of nodule PHN 1611 at 35 kbar

Run No.	P, kbar	T, °C	Run duration, min	Wt % melt	σ	Mineralogy
1611-W 12	35	1660	60	71.04	± 1.56	ol, opx, liq
1611-W 6	35	1645	60	48.13	± 0.03	ol, opx, liq
1611-W 5	35	1635	60	37.73	± 0.03	ol, opx, cpx, liq
1611-W 4	35	1625	60	21.32	± 0.03	ol, opx, cpx, liq
1611-W 8	35	1615	60	18.69	± 0.42	ol, opx, cpx, liq
1611-W 9	35	1605	60	14.68	± 0.59	ol, opx, cpx, liq
1611-W 10	35	1590	60	8.60	± 0.22	ol, opx, cpx, liq
1611-W 25	35	1585	60	8.00	± 0.19	ol, opx, cpx, gt, liq
1611-W 11	35	1580	60	2.29	± 0.04	ol, opx, cpx, gt, liq

Table 2. Rare earth element partitioning data

Run No.	P, kbar	T, °C	Run duration, min	Wt % melt	REE	Garnet,* ppm	Clino- pyroxene, ppm	Ortho- pyroxene, ppm	Olivine, ppm	Liquid, ppm
1611-Ce 20	35	1580	60	2.29	Ce	0.477 +0.016	11.337 +0.210	2.797 +0.192	1.550 +0.020	55.169 +0.953
1611-Ce 21	35	1585	60	8.00	Ce	0.173 +0.010	4.705 +0.113	1.092 +0.029	0.621 +0.012	19.649 +0.527
1611-Ce 27	35	1620	60	20.00	Ce	...	3.614 +0.072	0.826 +0.043	0.518 +0.049	11.516 +0.128
1611-Ce 26	35	1635	60	37.73	Ce	...	3.136 +0.113	n.d.**	0.311 +0.011	6.151 +0.139
1611-Sm 22	35	1580	60	2.29	Sm	4.732 +0.082	4.036 +0.142	0.672 +0.026	0.479 +0.031	16.148 +0.194
1611-Sm 23	35	1585	60	8.00	Sm	3.704 +0.092	3.569 +0.074	0.636 +0.032	0.384 +0.024	11.538 +0.242
1611-Sm 30	35	1620	60	20.00	Sm	...	2.466 +0.064	0.452 +0.021	0.294 +0.014	6.327 +0.290
1611-Sm 1	35	1635	60	37.73	Sm	...	1.634 +0.039	0.314 +0.007	0.222 +0.019	3.183 +0.018
1611-Tm 13	35	1580	60	2.29	Tm	1.794 +0.063	0.296 +0.009	0.068 +0.0002	0.050 +0.001	1.370 +0.043
1611-Tm 14	35	1585	60	8.00	Tm	1.625 +0.022	0.289 +0.005	0.061 +0.0006	0.045 +0.001	1.281 +0.035
1611-Tm 28	35	1620	60	20.00	Tm	...	0.260 +0.007	0.052 +0.0006	0.037 +0.001	0.8815 +0.033
1611-Tm 29	35	1635	60	37.73	Tm	...	0.243 +0.005	0.046 +0.0002	0.036 +0.0007	0.6194 +0.010

ature and compositional variables. The temperature difference between 20 and 37.7% melt is only 15°C, however, and can be realistically ignored.

A very low percentage of melt (e.g., 0.5%) was not used in partitioning experiments, even though such a melt would be more enriched in LREE than a melt produced by 2% melting. The melting interval immediately above the solidus will not show isobarically invariant behavior because PHN 1611 contains a few tenths of a percent of alkalis and these preferentially enter the first formed melt, having high activities in this melt. As a result, additional degrees of freedom (> four components and five phases) are probable in the initial melts. The presence of alkalis results in a steepening of the melting slope immediately above the solidus (Mysen and Kushiro, 1977), and the lowered temperatures, in addition to the high activities of alkalis in the melts, will have a significant effect on partitioning of REE. Because the melting curve has very slight temperature dependence between 2 and 8% melt (Fig. 1), it is assumed that the concentration

of alkalis is dilute relative to that of the major elements in these melts and that the natural system can thus be modeled by a four-component system.

Rare earth element partitioning

Partition coefficients and REE concentrations in phases are presented in Table 2. The concentrations given in each phase have been calculated to include the stable isotope present in the starting material (Shimizu, 1975) as well as the radioactive spike added.

Garnet-melt partition coefficients. Partition coefficients for Ce, Sm, and Tm between garnet and melt are shown in Figure 2A: $D_{Ce} = 0.008 \pm 0.003$ at both 2.3 and 8% melt, $D_{Sm} = 0.293 \pm 0.009$ at 2.3% melt and 0.321 ± 0.014 at 8% melt, and $D_{Tm} = 1.309 \pm 0.09$ at 2.3% melt and 1.268 ± 0.052 at 8% melt. Also shown, for comparison, in Figure 2B, are some other determinations of $D_{REE}^{garnet/melt}$ for similar pressures, temperatures, and compositions. In general, the agreement

Table 2 (continued)

Run No.	$D_{\text{gar/liq}}^{\text{gar}}$	$D_{\text{cpx/liq}}^{\text{cpx}}$	$D_{\text{opx/liq}}^{\text{opx}}$	$D_{\text{ol/liq}}^{\text{ol}}$	EF†	Calculated EF
1611-Ce 20	0.0087 +0.0003	0.206 +0.005	0.051 +0.004	0.028 +0.001	22.14	15
1611-Ce 21	0.0088 +0.0005	0.239 +0.009	0.056 +0.005	0.031 +0.001	7.93	7.9
1611-Ce 27	...	0.314 +0.010	0.072 +0.004	0.045 +0.001	4.62	...
1611-Ce 26	...	0.510 +0.022	...	0.049 +0.002	2.47	...
1611-Sm 22	0.293 +0.009	0.250 +0.009	0.042 +0.002	0.030 +0.002	10.68	10.5
1611-Sm 23	0.321 +0.014	0.309 +0.010	0.055 +0.004	0.033 +0.0003	7.63	6.85
1611-Sm 30	...	0.390 +0.021	0.071 +0.004	0.047 +0.004	4.18	...
1611-Sm 1	...	0.513 +0.032	0.099 +0.003	0.070 +0.006	2.10	...
1611-Tm 13	1.309 +0.090	0.216 +0.006	0.050 +0.002	0.037 +0.001	5.30	5.5
1611-Tm 14	1.268 +0.052	0.226 +0.007	0.048 +0.005	0.035 +0.002	4.95	4.9
1611-Tm 28	...	0.295 +0.013	0.059 +0.005	0.042 +0.003	3.41	...
1611-Tm 29	...	0.310 +0.008	0.059 +0.002	0.046 +0.002	2.40	...

*Concentrations calculated to include β isotope + stable isotope (from data of Shimizu, 1975).

†Enrichment factor = (radioactive REE in liquid)/(radioactive REE in starting mix).

**Not determined.

between investigations is good for light and intermediate REE. Shimizu and Kushiro (1975) found $D_{\text{Ce}} = 0.021$ and $D_{\text{Sm}} = 0.217$ for a garnet of composition pyrope₈₅grossular₁₅ at 30 kbar and 1275°C. Wood (1976) found $D_{\text{Sm}} = 0.197 \pm 0.013$ in a duplication of the experiments of Shimizu and Kushiro (1975). Harrison (1977, 1978, 1979b) and Harrison and Wood (1980) have observed that crystal trace element content may control $D_{\text{REE}}^{\text{garnet/melt}}$ within certain limits and that the Ca^{2+} content of pyrope garnets is more important in controlling the magnitude of $D_{\text{REE}}^{\text{garnet/melt}}$ than small changes in melt composition.

Partition coefficients for HREE are much more influenced by garnet trace element content and garnet calcium content than the light and intermediate REE. Partition coefficients for Ce, Sm, and Tm between a garnet selected from a nodule from kimberlite, PHN 1925 (Nixon and Boyd, 1973), and a coexisting melt at 1300°C and 30 kbar are shown in Figure 2B (Har-

rison, 1978, 1979b) to illustrate this point. When 50 ppm REE are contained in the garnet (pyrope₉₀), $D_{\text{Tm}} = 0.88$. The partition coefficient increases to 1.5 when the garnet contains 20 ppm REE and to 2.5 when the garnet contains 10 ppm REE. The increasing values are a consequence of non-Henry's law behavior of REE in garnets at low trace element concentrations (Harrison, 1977, 1978). Partition coefficients determined in this study and those determined by Shimizu and Kushiro (1975) and Harrison (1978, 1979b) for garnet crystals containing 20 ppm REE are in agreement.

Values of $D_{\text{REE}}^{\text{garnet/melt}}$ have been shown to be substantially greater when the melt composition is more silicic (see data and discussions of Irving and Frey, 1977, 1978; Irving, 1978; Mysen, 1978a); however, for the basic melts produced in these experiments (Mysen and Kushiro, 1977) it is believed that the partition coefficients determined in this study are re-

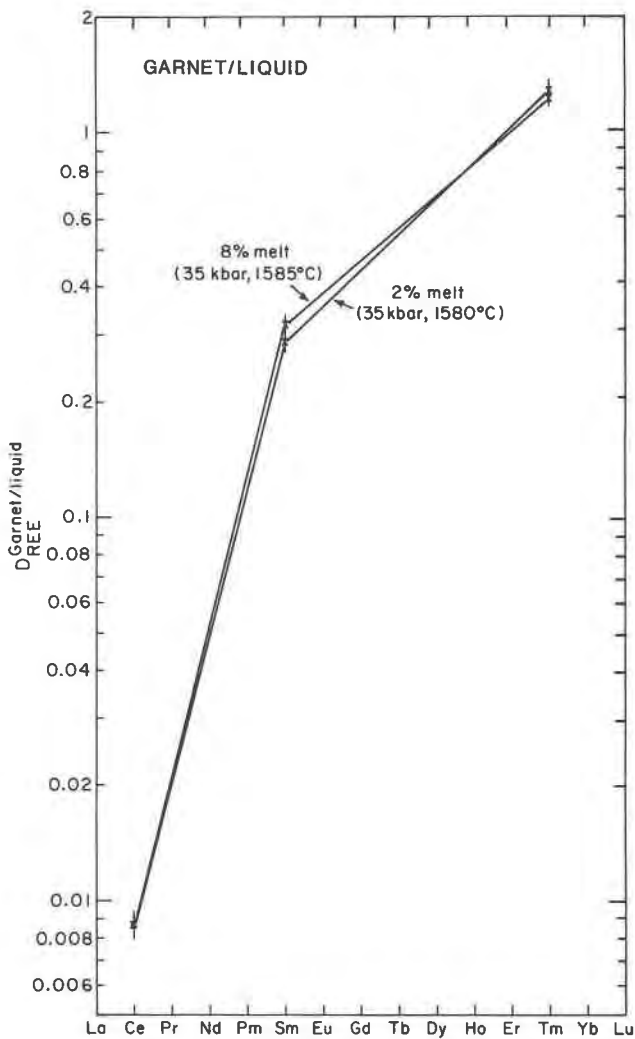


Fig. 2A. Partition coefficients for Ce, Sm, and Tm between garnet and melt produced by 2.3 and 8% partial melt of PHN 1611. Error bars $\pm 1\sigma$.

alistic values when garnet compositions and trace element concentrations are taken into consideration.

Clinopyroxene-melt partition coefficients. Partition coefficients for Ce, Sm, and Tm between clinopyroxene and a melt produced by 2.3, 8, 20, and 37.7% melting are shown in Figure 3. Values of D_{Ce} increase from 0.206 ± 0.005 at 2.3% melt to 0.510 ± 0.022 at 37.7% melt, D_{Sm} increases from 0.250 ± 0.009 at 2.3% melt to 0.513 ± 0.032 at 37.7% melt, and D_{Tm} increases from 0.216 ± 0.006 at 2.3% melt to 0.310 ± 0.008 at 37.7% melt.

These values are comparable with data from other systems (for review see Cullers *et al.*, 1973; Irving, 1978; Mysen, 1978a). Values of $D_{Ce}^{cpx/melt}$ fall in the range 0.05–0.4; D_{Sm} , 0.09–0.7; D_{Tm} , 0.04–0.4 for ba-

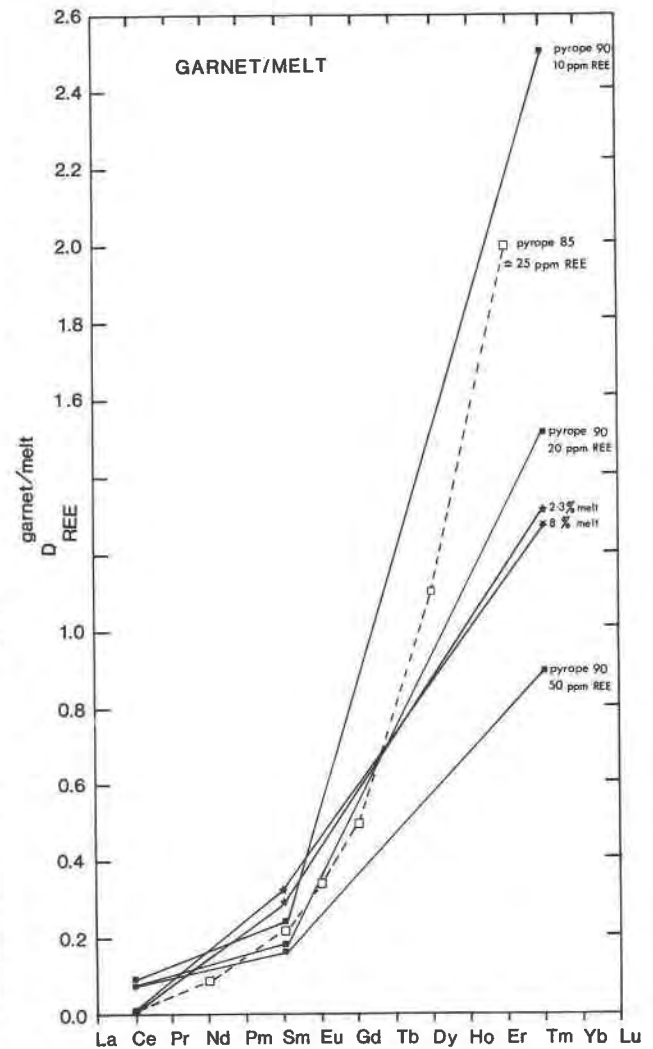


Fig. 2B. Partition coefficients determined in this study (Fig. 2A) compared with other experimentally determined values of $D_{garnet/melt}^{REE}$. Values for garnet composition pyrope₉₀ with 10, 20, and 50 ppm REE in the garnet at 1300°C and 30 kbar are from Harrison (1979b). The data indicated by dashed lines are from Shimizu and Kushiro (1975).

saltic-andesitic melts (the higher values are associated with more acidic melts). The melts that coexist with the clinopyroxenes in this study are probably alkali picritic (up to 9% melt) and olivine tholeiitic (10–40% melt) (Mysen and Kushiro, 1977), so it appears that the values of $D_{REE}^{cpx/melt}$ obtained here are somewhat higher than would be expected. Seitz (1974) determined $D_{Sm}^{cpx/melt} =$ about 0.09 at 20 kbar in equilibrium with a haplobasaltic melt in the system An–Ab–Di. Mysen (1978a) found $D_{Sm}^{cpx/melt} = 0.29$ at 15 kbar and 1450°C for clinopyroxene on the liquidus of Kilauea 1921 basalt. Grutzeck *et al.* (1974) deter-

mined $D_{Ce}^{diopside/melt} = 0.10$, $D_{Sm} = 0.26$, and $D_{Er} = 0.30$ at 1265°C and 1 atm for diopside crystals coexisting with a glass in the system $Ab_5-An_{30}-Di_{65}$.

There are, however, no determinations of $D_{REE}^{cpx/melt}$ at high pressures with which to compare these data. Drake and Holloway (1978) noted an apparent pressure dependence of $D_{Sm}^{cpx/melt}$ in a hydrous, Fe-free synthetic andesitic composition; D_{Sm} is observed to increase from 0.75 at 2 kbar and 1050°C to 0.85 at 5 kbar and 1050°C, and D_{Sm} is found to be 2.68 at 12 kbar and 900°C in a natural andesite. Some of the increase may be related to compositional differences, however. If a similar pressure dependence does occur in these experiments, where crystals coexist with anhydrous basaltic melts, then it is not surprising that

the observed partition coefficients are much higher than those determined in lower pressure experiments on basaltic compositions.

Clinopyroxene-garnet ratios. Ratios of REE in clinopyroxene to REE in garnet are as follows: For 2.3% melt, $D_{Ce}^{cpx/garnet} = 23.75$, $D_{Sm}^{cpx/garnet} = 0.85$, $D_{Tm}^{cpx/garnet} = 0.16$. For 8% melt, $D_{Ce}^{cpx/garnet} = 27.28$, $D_{Sm}^{cpx/garnet} = 0.96$, $D_{Tm}^{cpx/garnet} = 0.18$.

The ratios are shown in Figure 4 with a range of values calculated from REE analyses of peridotite nodules for comparison. The latter data have been accumulated from the analyses of Haskin *et al.* (1966), Nagasawa *et al.* (1969), Reid and Frey (1971), Philpotts *et al.* (1972), Ridley and Dawson (1975), Shimizu (1975), and Mitchell and Carswell (1976).

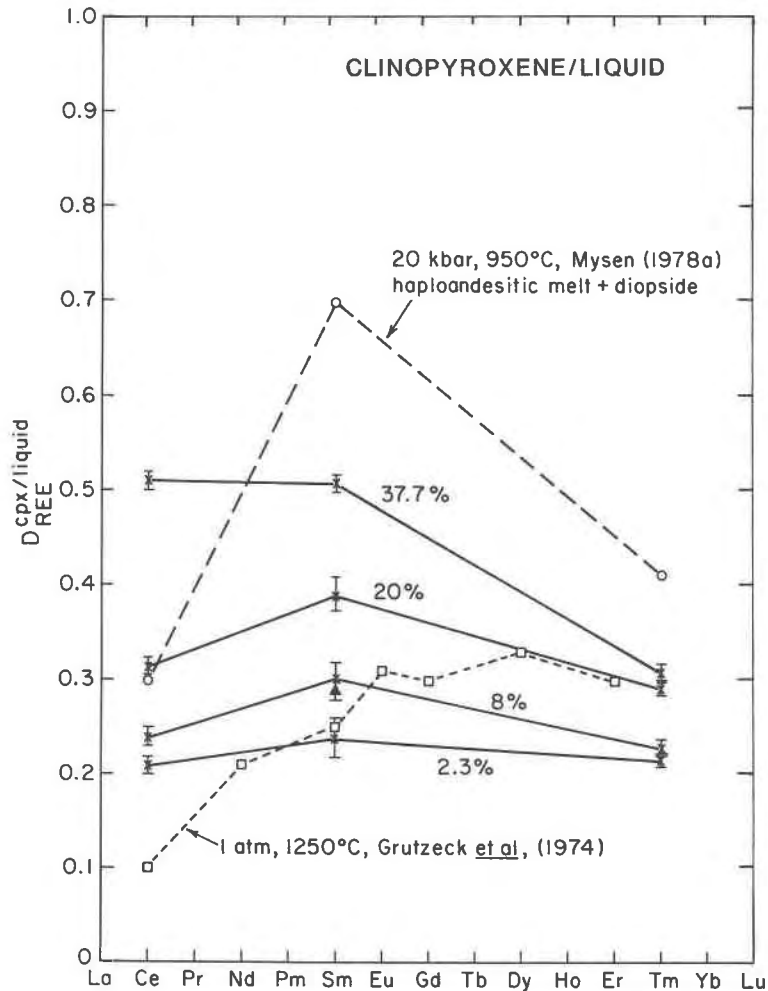


Fig. 3. Partition coefficients for Ce, Sm, and Tm between clinopyroxene and melts produced by 2, 8, 20, and 37.7% partial melting. Error bars are $\pm 1\sigma$. Also shown are data of Grutzeck *et al.* (1974) for diopside coexisting with a melt in the system $Ab-An-Di$ at 1 atm and 1250°C and data of Mysen (1978a) for diopside coexisting with a haploandesitic melt at 20 kbar and 950°C. The triangle denotes a value for D_{Sm} at 15 kbar, 1450°C, for diopside coexisting with a basaltic melt determined by Mysen.

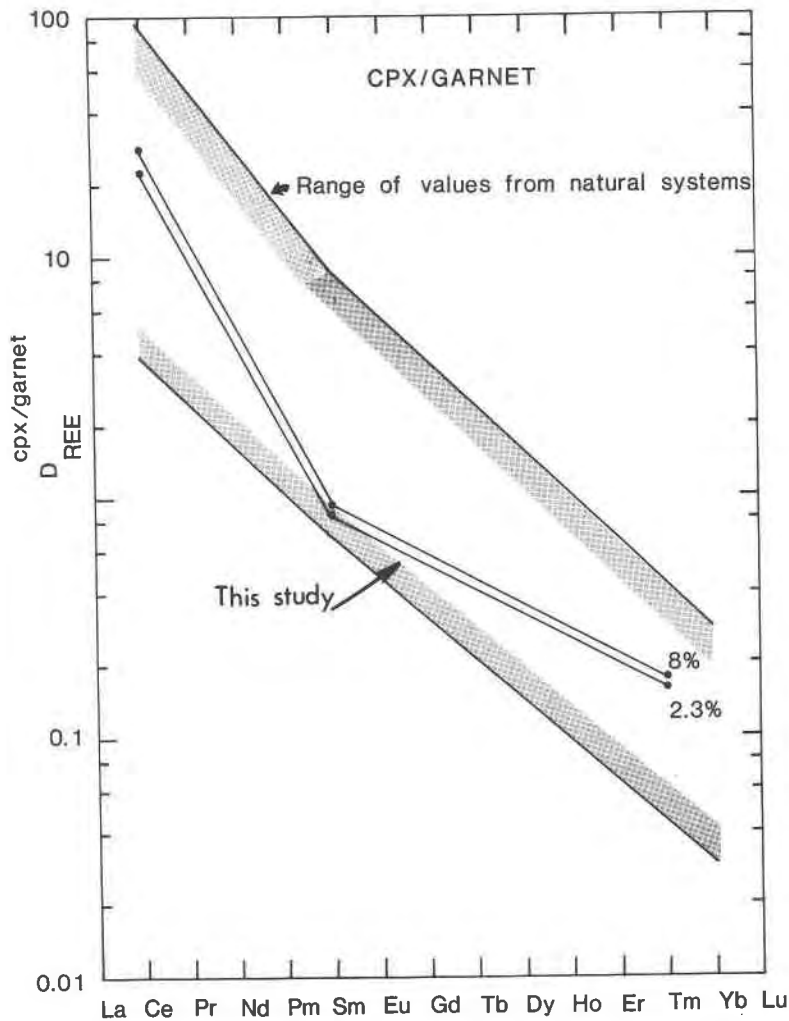


Fig. 4. Clinopyroxene/garnet REE ratios for 2.3 and 8% melt. A range of values calculated for REE analyses of peridotite nodules is also shown (see text).

The experimentally determined values in this study are in agreement with ratios from natural systems.

Orthopyroxene-melt partition coefficients. Figure 5 shows the values obtained for $D_{\text{REE}}^{\text{opx/melt}}$ as a function of the amount of melting. There is no analysis for $D_{\text{Ce}}^{\text{opx/melt}}$ at 37.7% melt. The partition coefficients increase with degree of melting. Values of D_{Ce} increase from 0.051 ± 0.004 at 2.3% melt to 0.072 ± 0.004 at 20% melt, D_{Sm} increases from 0.042 ± 0.002 at 2.3% melt to 0.099 ± 0.003 at 37.7% melt, and D_{Tm} increases from 0.050 ± 0.002 at 2.3% melt to 0.059 ± 0.002 at 37.7% melt. Except at 37.7% melt, there is relatively little fractionation of light or heavy REE by the crystal. The (M1) site onto which REE substitute is substantially smaller than the REE ions (ionic radii, 1.09, 1.04, and 0.96 \AA in octahedral coordination for Ce,

Sm, and Tm, respectively, and 0.80 \AA for Mg; Whittaker and Muntus, 1970), and although thulium is smaller than cerium it is unlikely that it approaches the Mg site size closely enough to have a substantial influence on D_{HREE} relative to D_{LREE} . Fractionation of the REE at 37.7% melting is probably due to liquid composition (e.g., Mysen *et al.*, 1979).

There is only one other investigation of partitioning of REE at high pressure between orthopyroxene and liquid. Mysen (1978a) investigated the behavior of REE at 10 and 20 kbar and 1025° and 1075°C . The melt with which his orthopyroxene crystals coexisted was haplobasaltic and contained 11–20 wt.% H_2O . Mysen's (1978a) data are shown in Figure 5 for comparison and are in agreement with partition coefficients determined in this study at low percentages of

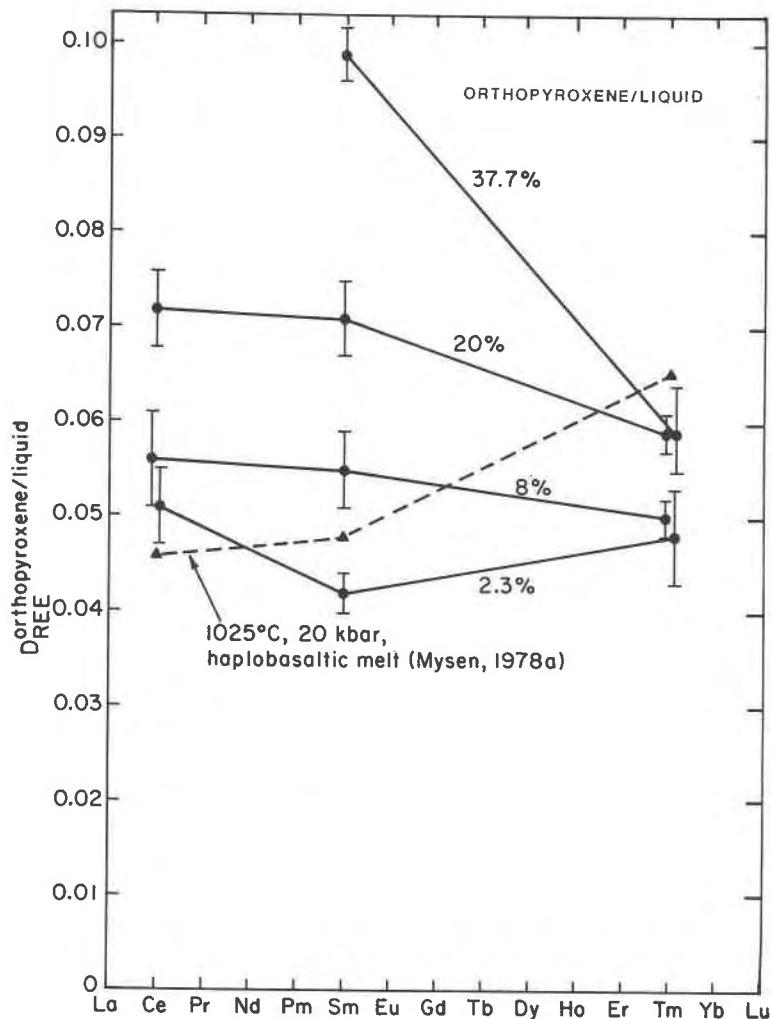


Fig. 5. Orthopyroxene/melt partition coefficients for Ce, Sm, and Tm at 2.3, 8, 20, and 37.7% partial melting. Error bars are $\pm 1\sigma$. Also shown are data of Mysen (1978a) in the system plagioclase₈₂-forsterite₁₆-silica₂ at 20 kbar and 1025°C.

melting. As there are differences in pressure, temperature, and composition (particularly H₂O content of the melt) between the two studies, the fact that these data are comparable must be fortuitous. Partitioning data at lower pressures between orthopyroxenes and melts and vapors have been reviewed by Cullers *et al.* (1973), Irving (1978), and Mysen (1978a). This study provides the first high-pressure data (35 kbar) on partition coefficients for REE between orthopyroxenes and melts; because the effect of pressure has not been evaluated, comparison with lower pressure data may not be meaningful.

Olivine-melt partition coefficients. Partition coefficients for Ce, Sm, and Tm between olivine and melt as a function of the amount of melting are shown in Figure 6. The value of D_{Ce} increases from 0.028 ± 0.001 at 2.3% melting to 0.049 ± 0.002 at 37.7%

melting, D_{Sm} increases from 0.030 ± 0.002 at 2.3% melting to 0.070 ± 0.006 at 37.7% melting, and D_{Tm} increases from 0.037 ± 0.001 at 2.3% melting to 0.046 ± 0.002 at 37.7% melting. The values of D_{REE} are close to those determined by Mysen (1978a). For 20 and 37.7% melt, D_{REE} are substantially higher than those determined by Mysen (1978a). As discussed above, Mysen's data are obtained at 20 kbar compared with 35 kbar in this study, and the crystals coexist with hydrous melts (20 wt.% H₂O). The data obtained at low pressure are reviewed by Irving (1978) and Mysen (1978a), and phenocryst-matrix data are summarized by Cullers *et al.* (1973). The values determined in this study are among the highest of any olivine-basaltic melt REE partition coefficients and are also determined under the highest pressure and temperature conditions.

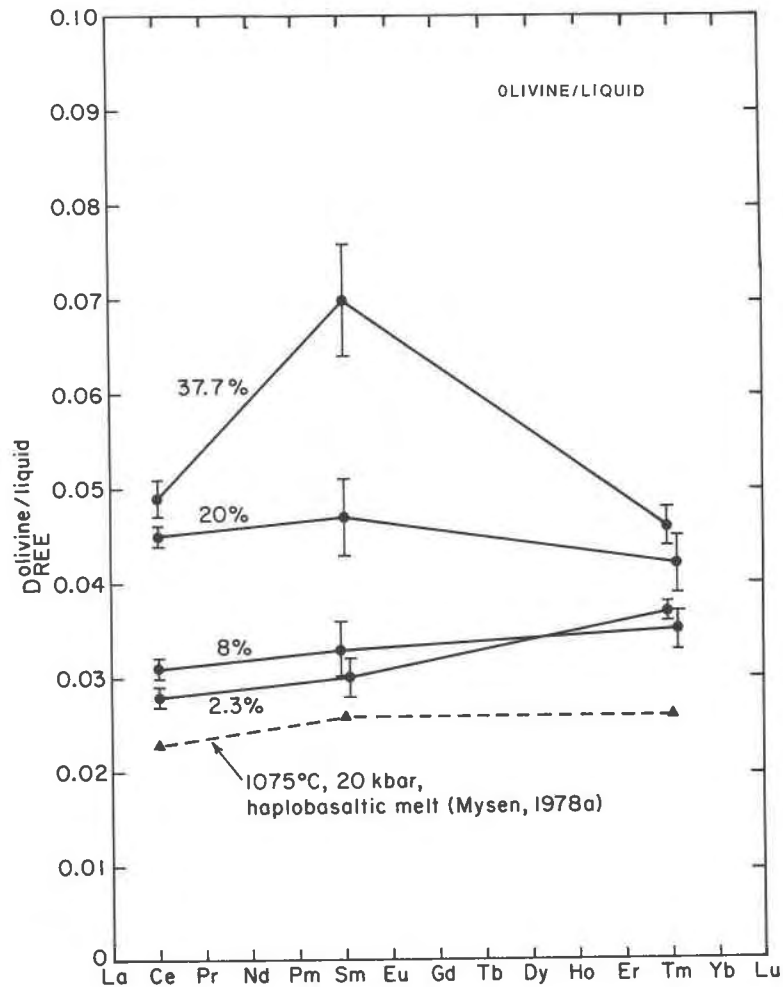
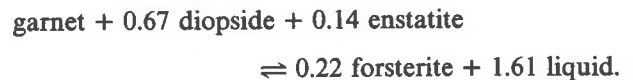


Fig. 6. Olivine/melt partition coefficients for Ce, Sm, and Tm at 2.3, 8, 20, and 37.7% partial melting. Also shown, for comparison, are the data of Mysen (1978a) for forsterite coexisting with a haplobasaltic, hydrous melt at 20 kbar and 1075°C.

Liquids. In Figure 7 the enrichment of radioactive Ce, Sm, and Tm in the melts relative to the initial spike is depicted; this experimentally determined enrichment factor, EF (Table 2), is equivalent to the chondrite-normalized REE pattern of partial melts of the nodule (Mysen and Holloway, 1977).

Also shown in Figure 7 are calculated enrichments of REE in 2.3 and 8% partial melts. The equation of Shaw (1970) for equilibrium partial melting (which is the case defined by these experiments) was used. Partition coefficients used in the calculations were those determined in this study (Table 2). The real phase proportions contributing to the melt are unknown, but as a first approximation the reaction stoichiometry for invariant melting in the system CaO–MgO–Al₂O₃–SiO₂ may be used. Mysen (1977a) has calculated the following reaction stoichiometry based

on mineral analyses and calculated liquid compositions in the system CMAS at high pressure:



The initial modal composition of the nodule was 10% garnet, 10% clinopyroxene, 20% orthopyroxene, 60% olivine (Nixon and Boyd, 1973; Shimizu, 1975). The calculated enrichments of Ce, Sm, and Tm in the 2.3% melt are, respectively, 15, 10.5, and 5.5 (Ce/Tm = 2.7) compared with the experimentally determined enrichments of 22, 10.7, and 5.3 (Ce/Tm = 4.15).

The lower value for cerium enrichment calculated from the reaction stoichiometry of the iron-free, synthetic system implies that more garnet must be entering the melt relative to clinopyroxene in the natural

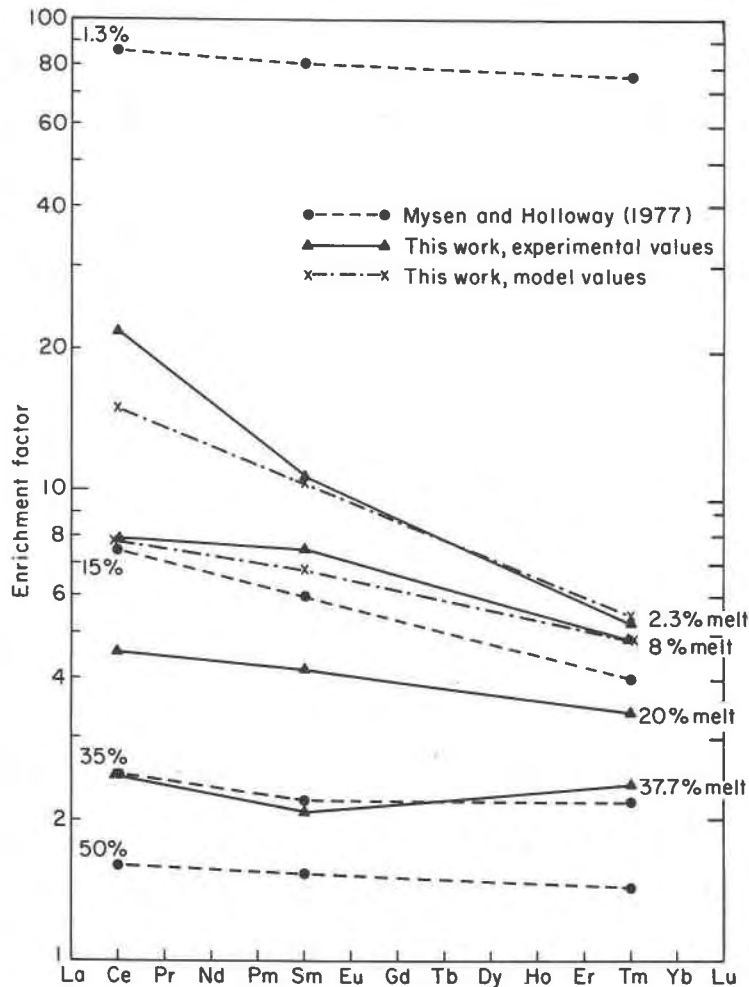


Fig. 7. Enrichment factors of Ce, Sm, and Tm in melts produced by 2.3, 8, 20, and 37.7% partial melting of PHN 1611 at 35 kbar, denoted by triangles. Also shown are the enrichment factors for 2.3 and 8% partial melts calculated for equilibrium partial melting denoted by crosses (see text). Data from Mysen and Holloway (1977) are indicated by dashed lines; enrichment factors for 1.3, 15, 35, and 50% partial melts at 20 kbar for PHN 1611 are shown.

system; *i.e.*, the presence of Fe has a greater effect in reducing the stability of garnet than it does in reducing the stability of clinopyroxene. Alternatively, the initial modal mineralogy may not be 10% clinopyroxene and 10% garnet as estimated by Nixon and Boyd (1973) and Shimizu (1975) but would have garnet in excess of 10% and clinopyroxene less than 10%.³ The first alternative is probably more reasonable. Of note, however, is the close agreement that exists between the experimentally determined patterns of REE enrichment and the calculated values. This agreement lends support both to the application of an invariant-

type melting interval when garnet is present and to the application of the melting reaction stoichiometry determined in CMAS by Mysen (1977a) to more complex, natural systems.

The 8% partial melt has a less fractionated pattern. Experimentally determined enrichment factors for Ce, Sm, and Tm are, respectively, 7.9, 7.6, and 4.95 ($Ce/Tm = 1.6$). Cerium enrichment is controlled by the percentage of melt present, *i.e.*, the cerium content at 8% melt is diluted relative to 2.3% melt, whereas thulium enrichment is controlled by the garnet/melt partition coefficients and remains relatively constant in the garnet melting interval. The lower value of Ce/Tm at 8% melt relative to 2.3% melt therefore reflects the increased percentage of melt and the lowering ratio of garnet/clinopyroxene. The

³ The use of other estimates of the modal mineralogy of PHN 1611 (*e.g.*, Boyd and McCallister, 1976) does not improve the fit of the data significantly.

calculated REE enrichment in an 8% partial melt is in close agreement with the experimentally determined pattern. It is to be expected that most deviation from the ideal behavior predicted from the CaO–MgO–Al₂O₃–SiO₂ reaction stoichiometry would be obtained at the lowest amounts of melting as initial melts will be relatively alkali and iron rich.

Between 20 and 37.7% melting, clinopyroxene is progressively removed. It is not surprising that the 20% melt is slightly LREE enriched, Ce/Tm = 1.34, whereas the 37.7% melt, close to the limit of clinopyroxene stability, has Ce/Tm ≈ 1.0. The difference in REE enrichment in the two percentages of melting reflects the dilution produced by increasing the amount of melt because neither orthopyroxene nor olivine fractionates REE significantly ($D_{\text{REE}}^{\text{opx/melt}}$ and $D_{\text{REE}}^{\text{ol/melt}}$ are both small).

No theoretical calculations of REE enrichment are possible at 20 and 37.7% melting because the melting reaction is unknown. Quench problems preclude microprobe analysis of phase compositions from which the melting reaction could be estimated.

Also shown in Figure 7 are the REE enrichment patterns of 1.3, 15, 35, and 50% partial melts of nodule PHN 1611 at 20 kbar determined by Mysen and Holloway (1977). At 20 kbar, garnet is replaced by spinel; consequently the heavy rare earth depletion in low percentage melts is not observed. The 1.3% melt has Ce/Tm = 1.3 compared with Ce/Tm = 4.2 in this study at 2.3% melting although the total REE enrichment is higher at 20 kbar. The two sets of data are in close agreement at 35 and 37.7% melt. At 20 kbar and 35% melt no clinopyroxene is melting; at 35 kbar and 37.7% melt, clinopyroxene is at the end of its stability field. In view of the small pressure dependence of olivine/melt and orthopyroxene/melt partition coefficients for REE (Mysen, 1978a), the agreement between the data in this paper and those of Mysen and Holloway (1977) implies that the melt compositions at 20 and 35 kbar cannot be very different from each other, a conclusion also reached by Mysen and Kushiro (1977).

Discussion

Partition coefficients for REE between garnet lherzolite minerals and melts

The partition coefficients determined in this work for three REE between olivine, orthopyroxene, clinopyroxene, garnet, and various percentages of melting

at high pressures and temperatures provide a coherent set of data that is complementary to the studies in synthetic systems by Mysen (1978a). Values of D_{REE} are, in general, close to those determined at similar pressures and temperatures in synthetic systems and fall within the much broader range of values defined from analyses of natural systems.

Partition coefficients vary as a function of degree of partial melting of garnet lherzolite. This relationship is predictable in view of the changing melt compositions (Mysen and Kushiro, 1977; Wendlandt and Mysen, 1978), increasing temperatures (1580°C at 2.3% melt to 1635°C and 37.7% melt), and changing trace element concentrations in all phases. Evidently the assumption made in most petrogenetic models that $D_{\text{REE}}^{\text{crystal/melt}}$ are constant is unrealistic. In the absence of more comprehensive partitioning data, modeling is constrained to this assumption. It is important to note that the variation in $D_{\text{REE}}^{\text{crystal/melt}}$ with the amount of melting is frequently negligible, e.g., $D_{\text{Ce}}^{\text{garnet/melt}}$ (Fig. 2A), $D_{\text{Tm}}^{\text{px/melt}}$ between 2.3 and 8% melt (Fig. 3), $D_{\text{Ce,Tm}}^{\text{opx/melt}}$ between 2.3 and 8% melt, $D_{\text{Tm}}^{\text{opx/melt}}$ between 20 and 37.7% melt (Fig. 5), $D_{\text{Ce,Sm,Tm}}^{\text{ol/melt}}$ between 2 and 8% melt, and $D_{\text{Tm}}^{\text{ol/melt}}$ between 20 and 37.7% melt (Fig. 6). For some REE and some minerals the assumption that D_{REE} are constant during magma generation and evolution may be realistic.

Partition coefficients at 2.3 and 8% melting. Between 2.3 and 8% melting, both temperature (1580° and 1585°C, respectively) and melt composition (melting is invariant-like at constant pressure) are essentially constant. It has been observed that $D_{\text{REE}}^{\text{crystal/melt}}$ may increase between the two melting fractions, however. Two variables may contribute to this increase. First, the Fe/Mg in crystals and melts changes, the ratio falling as the amount of melting is increased (see data of Mysen and Kushiro, 1977). Simple site-size considerations indicate that REE should substitute more readily onto an Fe-bearing site than an Mg-bearing site. Considering the influence of crystal structure alone, it is to be expected that as melting proceeds and the minerals become more Mg-rich $D_{\text{REE}}^{\text{crystal/melt}}$ will decrease. The reverse trend is observed; however, the melt Fe/Mg decreases at a faster rate than the crystal ratio, and the effect of melt composition on D_{REE} cannot be evaluated. Second, the REE concentrations in crystals and melts decrease as the amount of melt increase (Table 2). If Henry's law is not obeyed, $D_{\text{REE}}^{\text{crystal/melt}}$ will increase as the REE concentrations decrease. Mysen (1978a) has observed that Henry's law is obeyed only at very low concentrations of REE in olivines and orthopyroxenes (< 1–2

ppm), and Harrison (1978) has found that Henry's law is not obeyed for REE concentrations < 10–20 ppm in clinopyroxenes and garnets. It is suggested that the observed increases in D_{REE} between 2.3 and 8% melting are due to non-Henry's law behavior of REE. Partition coefficients for thulium are essentially constant, and it is suggested that as a result of the low concentrations in the crystals (Table 2), Henry's law behavior is obtained for this element. The increase in $D_{\text{Ce}}^{\text{crystal/melt}}$ is not greatly in excess of experimental error, and the assumption of constant partition coefficients in model calculations should not result in significant error. Partition coefficients for samarium show a significant increase as the melting event proceeds; evidently the Sm concentrations in the phases are outside the limits of Henry's law.

Partition coefficients at 20 and 37.7% melting. Values of $D_{\text{REE}}^{\text{crystal/melt}}$ vary much more between 20 and 37.7% melting than they do at the low percentages of melt. Unlike the lower melting interval, the variation in melt composition and, to a lesser extent, temperature (1620°–1635°C) is significant, and so the two sets of partition coefficients cannot be rigorously compared either with each other or with the lower percentage melt experiments.

Temperature may be considered an insignificant variable because of the small melting interval involved (15°C). Values of D_{REE} in these experiments appear to increase with increasing temperature although there is some consensus that D_{REE} decrease with increasing temperature (e.g., Irving, 1978; Mysen, 1978a). This increase must be interpreted in terms of changing melt and mineral compositions. Because melt compositions in these experiments are not characterized, no further discussion can usefully be made. Mysen and Kushiro (1977) suggested that the melt that coexists with the phases olivine + orthopyroxene + clinopyroxene at 35 kbar is olivine tholeiitic (10–39% melt). It is evident from Figures 2–6 that the difference in some partition coefficients between 20 and 38% melt is not so great as that between 8 and 20% melt; $D_{\text{Tm}}^{\text{opx/melt}}$, $D_{\text{Ce,Tm}}^{\text{ol/melt}}$, and $D_{\text{Tm}}^{\text{opx/melt}}$ do not have significantly different values between 20 and 37.7% melt. In view of the well-documented dependence of partition coefficients on melt composition (Watson, 1976; Irving and Frey, 1978; Ryerson and Hess, 1978), it is concluded that the melt composition between 20 and 37.7% melting probably is relatively constant. The bigger difference in partition coefficients between 8 and 20% melt is related to a major change in melt composition that results from the loss of garnet as a liquidus phase at 9% melting.

Application of these partition coefficients to other systems

The determination of D_{REE} for natural, garnet-lherzolite minerals and coexisting melts at high pressure and temperature in a normal REE concentration range provides a set of data that should be applicable to many problems of magma origin and evolution. The principal limitation of these data is that they pertain to a volatile-free system.

Anhydrous melting of peridotite undoubtedly produces many continental and oceanic basalts (Kushiro, 1972; Yoder, 1976; Mysen and Kushiro, 1977; Presnall *et al.*, 1978), and for such cases the partition coefficients determined here may be applicable when suitable corrections for pressure and temperature differences are made.

Melting in the mantle in the presence of volatiles such as CO₂ and H₂O may generate more unusual magmas at low percentages of melt (e.g., kimberlites, carbonatites, ultra-alkalic basalts; Eggler and Holloway, 1977; Mysen and Boettcher, 1975a,b; Wendlandt and Mysen, 1978; Wendlandt and Eggler, 1980a,b). The presence of CO₂ and H₂O in the magma source region will place serious limitations on the use of these partitioning data; the volatiles change melt structures (e.g., Mysen, 1977b) and phase relationships (Eggler, 1978; Mysen and Boettcher, 1975a,b) and reduce melting temperature (Mysen and Boettcher, 1975a,b; Wendlandt and Mysen, 1978). Watson (1976, 1977) and Mysen and Kushiro (1978) have shown that changes in melt structure have a strong influence on partition coefficients. For small amounts of melting where liquids may be volatile-saturated (Eggler and Holloway, 1977) and alkali-rich (Mysen and Kushiro, 1977; Eggler, 1974, 1977), the strong preference of REE for both H₂O and CO₂ vapor phases relative to minerals and melts (Mysen, 1979; Wendlandt and Harrison, 1979) and the influence of alkalis on REE solubilities in melts (Robinson, 1974a,b) place limitations on the use of the data obtained here.

At high percentages of melting, volatiles are diluted in the melts and their effects on partitioning may be much reduced. The data obtained here, when corrected for the reduced melting temperatures of a volatile-bearing peridotite (Mysen and Boettcher, 1975a,b; Wendlandt and Mysen, 1978), may thus be applicable to high percentages of melting of such a peridotite.

The effect of temperature on partition coefficients is not well defined; experimental studies of temperature dependency invariably involve changes in an-

other parameter (Weill and McKay, 1975; Harrison, 1977; Leeman and Lindstrom, 1978). Watson (1977) determined that $D_{Mn}^{ol/melt}$ decreases with increasing temperature and has evaluated this effect independently of melt compositional changes. Because changes in temperature of melting in this nodule will probably produce changes in melt composition also, it is impossible to predict how the partition coefficients determined in these anhydrous experiments would vary under different temperature regimes.

Implications for the genesis of alkali basalts

It has been suggested that alkali basalts may be generated by only a few percent of partial melting of a garnet-bearing source, owing to their enrichment in LREE (Gast, 1968; Kay and Gast, 1973; Shimizu and Arculus, 1975). Alkali basalts have chondrite-normalized Ce/Tm of 2–15 and LREE chondrite-normalized abundances of 40–200 (Schilling and Winchester, 1969; Kay and Gast, 1973; Shimizu and Arculus, 1975; Frey *et al.*, 1978). Values of Ce/Tm determined in these experiments are 4.18 (2.3% melt), 1.60 (8% melt), 1.35 (20% melt), and 1.03 (37.7% melt), and LREE chondrite-normalized abundances are ≤ 22 . Evidently, the LREE enrichment typical of alkali basalts *cannot* be generated even by very small degrees of anhydrous partial melting of a garnet lherzolite source with chondritic REE abundances, on the basis of the experiments presented in this paper. Two possible explanations arise. First, the crystal/melt partition coefficients, in particular, garnet/melt partition coefficients for HREE, used in modeling alkali basalt genesis need modifying (*e.g.*, Kay and Gast, 1973; Shimizu and Arculus, 1975). Investigations of $D_{REE}^{garnet/melt}$ have shown that order-of-magnitude variation may result from pressure, temperature, and

phase composition changes (Shimizu and Kushiro, 1975; Harrison, 1978; Irving and Frey, 1978). Because the melt REE pattern is principally controlled by the value of $D_{REE}^{garnet/melt}$ for small amounts of melting, it is crucial that D_{REE} , and in particular D_{HREE} , should be closely constrained in petrogenetic models.

Second, the mantle source region for alkali basalts may not have chondritic REE abundances but may be LREE enriched. The REE enrichments calculated in this paper are equivalent to those that would be obtained if the REE pattern for nodule PHN 1611 is chondritic; Shimizu (1975) derived such a pattern by analysis of garnet and clinopyroxene. An initial REE pattern of 3–5 times LREE enrichment and 1.5–2 times HREE enrichment would yield REE abundances typical for alkalic magmas if the partition coefficients determined in this work and reaction stoichiometry of Mysen (1977a) are used. A mantle REE enrichment of this magnitude, also predicted from the theoretical analysis of Minster and Allègre (1978) and Frey *et al.* (1978) and isotopic studies by Menzies and Murthy (1980), may be produced by a metasomatic event involving, for example, a CO₂–H₂O fluid phase (Mysen, 1979; Wendlandt and Harrison, 1979).

If PHN 1611 has undergone metasomatism (as suggested by its K₂O content of 0.14 wt.%), and intergranular deposition of REE has occurred, a REE analysis by phase separation will yield erroneous results. A recent whole-rock analysis by Morgan *et al.* (1980), reproduced in Table 3, shows that nodule PHN 1611 is enriched in LREE 3.5 times relative to chondrites and enriched in HREE 2 times relative to chondrites. The experimentally determined enrichment factors may be used to calculate the REE abundances that could be obtained from the enriched source (or, indeed, any source). The new values for nodule PHN 1611 (Table 3) are similar to those for alkali basalts.

Conclusions

1. Partial melting of a garnet lherzolite nodule, PHN 1611, for which iron loss to noble-metal capsules is avoided, occurs at temperatures at least 30°C lower than melting in the same nodule when iron loss is not avoided. Additionally, the phase field for garnet extends to only 10% melting, and the phase field for clinopyroxene extends to only 39% melting.

2. Partition coefficients for Ce, Sm, and Tm between garnet, clinopyroxene, orthopyroxene, olivine, and a coexisting melt have been determined for 2.3, 8, 20, and 37.7% melting of the nodule. Crystal-melt partition coefficients vary as a function of the amount of melting. Variations between 2 and 8%

Table 3. REE enrichments calculated from data of Morgan *et al.* (1980)

REE, ppm*	Cl-normalized†	Enrichment Factors			
		2.3% melt	8% melt	20% melt	37.7% melt
La	0.890	3.639			
Ce	2.250	3.527	78.1	26.9	16.3
Nd	1.650	3.483			8.7
Sm	0.470	3.052	32.6	23.2	12.8
Eu	0.173	2.982			6.4
Gd	0.065	0.318			
Tb	0.100	0.267			
Ho	0.130	2.293			
Tm	no data	2.100**	11.1	10.4	7.2
Yb	0.330	1.999			5.0
Lu	0.052	2.048			

*Data of Morgan *et al.* (1980).

†Normalized to Cl average of Evensen *et al.* (1978).

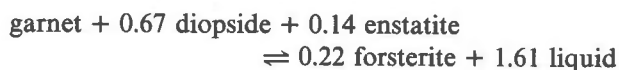
**Estimated value.

melting may be ascribed to non-Henry's law behavior of REE in the minerals as the melt composition and temperature remain essentially constant. Increasing partition coefficients from 8 to 37.7% melt reflect changes in melt composition, temperature (1585°–1635°C), and non-Henry's law behavior of REE. The total increase in $D_{\text{REE}}^{\text{crystal/melt}}$ may be up to a factor of 2 from 2 to 37.7% melt; however, some values of $D_{\text{REE}}^{\text{crystal/melt}}$ do not change significantly.

3. The assumption that $D_{\text{REE}}^{\text{crystal/melt}}$ remains constant during partial melting (and, presumably, fractional crystallization) is an oversimplification. Within certain melting intervals and for some REE, however, this assumption does not necessarily result in very poorly constrained models of basalt petrogenesis. It is particularly important that $D_{\text{REE}}^{\text{garnet/melt}}$ be well defined.

4. The REE patterns of the melts investigated do not show the fractionation and LREE enrichment typical of alkali basalts, and it is considered unlikely that such magmas may be generated by small percentages of melting of a garnet-bearing source with chondritic REE abundances. A garnet-bearing source with 3–5 times enrichment in LREE and 1.5–2 times enrichment in HREE relative to chondritic abundances would produce melts containing REE abundances appropriate for alkali basalts. A metasomatic event may produce the necessary REE enrichment of the mantle source region.

5. The REE patterns of 2.3 and 8% melts may be modeled adequately with an equilibrium partial melting model and a melting reaction that has the stoichiometry



in the system CaO–MgO–Al₂O₃–SiO₂ (Mysen, 1977a), providing further confirmation of the principle that melting behavior in natural systems may be modeled by simple systems.

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