Experimental study on rare-earth element partitioning in minerals formed at 20 and 30kb for basaltic systems

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Crystal/glass partition coefficients of rare-earth elements (REE), Ba and Sr were precisely determined for the systems prepared by partial melting and partial solidification of high-alumina basalt at 30kb and alkali olivine basalt at 20 and 30kb.

At 30kb partial melting produced garnet and clinopyroxene as the solid phase, while partial solidification at the same pressures produced only clinopyroxene as an essential mineral. The difference in mineral composition of the solid phase appears to be due to the difficulty of nucleation of garnet from the melts. Because of the higher tendency of garnet to enrich heavy REE compared with clinopyroxene, the bulk solid phase produced by partial melting shows much higher enrichment of heavy REE compared with that produced by partial solidification.

At 20kb both partial melting and partial solidification produced only clinopyroxene as the essential mineral. However, partition patterns for the systems produced by partial melting and those by partial solidification show small but systematic differences.

REE partition patterns are terrace-shaped for clinopyroxenes, which are formed by partial solidification at 30kb and by partial melting at 20kb, while REE partition pattern is modified peak-shaped for clinopyroxene formed by partial solidification at 20kb. But, rectilinear character with atomic number is commonly observed for these two REE partition patterns for clinopyroxenes. In partial melting at 30kb which produced garnet and clinopyroxene as the solid phase, on the other hand, REE partition pattern for the total solid is smoothly curved with atomic number and *schanze*-shaped.

The results of the present work suggest that liquid magmas produced by partial melting and partial solidification at the same temperatures and pressures from the initial material with the same chemical composition could show widely different trace element abundances. It should also be emphasized that such kinetic effect on both mineral assemblage in the solid phase and on the (bulk solid)/(liquid) partition coefficients must be taken into account in discussing the origin and evolution of magmas on the basis of trace element partitioning. Further, it should be added that, in partial solidification, formation of clinopyroxene essentially free from other minerals prevails in wide fields of chemical composition of liquid and physical conditions of pressure and temperature. It is emphasized in this study that rectilinear natures of REE partitioning for this clinopyroxene are very favorable in interpreting REE patterns of many igneous rocks.

INTRODUCTION

Recognition of importance of rare-earth element (REE) geochemistry in petrogenesis has stimulated researchers to investigations on REE partitioning among coexisting phases. Investigation of REE partitioning for natural coexisting phases is one of the possible approaches in this field and has been carried out by a number of researchers (e.g., ONUMA *et al.*, 1968; SCHNETZLER and PHILPOTTS, 1968, 1970; HIGUCHI and

NAGASAWA, 1969; NAGASAWA and SCHNETZLER, 1971; PHILPOTTS *et al.*, 1972; NAGASAWA, 1973; SHIMIZU, 1975, and LARSEN, 1979). Another approach is to study the REE partitioning under experimentally controlled conditions. This approach could be much significant and several experimental studies have been made: MASUDA and KUSHIRO (1970), CULLERS *et al.* (1973), GRUTZECK *et al.* (1974), SHIMIZU and KUSHIRO (1975), TANAKA and NISHIZAWA (1975), MASUDA *et al.* (1977), RYERSON and HESS (1978), TERA-

KADO and MASUDA (1979), MYSEN (1979), WENDLANDT and HARRISON (1979), NICOLLS and HARRIS (1980) and HARRISON and WOOD (1980). It is true that these investigations greatly contributed to REE geochemistry on petrogenesis. But, many essential and fundamental problems concerning the REE partitioning still remain unsolved or untouched after these studies.

In general, many reserchers have interpreted the REE patterns of igneous rocks on the basis of the following premises; both processes of partial melting and partial solidification produce the same mineral assemblage and the effective REE partition patterns between solid and liquid phases agree with each other; trace element partitioning is controlled solely by crystal structure of mineral under consideration; REE patterns of igneous rocks can be interpreted by the combination of partitioning coefficients of associated minerals (ONUMA *et al.*, 1968; GAST, 1968; SHAW, 1970; JENSEN, 1973; MATSUI *et al.*, 1977, and ALLEGRE and MINSTER, 1978). On the other hand, MASUDA (1963, 1978, 1979a) has placed emphasis on that many REE patterns of igneous rocks, having logarithmic linearity, are quantitatively explained only if the bulk partition coefficients between solid and liquid are rectilinear with the atomic numbers of REE. MASUDA designated such characters of bulk partition coefficients as an integer effect. In addition, he meant an aspect of this effect as comprising appearance of turning point of bulk partition pattern at a position of atomic number. Further, MASUDA stressed that partial solidification and partial melting cannot always stand in mutually reversible relation in effect.

In natural processes, thermodynamic equilibrium might not be attained and metastable phases could play a potential role in generating natural rocks we observe. Many petrological problems are treated as phases being in equilibrium state. It is true that these treatments have been successful in many cases. But, to comprehend wider aspects or mechanism of the naturally occurring problems, it would be necessary to accumulate information not only on equilibrium state but also on the nonequi-

librium one in which metastable phases appear.

Experimental studies on REE partitioning with high precision are needed to examine these unsolved problems, even if there remains a question concerning time scale. Detailed discussions would be possible only on the basis of the results precisely determined under the controlled conditions. Many of the experimental studies on REE partitioning in the past are unsatisfactory in precision on REE determination and some are insufficient in major element analysis to discuss problems as stated above.

In this study, partition coefficient patterns of REE, Ba and Sr are precisely determined for pairs of glass and crystal phases prepared at 20 and 30 kb for natural basaltic systems. On the basis of these results together with the major element analysis, REE partitioning will be discussed with special reference to the following fundamental problems: reversibility of REE partitioning between melting and solidification process, relation of REE partitioning to the major element partitioning or crystal structure and connection with the bulk REE patterns of igneous rocks.

EXPERIMENTAL

Two kinds of basalts were used as starting materials; one is high-alumina basalt of Mt. Fuji from Mishima and another is alkali olivine basalt from the Oki-Dogo islands, Japan. Table 1 shows the major element compositions and concentrations of REE, Ba and Sr in basalt employed for the present purpose. A piston-cylinder type apparatus was used for the high pressure experiments and sample powder was enveloped in molybdenum foil. Table 2 shows experimental conditions and run products obtained. In "D-series" experiments, powder of basalt was completely molten at high pressures in a piston-cylinder apparatus and then temperature was slowly lowered to cause the partial solidification and maintained constant for one hour. After that, the whole system was quenched. In "E-series" experiments, temperature was maintained for one hour at desired

Table 1. Major chemical compositions (wt. %) and concentrations (ppm) of REE, Ba and Sr in starting materials

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
High-alumina basalt	49.33	1.46	17.55	11.25	0.14	5.39	9.59	2.70	0.71	98.12
Alkali olivine basalt**	47.53	2.31	15.45	9.45	0.15	9.88	7.66	3.84	1.91	98.18

	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	Ba	Sr
High-alumina basalt	7.71	19.63	14.89	4.04	1.306	4.41	4.40	2.54	2.41	0.365	218	406
Alkali olivine basalt	27.6	55.6	27.2	5.73	1.931	5.19	4.03	1.826	1.505	0.217	492	558

* Total iron as FeO.

** TAKAHASHI (1978).

Table 2. Details of high pressure experiments

Run No.	P (kb)	Temperature (°C) and time (min)	Starting material	Phases present
D-H-30-25	30	1500° (5 min) — (30 min)	high-alumina basalt	cpx + gl
D-H-30-40	30	1500° (5 min) — (60 min)	"	cpx + gl
E-H-30-33	30	1375° (60 min)	"	cpx + ga + gl
E-H-30-36	30	1400° (60 min)	"	cpx + ga + gl
D-A-30-56	30	1500° (5 min) — (30 min)	alkali olivine basalt	cpx + gl
D-A-30-73	30	1500° (5 min) — (30 min)	"	cpx + gl
E-A-30-54	30	1400° (60 min)	"	cpx + ga + gl (+ qch + residual ol)
E-A-30-72	30	1430° (60 min)	"	cpx + ga + gl (+ qch + residual ol)
D-A-20-62	20	1400° (5 min) — (30 min)	"	cpx + gl
D-A-20-77	20	1400° (5 min) — (30 min)	"	cpx + gl
E-A-20-60	20	1260° (60 min)	"	cpx + gl (+ residual ol)
E-A-20-76	20	1230° (60 min)	"	cpx + gl (+ residual ol)

Note: cpx, clinopyroxene; ga, garnet; gl, glass; residual ol, residual olivine phenocryst from starting material; qch, quench crystal; D, D-series (partial solidification); E, E-series (partial melting); H, high-alumina basalt; A, alkali olivine basalt.

points to allow crystalline phase to coexist with silicate melt produced by partial melting.

For the system of alkali olivine basalt, both D-series (partial solidification) and E-series (partial melting) experiments were performed at 20 and 30 kb. These experimental runs are named "D-A-30-series" (D-series for alkali olivine basalt at 30 kb), "E-A-30-series" (E-series for alkali olivine basalt at 30 kb), "D-A-20-series" (20 kb) and "E-A-20-series". High pressure experiments in the system of high-alumina basalt were carried out at 30 kb and they are called "D-H-30-series" (D-series for high-alumina basalt at 30 kb) and "E-H-30-series" (E-series for high-alumina basalt at 30 kb). Each series was repeated twice and experimental results of two runs in each series are generally in good agreement as shown later.

The phase separation was carried out with methylene iodide and acetone after crushing the run products. The concentrations of REE, Ba and Sr in separated fractions were determined by mass-spectrometric stable isotope dilution technique. In most cases, REE, Ba and Sr abundances were determined with accuracies better than 1%. The effect of impurity corrections for reagents used were usually below 1% with REE, Ba and Sr. Major element compositions were determined by an electron microprobe. Weight ratios of glass to mineral phases in each run were estimated by microscopic observations covering wide areas.

RESULTS

Mineral assemblage As shown in Table 2, a difference in mineral assemblage was observed at 30 kb, depending on experimental procedure, i.e., D-series (partial solidification) and E-series (partial melting) experiments. This difference in mineral assemblage is common to both systems of high-alumina basalt and alkali olivine basalt. In E-A-30 and E-H-30, garnet and clinopyroxene coexist with glass, as expected by the results of GREEN and RINGWOOD (1967). The garnet is about 30-50 μm in size and appears euhedral. The clinopyroxene is about 10 μm in

size and its crystals stick together into a cluster. In D-A-30 and D-H-30, clinopyroxene only coexists with glass and garnet is not found even at 30 kb. This clinopyroxene is several hundred μm in size and euhedral. Electron microprobe and optical studies did not reveal substantial zoning in this large clinopyroxene. In D-A-20 (partial solidification for alkali olivine basalt at 20 kb), clinopyroxene is the only crystal coexisting with melt in the same way as in 30 kb experiments of D-series. The size and shape of the clinopyroxene for D-A-20-series experiments are similar to those of clinopyroxene obtained in D-A-30 and D-H-30 experiments. In E-A-20, also clinopyroxene coexists with melt, but this clinopyroxene is relatively small in size, that is, about 10 μm . A little fraction of olivine phenocryst in starting material remained as a relict in E-A-20 and E-A-30 and, besides, quench crystals were observed in E-A-30. Corrections were made for the effects of these appendant minerals. However, effects of these corrections were almost negligible and had no essential effects on the following discussions. Very small amounts of opaque minerals were present in some of E-series runs.

Major element compositions Table 3 shows the major element compositions of crystal and glass phases. It is observed that total FeO content of run products is smaller than that of starting materials in some of runs, especially in D-series runs. This decrease of FeO content would be due to reaction of FeO in starting materials with molybdenum vessel used for high pressure experiments.

Clinopyroxene obtained from high-alumina basalt contains 16-17% Al_2O_3 and 7-10% MgO; clinopyroxene in the runs of alkali olivine basalt contains 9-12% Al_2O_3 and 12-18% MgO. Both clinopyroxenes are highly aluminous and rich in sodium. (GREEN and RINGWOOD, 1967, reported high Al_2O_3 content of 7-11% in clinopyroxene formed at 13-18 kb. NAKAMURA and MASUDA, 1976, also reported that clinopyroxene formed at 20 kb contained 13-15% Al_2O_3 .) As shown in Table 4, Ca/Mg atomic ratio of clino-

Table 3a. Major element compositions for clinopyroxene, garnet and glass formed in 30kb experiments on high-alumina basalt

	D-H-30-25	D-H-30-25	D-H-30-40	D-H-30-40	E-H-30-33	E-H-30-33	E-H-30-33	E-H-30-36	E-H-30-36	E-H-30-36
	glass	cpx	glass	cpx	glass	garnet	cpx	glass	garnet	cpx
SiO ₂	55.87	48.13	52.48	48.09	57.28	39.34	47.41	54.79	39.03	47.71
TiO ₂	1.79	1.20	1.50	1.24	1.51	1.14	0.81	1.71	0.88	0.95
Al ₂ O ₃	17.31	16.59	17.52	16.36	17.60	21.10	16.71	17.29	21.34	17.14
FeO*	9.63	9.47	7.85	6.97	7.15	20.33	10.43	8.47	18.07	7.63
MnO	0.14	0.21	0.10	0.18	0.06	0.46	0.14	0.08	0.41	0.14
MgO	2.70	8.72	4.17	9.74	2.35	8.10	7.01	2.70	9.40	7.41
CaO	7.46	13.17	8.98	14.17	8.23	9.81	14.37	8.63	9.49	15.23
Na ₂ O	2.91	2.23	2.95	2.35	3.90	0.08	2.83	3.58	0.07	2.83
K ₂ O	1.16	0.01	0.80	0.01	1.21	0.01	0.02	1.10	0.01	0.02
Total	98.97	99.73	96.35	99.10	99.29	100.37	99.73	98.35	98.70	99.06

* Total iron as FeO.

Table 3b. Major element compositions for clinopyroxene, garnet and glass formed in 30kb experiments on alkali olivine basalt

	D-A-30-56	D-A-30-56	D-A-30-73	D-A-30-73	E-A-30-54	E-A-30-54	E-A-30-54	E-A-30-72	E-A-30-72	E-A-30-72
	glass	cpx	glass	cpx	glass	garnet	cpx	glass	garnet	cpx
SiO ₂	52.04	51.72	53.22	51.46	49.82	42.00	50.87	48.95	39.65	49.55
TiO ₂	2.63	1.48	3.26	1.52	2.51	1.09	1.06	3.00	1.40	1.36
Al ₂ O ₃	17.51	11.29	16.23	12.13	15.02	22.08	12.05	15.96	22.88	11.86
FeO*	3.94	4.67	7.72	7.49	7.22	10.77	6.07	7.57	10.76	6.17
MnO	0.06	0.12	0.14	0.20	0.09	0.26	0.10	0.15	0.31	0.16
MgO	7.22	16.35	3.79	15.38	8.39	17.79	14.15	6.58	17.19	13.67
CaO	6.28	10.27	4.40	9.69	7.41	6.33	12.46	6.77	6.44	13.24
Na ₂ O	4.20	2.54	4.81	2.36	4.15	0.07	2.54	4.43	0.08	2.76
K ₂ O	2.50	0.01	3.21	0.02	1.96	0.02	0.04	2.40	0.01	0.03
Total	96.38	98.45	96.78	100.25	96.57	100.41	99.34	95.81	98.71	98.80

* Total iron as FeO.

Table 3C. Major element compositions for clinopyroxene and glass formed in 20kb experiments on alkali olivine basalt

	D-A-20-62	D-A-20-62	D-A-20-77	D-A-20-77	E-A-20-60	E-A-20-60	E-A-20-76	E-A-20-76
	glass	cpx	glass	cpx	glass	cpx	glass	cpx
SiO ₂	49.48	49.80	49.22	48.76	49.20	48.76	51.33	47.60
TiO ₂	2.91	1.65	2.98	1.42	2.86	1.70	2.91	2.43
Al ₂ O ₃	17.64	10.57	18.29	11.76	18.40	10.71	19.18	9.76
FeO*	8.09	7.61	9.36	8.60	9.10	7.86	8.19	7.68
MnO	0.10	0.17	0.07	0.14	0.12	0.19	0.15	0.21
MgO	6.04	17.90	4.06	16.82	5.10	14.79	3.80	12.42
CaO	6.29	10.32	4.54	9.90	5.98	13.93	5.09	17.25
Na ₂ O	4.65	1.34	5.35	1.54	4.96	1.54	5.17	2.01
K ₂ O	2.51	0.01	3.45	0.02	2.62	0.03	2.93	0.04
Total	97.71	99.37	97.33	98.96	98.34	99.51	98.75	99.40

* Total iron as FeO.

Table 4. Formulas of clinopyroxene on the basis of 6 oxygens

	D-H-30-25	D-H-30-40	E-H-30-33	E-H-30-36	D-A-30-56	D-A-30-73	E-A-30-54	E-A-30-72	D-A-20-62	D-A-20-77	E-A-20-60	E-A-20-76
Si	1.753	1.749	1.745	1.748	1.853	1.830	1.831	1.805	1.797	1.774	1.774	1.782
Al	0.247	0.251	0.255	0.252	0.147	0.170	0.169	0.195	0.203	0.226	0.218	0.233
Al	0.465	0.451	0.470	0.488	0.330	0.339	0.342	0.315	0.246	0.278	0.243	0.193
Ti	0.033	0.034	0.022	0.026	0.040	0.041	0.029	0.037	0.045	0.039	0.047	0.068
Fe	0.288	0.212	0.321	0.234	0.140	0.223	0.183	0.188	0.230	0.262	0.240	0.238
Mn	0.007	0.006	0.004	0.004	0.004	0.006	0.003	0.005	0.005	0.004	0.006	0.007
Mg	0.473	0.528	0.385	0.405	0.873	0.815	0.759	0.742	0.962	0.912	0.806	0.687
Ca	0.514	0.552	0.567	0.598	0.394	0.369	0.480	0.517	0.399	0.386	0.545	0.686
Na	0.158	0.166	0.202	0.201	0.177	0.163	0.177	0.195	0.094	0.108	0.109	0.145
K	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.002
Z	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
X + Y	1.938	1.949	1.972	1.957	1.957	1.957	1.974	2.000	1.981	1.990	1.996	2.023
Atomic ratio												
Ca/Mg	1.09	1.05	1.47	1.48	0.451	0.453	0.632	0.697	0.415	0.423	0.676	0.999
Na/(Ca + Mg)	0.160	0.154	0.212	0.200	0.140	0.138	0.143	0.155	0.069	0.083	0.081	0.106
NaAlSi ₂ O ₆	0.16	0.17	0.20	0.20	0.18	0.16	0.18	0.19	0.09	0.11	0.11	0.14
CaAl ₂ SiO ₆	0.28	0.27	0.26	0.27	0.15	0.18	0.17	0.16	0.18	0.20	0.18	0.15

pyroxene of E-series (partial melting) is higher than that of clinopyroxene of D-series (partial solidification), e.g., 0.42-0.45 in D-A-20 and D-A-30 and 0.63-1.0 in E-A-20 and E-A-30 (Table 4). Further, E-series clinopyroxene is somewhat rich in sodium compared with D-series clinopyroxene, e.g., numbers of sodium atoms in clinopyroxene on the basis of 6 oxygens are 0.16 in D-H-30 and 0.20 in E-H-30. The proportion of jadeite component in clinopyroxene at 30 kb is larger than in clinopyroxene at 20 kb, e.g., 0.09-0.14 at 20 kb and 0.16-0.19 at 30 kb in runs for alkali olivine basalt. Besides, the Al content of the four-coordination site in the clinopyroxene at 20 kb is larger than that of the clinopyroxene at 30 kb, corresponding to the decrease of tschermak molecule in clinopyroxene with increased pressure.

Garnet obtained by employment of alkali olivine basalt as a starting material has the compositions of $\text{Fe}_{21}\text{Mg}_{63}\text{Ca}_{16}$ and $\text{Fe}_{22}\text{Mg}_{63}\text{Ca}_{16}$ in atomic ratios, whereas the compositions of garnet from high-alumina basalt are $\text{Fe}_{43}\text{Mg}_{31}\text{Ca}_{26}$ and $\text{Fe}_{38}\text{Mg}_{36}\text{Ca}_{26}$ in atomic ratios. This difference in atomic ratios between these two kinds of garnet is larger than the difference between the starting materials ($\text{Fe}_{25}\text{Mg}_{48}\text{Ca}_{27}$ for alkali olivine basalt and $\text{Fe}_{34}\text{Mg}_{29}\text{Ca}_{37}$ for high-alumina basalt). Concentration ratios of components between garnet and glass are 1.4-1.5 for FeO, 2.1-2.6 for MgO and 0.85-0.95 for CaO in alkali olivine basalt and 2.1-2.8 for FeO, 3.4 for MgO and 1.1 for CaO in high-alumina basalt. The partitioning of these components between garnet and liquid seems to depend strongly on the chemical composition of liquid.

Concentration ratios of SiO_2 between crystal and glass phases are 0.77-0.91 in runs of high-alumina basalt and are 0.95-1.0 in most runs of alkali olivine basalt. Glasses from high-alumina basalt turn out to have normative quartz, while the starting material has normative olivine. In runs of alkali olivine basalt, on the other hand, glass phases have similar SiO_2 content to those of crystal phases and all glasses are nepheline-normative. In contrast to the case of SiO_2 content, Al_2O_3 concentration ratios of crystal to

glass are close to unity in run products of high-alumina basalt. In the case of alkali olivine basalt, on the other hand, Al_2O_3 concentration ratio of clinopyroxene to glass is about 0.6 in most runs of D-A-20, D-A-30 and E-A-20 series (clinopyroxene is the only essential mineral in these experiments). Glass of E-A-30 experiments, where garnet as well as clinopyroxene crystallized, contains about 15% Al_2O_3 , which is low compared with the other glasses from alkali olivine basalt.

Partitioning of REE, Ba and Sr Table 5 shows partition coefficients of REE, Ba and Sr. In this paper, unless otherwise noted, the "partition coefficient" means the concentration ratio between crystalline and glass phases. Concentrations in a composite of garnet and clinopyroxene are calculated from concentrations in each of the two phases and their estimated ratios. Solid fractions, which were separated by heavy liquid and composed of garnet and clinopyroxene, have been also analyzed to refine the calculation.

Partition coefficients between clinopyroxene and liquid for Ba, Sr and La are similar in all runs. Ratios of the partition coefficient of Ba to Sr lie in the range of 0.74-1.23. Similar values ranging from 0.65-0.76 have been obtained in high-pressure experimental studies by TANAKA and NISHIZAWA (1975) and MASUDA *et al.* (1977). On the other hand, SHIMIZU (1974) obtained also by high-pressure experiments smaller partition coefficients between clinopyroxene and liquid for Sr and Ba. That is, the coefficients lie in the ranges 0.054-0.081 for Sr and 0.00078-0.0023 for Ba; ratios of the partition coefficient of Ba to Sr are 0.015-0.028. These disagreements should be attributed to difference in phase separation technique for high-pressure run products. In the present work, phase separation was carried out with heavy liquid, while SHIMIZU (1974) employed the differential dissolution technique. If inclusions and defects rich in large-ion lithophile (LIL) elements exist inside crystals, effective partition coefficients of these elements should come out different for these two separation techniques.

Table 5A. Partition coefficients of REE, Ba and Sr for crystal-glass pairs formed in 30kb experiments on high-alumina basalt

	D-H-30-25 clino- pyroxene*	D-H-30-40 clino- pyroxene*	E-H-30-33 garnet + cpx	E-H-30-33 garnet	E-H-30-33 clino- pyroxene	E-H-30-36 garnet + cpx	E-H-30-36 garnet	E-H-30-36 clino- pyroxene
La	0.294	0.449	0.379	0.236	0.587	0.472	0.188	0.695
Ce	0.331	0.447	0.379	0.223	0.606	0.486	0.193	0.715
Nd	0.426	0.489	0.435	0.286	0.652	0.510	0.257	0.708
Sm	0.552	0.591	0.658	0.635	0.692	0.634	0.566	0.687
Eu	0.441	0.440	0.795	0.845	0.722	0.716	0.719	0.713
Gd	0.686	0.709	1.16	1.43	0.755	0.937	1.27	0.672
Dy	0.826	0.810	2.24	3.23	0.810	1.60	2.89	0.580
Er	0.848	0.862	3.43	5.21	0.833	2.57	5.30	0.427
Yb	0.855	0.851	4.09	6.48	—	3.65	7.90	0.313
Lu	0.849	0.869	4.23	6.64	0.722	3.90	8.53	0.273
Ba	0.274	0.441	0.421	0.278	0.629	0.325	0.0954	0.506
Sr	0.308	0.360	0.344	0.167	0.601	0.444	0.146	0.680

* Apparently free from garnet.

Table 5B. Partition coefficients of REE, Ba and Sr for crystal-glass pairs formed in 30kb experiments on alkali olivine basalt

	D-A-30-56 clino- pyroxene*	D-A-30-73 clino- pyroxene*	E-A-30-54 garnet + cpx	E-A-30-54 garnet	E-A-30-54 clino- pyroxene	E-A-30-72 garnet + cpx
La	0.288	0.355	0.422	0.121	0.700	0.179
Ce	0.303	0.387	0.511	0.144	0.848	0.216
Nd	0.379	0.497	0.574	0.232	0.888	0.360
Sm	0.476	0.641	0.768	0.541	0.978	0.649
Eu	0.354	0.512	0.780	0.623	0.925	0.669
Gd	0.561	0.795	1.03	1.19	0.889	1.25
Dy	0.663	0.940	1.64	2.56	0.790	2.31
Er	0.706	0.992	2.33	4.24	0.566	3.52
Yb	0.719	0.990	2.95	5.73	0.393	4.57
Lu	0.719	0.968	3.17	6.30	0.297	4.68
Ba	0.250	0.282	0.440	0.109	0.744	0.143
Sr	0.296	0.348	0.465	0.117	0.785	0.162

* Apparently free from garnet.

Table 5C. Partition coefficients of REE, Ba and Sr for clinopyroxene-glass pairs formed in 20kb experiments on alkali olivine basalt

	D-A-20-62 clino- pyroxene*	D-A-20-77 clino- pyroxene*	E-A-20-60 clino- pyroxene*	E-A-20-76 clino- pyroxene*
La	0.316	0.332	0.316	0.288
Ce	0.354	0.378	0.350	0.336
Nd	0.468	0.504	0.464	0.455
Sm	0.619	0.668	0.599	0.590
Eu	0.490	0.521	0.559	0.508
Gd	0.776	0.818	0.731	0.725
Dy	0.891	0.960	0.852	0.828
Er	0.923	0.964	0.873	0.867
Yb	0.930	0.844	0.868	0.864
Lu	0.835	0.794	0.890	0.860
Ba	0.267	0.291	0.258	0.220
Sr	0.301	0.351	0.292	0.239

* Apparently free from other minerals.

In the separation using heavy liquid, LIL elements in these inclusions and defects may be involved in the solid fraction, while, in the separation using differential dissolution technique, LIL elements in such inclusions and defects may be included in the liquid fraction. To find which separation technique is better for understanding the naturally occurring processes, we need to clarify the mechanism of partitioning of trace elements. If it is assumed that the presence of small inclusions and defects rich in LIL elements is intrinsic features of crystals forming from magmas in nature, these inclusions and defects rich in LIL elements should be included in the solid fraction rather than in the liquid fraction. (Similarly, if there exist grain boundary layers rich in LIL elements, the elements in these layers should be treated in the same fashion as the case of LIL elements in inclusions and defects in crystals.)

MASUDA *et al.* (1977) classified REE partitioning patterns into three groups: terrace-shaped, peak-shaped and *schanze*-shaped. It is observed that bulk REE partition patterns, i.e., between total solid and liquid, depend on mineral assemblages. When clinopyroxene and garnet coexist with liquid (e.g., E-A-30 and E-H-30), the bulk REE partitioning pattern is *schanze*-shaped as seen in Figs. 1 and 2. The pattern shows a kind of S-shaped smooth curve and the heaviest REE has the largest partition coefficient. Partition coefficients of heavy REE exceed unity. The pattern resembles the one for M-3 by MASUDA *et al.* (1977), although there are differences in absolute magnitude among them.

The *schanze*-shaped pattern is understood to be ascribed to the presence of garnet. As shown in Figs. 1 and 2, partition patterns of garnet separated here are also *schanze*-shaped and their inclinations are steeper than those of partition patterns for crystalline mixture of garnet and clinopyroxene. The REE partition pattern for garnet of this study is qualitatively similar to previous results for synthetic systems by SHIMIZU and KUSHIRO (1975) and for natural rocks by SCHNETZLER and PHILPOTTS (1970),

Fig. 1. Partition coefficient patterns of REE, Ba and Sr for crystal-glass pairs formed in partial melting experiments at 30 kb on high-alumina basalt. Ga, garnet; Cpx, clinopyroxene; Ga + Cpx, mixture of crystal phases composed of garnet and clinopyroxene.

though there are considerable differences in absolute magnitudes and curving features. Figure 1 and 2 show also the partition coefficient patterns of clinopyroxene coexisting with garnet in E-H-30 and E-A-30-series. The partition coefficients of these clinopyroxenes are smaller than unity and are peak-shaped. Because of difficulty of complete separation of clinopyroxene from garnet, the fine structures of the REE partition patterns cannot be revealed. It is certain, however, being indifferent to the effect of garnet as a possible impurity, that the partition coefficients of light REE for clinopyroxene coexisting with garnet are larger than those for clinopyroxene free from garnet.

MASUDA (1967b) dealt with the REE concentration ratios between clinopyroxene and garnet and pointed out a general simple relationship between them. Figure 3 shows the REE concentration ratios between coexisting clinopyroxene and garnet obtained experimentally in this study and the corresponding ratios between naturally coexisting clinopyroxene and garnet reported by PHILPOTTS *et al.* (1972) and SHIMIZU (1975). All of these patterns in Fig. 3 are very similar to each other. It draws our attention that the clinopyroxene-garnet REE ratios are practically identical in both systems of high-alumina basalt and alkali olivine basalt and it would be much significant that the ratios experimentally secured here are in good agreement with the corresponding previous values for natural systems.

In partial solidification experiments of D-H-30- and D-A-30-series, only clinopyroxene coexists with liquid and garnet is absent even at 30 kb. Patterns of partition coefficients are

Fig. 2. Partition coefficient patterns of REE, Ba and Sr for crystal-glass pairs formed in partial melting experiments at 30 kb on alkali olivine basalt. Labels as for Fig. 1.

terrace-shaped and the coefficients are below unity (Fig. 4). The patterns display flatness over the span of heavy REE. They appear to be composed of three linear segments, having two inflection points: Nd and Dy for D-H-30-25 and Pr and Ho for D-H-30-40, D-A-30-56 and D-A-30-73. Their essential features are common to those reported by TANAKA and NISHIZAWA (1975) and those for B-3 and MM by MASUDA *et al.* (1977). Thus, at 30 kb experiments of high-alumina basalt and alkali olivine basalt, bulk REE partitioning patterns differ clearly among run products of partial melting and partial solidification, owing to the difference in mineral assemblages: garnet and clinopyroxene for partial melting and solely clinopyroxene for partial solidification.

As for 20 kb experiments of alkali olivine basalt, clinopyroxene is an essential mineral in both processes of partial melting and partial solidification, but REE partition patterns somewhat differ between the two kinds of clinopyroxene. In runs of partial melting (E-A-20-series), the patterns are terrace-shaped and

Fig. 3. REE and Ba concentration ratios of clinopyroxene to garnet. Numerical symbols 33, 36 and 54 refer to run products of E-H-30-33, E-H-30-36 and E-A-30-54, respectively, of this study; 155, eclogite reported by PHILPOTTS *et al.* (1972); 1611, garnet lherzolite (PHN 1611) by SHIMIZU (1975).

horizontal linear segments over the heavy REE appear to have inflection at or near Dy (Fig. 5). In runs of partial solidification (D-A-20-series), on the other hand, the REE partition patterns are modified peak-shaped. There appears a maximum plateau in these modified peak-shaped REE partition patterns as shown in Fig. 5. If extensions are drawn from both slopes adjacent to the plateau, they intersect at Ho or Er.

The clinopyroxenes free from garnet have relatively narrow ranges of the partition coefficient values for each REE and have similar inclinations in the Nd-Gd segment in their REE partition patterns; ratios of partition coefficient of Nd to Gd are 0.60-0.63 for six clinopyroxenes under consideration and 0.68-0.69 for the other two (D-H-30-40 and D-A-30-56). MASUDA (1979b) proposed to express the partition coefficients for the rectilinear segment covering light (and middle) REE in a form given by $A(\alpha + n)/(\alpha + 14)$, where A and α are variable constants and n 's are integers for elements corresponding to their atomic number differences starting from La ($n=0$ for La). For Nd-Gd segment except

for Eu, the values of α are around 4.0 and those of A are about 1.2 in most cases for the partition patterns of clinopyroxenes free from garnet in this study. It is interesting that the value of $\alpha=4$ in this study is close to that of $\alpha=3.3$ obtained mathematically by MASUDA (1967a).

Production of the Nd-Gd linear segment and that of the heavy REE segment intersect at Ho in D-A-30-series and at Dy or Tb in D-A-20- and E-A-20-series. This difference in the intersection or inflection point would be attributed to the difference in pressure under which clinopyroxenes were formed. It is interesting that the intersection point shifts to the position of larger atomic number at higher pressures.

REE partition patterns display negative Eu anomalies of about 15% for six runs of E-series (partial melting) and of about 30% for six runs of D-series (partial solidification). These Eu anomalies may be due to divalent valency state of part of Eu in these experiments as discussed

Fig. 4. Partition coefficient patterns of REE, Ba and Sr for clinopyroxene-glass pairs formed in partial solidification experiments at 30kb on high-alumina basalt (D-H-30) and alkali olivine basalt (D-A-30).

Fig. 5. Partition coefficient patterns of REE, Ba and Sr for clinopyroxene-glass pairs formed in partial solidification (D-A-20) and partial melting (E-A-20) experiments at 20kb on alkali olivine basalt.

Fig. 6a

Fig. 6b

Fig. 6a and 6b. Partition coefficient-ionic radius diagrams for garnet-glass pairs.

by TANAKA and NISHIZAWA (1975).

DISCUSSION

Partition coefficient-ionic radius diagram (PC-IR diagram) In Figs. 6, 7 and 8, the partition coefficients are plotted against ionic radii in the same manner as ONUMA *et al.* (1968), JENSEN (1973) and MATSUI *et al.* (1977). These authors concluded that partition coefficient is controlled by the crystal structure and PC-IR diagrams give smooth parabola-like peak.

In PC-IR diagrams of this study, ionic radii by SHANNON and PREWITT (1970) were used and iron was assumed as ferrous state. For garnet of E-H-30-33, the REE curve and the curve of Sr-Ca-Mn look to be subparallel. The latter curve has a peak maximum near Mn. For garnet of E-A-30-54, however, the two curves intersect. For clinopyroxene having the modified peak-shaped REE partition pattern such as D-A-20-62 and D-A-20-77, the two partition curves for Sr-Ca-Mn-Fe and for REE run subparallel and

have peak maxima at nearly the same ionic radius. (For D-A-20-62, note that the peak top span, Dy-Er-Yb, is horizontal.) For clinopyroxene having terrace-shaped REE partition pattern such as D-H-30, D-A-30 and E-A-20, the curves of REE in PC-IR diagrams appear conformable in a broad sense to those of divalent cations. At the same time, horizontality for heavy REE span and a sharp turning to flatness are noteworthy. As shown in Figs. 7 and 8, PC-IR diagrams for the two kinds of clinopyroxenes with modified peak-shaped and terrace-shaped REE partition patterns demonstrate essentially the same features for curves of divalent and monovalent cations. The difference in REE partition pattern seems to be correlated with a difference in the relative position of two curves for divalent cations and REE. In a case, that the partition coefficient of Fe is smaller than the largest value of REE partition coefficients, the REE partitioning pattern tends to be peak-shaped rather than terrace-shaped.

GRUTZECK *et al.* (1974) and TERAKADO and

Fig. 7a

Fig. 7b

Fig. 7a and 7b. Partition coefficient-ionic radius diagrams for clinopyroxene-glass pairs. REE partition pattern for clinopyroxene in these figures is modified peak-shaped.

MASUDA (1979) reported REE partition coefficients for diopside prepared experimentally at atmospheric pressure and showed that the REE partition pattern has two peaks corresponding to M1 and M2 sites in the pyroxene structure. Clinopyroxenes formed at 20-30kb have terrace-shaped or peak-shaped partition patterns and possess no peak attributable to M1 site (MASUDA and KUSHIRO, 1970; TANAKA and NISHIZAWA, 1975; MASUDA *et al.*, 1977, and this study).

The REE partition patterns (Figs. 1, 2, 4 and 5) and PC-IR diagrams (Figs. 6, 7 and 8) would enable us to conclude that REE partition coefficient patterns are approximately conformable with the crystal structures and, at the same time, exhibit the atomic number or "integer" characters such as rectilinear features of REE partition patterns having sharp inflection points in terms of the atomic number array.

Significance of rectilinear character in REE partitioning Figure 9 shows that REE, Ba and

Sr patterns normalized by the relevant starting material. This type of illustration is useful in comparing the results obtained in this study with REE patterns of natural rocks normalized by chondrite. The REE partition pattern is *schanze*-shaped for E-H-30-33, modified peak-shaped for D-A-20-77 and terrace-shaped for E-A-20-62 and D-A-30-73 (Figs. 1, 2, 4 and 5). The first system (E-H-30-33) comprises garnet and clinopyroxene in its mineral phase, whereas the latter three systems comprise clinopyroxene only in their solid phases. The REE patterns for glass phases of the latter three systems appear to consist of two rectilinear segments, being inflected sharply at Dy or Ho; the pattern of D-A-20-77 is almost symmetrical with the possible inflection point at Ho, while heavy REE spans for E-A-20-60 and D-A-30-73 are represented by horizontal lines. These represent typical features of liquid-type REE patterns (MASUDA, 1969, 1979b). As noted by MASUDA (1978, 1979a), REE in many igneous rocks nor-

Fig. 8a

Fig. 8b

Fig. 8c

Fig. 8a, 8b and 8c. Partition coefficient-ionic radius diagrams for clinopyroxene-glass pairs. REE partition pattern for clinopyroxene in these figures is terrace-shaped.

malized by chondrite have logarithmically linear patterns with or without inflection points. These patterns in igneous rocks can be considered to reflect essentially the same effects as obtained for experiments E-A-20-60, D-A-20-77 and D-A-30-73 and could be explained only by the rectilinear form of REE partition pattern, not by the curved ones.

As shown in Fig. 9, REE patterns of solid phase from E-H-30-33 also distinctly differ from solid phase patterns of E-A-20-60, D-A-20-77 and D-A-30-73. In the lighter and middle REE span, solid phase for E-H-30-33 shows downward convex curve, while solid phases for the other runs under consideration show upward convex curves. REE patterns of many abyssal tholeiites and island arc tholeiites display upward convex curves in the light and middle REE span in the same fashion as the pattern of solid phases of E-A-20-60, D-A-20-77 and D-A-30-73 (FREY and HASKIN, 1964; MASUDA, 1966 and 1968; KAY *et al.*, 1970; SCHILLING, 1971; MASUDA *et al.*, 1977; KAY and HUBBARD, 1978, and SHIMIZU *et al.*, 1980). REE patterns of these tholeiites could be explained in terms of the rectilinear REE

Fig. 9a

Fig. 9b

Fig. 9a and 9b. REE, Ba and Sr patterns of glass and crystal phases normalized by the relevant starting material.

partition patterns only.

REE patterns in igneous rocks are interpreted by many authors on a basis of a combination of partition coefficients of constituent minerals (e.g., GAST, 1968; SHAW, 1970, and ALLEGRE and MINSTER, 1978). But, as aforementioned, the rectilinear partitioning for clinopyroxene formed free from other minerals can quantitatively and simply explain the features in REE patterns such as the marked rectilinearity, the sharp break and the horizontality for heavy REE span. The aforementioned authors did not pay any attention to these features. Moreover, it should be noted emphatically that the major element compositions of glasses and clinopyroxenes for D-H-30, D-A-30-, D-A-20- and E-A-20- series are in a range of basaltic rocks (and andesitic rocks for glass of D-H-30-series).

Stability of clinopyroxene formed by partial solidification It would draw attention that clinopyroxene prevails as the only essential mineral in D-series (partial solidification) experiments (this study, TANAKA and NISHIZAWA, 1975, and MASUDA *et al.*, 1977). As stated before,

clinopyroxene in these runs shows the rectilinear REE partition pattern. In contrast to results by GREEN and RINGWOOD (1967), garnet does not appear even at 30kb. In order to examine the stability of the clinopyroxene in D-series, the following four additional 30kb experiments were tried by employment of high-alumina basalt.

In the first experiment, glass was prepared by fusing high-alumina basalt at 1 atmosphere, 1,300°C in a piston-cylinder apparatus. Quenched glass was taken out, pulverized and used for high pressure run at 30kb and 1,385°C. In the second experiment, high-alumina basalt was fused in the same fashion as that of the first experiment. The whole system was quenched once, left as it was for 10 minutes, then the system was brought to 30kb and 1,400°C, and kept for one hour. That is, unlike in the first experiment, glass formed at 1 atmosphere was not pulverized in the second experiment. In the third experiment, glass was prepared by fusing high-alumina basalt at 30kb and 1,500°C. After quenching, glass was taken out, pulverized, and used for a high pressure experiment at 30kb and 1,385°C. In the fourth experiment, high-alumina basalt was fused at 30kb and 1,500°C

and, after quenching the whole system, the system was kept at 30kb and at a room temperature for 10 minutes. Then the system was again brought to 30kb and 1,400°C. The difference between the third and fourth experiments, in both of which the glass was prepared at 30kb, is also whether glass was pulverized or not. Garnet appeared in the second and fourth experiments, but not in the first and third ones.

The following facts were revealed from these four experiments in addition to foregoing 30kb D- and E-series experiments. Garnet would not nucleate either from melt or from unpulverized glass even at 30kb, while clinopyroxene never fails to appear coexisting with silicate melt in both cases. When pulverized glass or powder of rocks is used as starting material, garnet as well as clinopyroxene appears coexisting with silicate melt at 30kb. BOYD and ENGLAND (1959) and COHEN *et al.* (1967) pointed out the difficulty of garnet nucleation. Thus, the clinopyroxene formed free from garnet is not regarded as an ultimately stable phase in a thermodynamic sense, but the clinopyroxene is a metastable phase to crystallize persistently from a basaltic *homogeneous* system even at 30kb. This can be interpreted as related with close resemblance in atomic structure between the metastable clinopyroxene and the basaltic melt under high pressures. Appearance or nonappearance of garnet can be ascribed to whether nucleation occurs in a heterogeneous system or homogeneous one. Needless to say, the powder of basalt is heterogeneous in chemical composition. Besides, powder of chemically homogeneous glass can be regarded as energetically heterogeneous because of the surface energy. It would be reasonable that it is very difficult to develop a heterogeneous solid phase from the system which is completely homogeneous in both physical and chemical senses.

It may be suspected that, in experiments of partial solidification, the loss of FeO into capsules during total melting thwarts the crystallization of garnet because of the decrease of garnet stability field in FeO-poor systems. How-

ever, D-A-30-73 produces clinopyroxene only, although the loss of FeO is negligibly small. Therefore, it is hard to consider that the decrease of FeO content during high pressure experiment is a cause for prevailing appearance of clinopyroxene in partial solidification. (The results of additional four high pressure experiments mentioned above also confirm this conclusion.)

Further, it has been observed in experiments at 10kb on picrite basalt that clinopyroxene is an essential mineral in the partial solidification, while partial melting produces olivine and clinopyroxene as crystalline phase coexisting with silicate melt (MASUDA, SHIMIZU and SANGEN, unpublished). Thus, it would be considered that partial solidification prevalently produces metastable clinopyroxene essentially free from other minerals in wide fields of chemical compositions and physical conditions. On the other hand, partial melting would give rise to diversification in a solid phase, producing thermodynamically stable assemblages: for example, garnet and clinopyroxene at 30kb, clinopyroxene at 20kb and olivine and clinopyroxene at 10kb in some basaltic systems. Moreover, it would be worthwhile noting that the metastable clinopyroxene formed by partial solidification has always rectilinear REE partition pattern, while REE partition patterns for products of partial melting vary with the change of mineral assemblage. For instance, the REE partition pattern for products of partial melting is curved one at 30kb because garnet is included, but the pattern is rectilinear one at 20kb because clinopyroxene is the only crystalline phase. Further, it would be added that REE partition pattern is modified peak-shaped for clinopyroxene of partial solidification in the alkali olivine basalt at 20kb and the pattern is terrace-shaped for clinopyroxene of partial melting in the same basalt at the same pressure. It is concluded from these results that REE partition patterns of partial solidification and partial melting do not always agree with each other.

MASUDA (1978) suggested that REE patterns for whole rocks were determined by a process to separate single-phase solid precursor from the

true melt. The metastable clinopyroxene in partial solidification might be regarded as corresponding to this solid-precursor. Of course, it is likely that some stimulus of change in physical conditions causes an irreversible disintegration of the metastable clinopyroxene into garnet-clinopyroxene system at 30 kb or other mineral assemblages thermodynamically stable at given temperatures and pressures. However, it should be noted that such a secondary solid-state reaction would not change the bulk REE pattern for a whole rock and the overall effect reflecting the property of the metastable clinopyroxene would remain as bold lines.

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