RARE-EARTH GEOCHEMISTRY OF ANTARCTIC DIOGENITES

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Abstract : Rare-earth elements (REE) were determined for seven diogenite samples (four whole rock samples, two separate fractions and one handpicked orthopyroxene sample), prepared from Yamato-74010, -74013, -74037 and -74136. Diogenites, Yamato-74037 and -74136, have positive Ce anomalies of 14 and 17%, respectively. REE distribution has been found to be heterogeneous even in the same sample (Yamato-74010) of the size less than 2 g without any apparent distinctions in itself. The Lu contents are generally lower than in diogenites studied by Fukuoka *et al.* (1977) and Schmitt *et al.* (1963). Unlike diogenites examined by these authors, REE patterns of a large fraction of Antarctic diogenites show marked turning-up toward the lightest REE.

Diogenite Yamato-74010 was separated into four fractions, with the special aim of collection of a floating ultrafine-grained fraction. This fraction and a coarse-grained one display contrasting differences in Eu anomaly as well as Na content.

Assuming that, in ideally the simplest case, the REE partition coefficient function for orthopyroxene is a logarithmically linear function of difference in atomic number, a function responsible for turning-up towards the lighter REE was evaluated. Regardless of mutually opposite signs, the absolute magnitude of inclination coefficient for this function is similar to that for the function ideally assumed for simple orthopyroxene effect.

1. Introduction

Diogenites composed of orthopyroxene are one of major achondrites (Mason, 1962; McCarthy *et al.*, 1973; Fukuoka *et al.*, 1977). According to the information from the National Institute of Polar Research (*cf.* Takeda *et al.*, 1978, 1979), diogenites are relatively abundant in Antarctic meteorite collection to other achondrites such as eucrites and howardites. [Genetic relations among these achondrite groups were discussed by researchers including McCarthy *et al.* (1973) and Takeda *et al.* (1976).] Therefore, it can be said that the collection of Yamato meteorites has supplied us with copious samples to gain a deeper insight into origin and nature of diogenites.

However, the Yamato diogenites are unique diogenites with a non-brecciated

granoblastic texture (TAKEDA *et al.*, 1975, 1978, 1979). Rare earth data may provide us with a clue to the nature of reheating event that caused recrystallization of the Yamato diogenites.

SCHMITT *et al.* (1963) were the first to determine rare-earth elements (REE) in diogenites, Johnstown and Shalka. Recently FUKUOKA *et al.* (1977) performed the geochemical investigation of howardites, diogenites and eucrites, determining many elements with emphasis on REE. Also MASUDA and TANAKA (1978) analyzed a diogenite Yamato-692 or Yamato-6902 for REE, which was formerly called Yamato-b.

2. Experimental

Here we have carried out the REE determination in several diogenites, employing the stable isotope dilution. Corrections have been made for blank values for reagents used. The blank corrections are at most 3% of uncorrected values. For some fractions separated in unique manner as shown in Fig. 1, Al_2O_3, FeO,
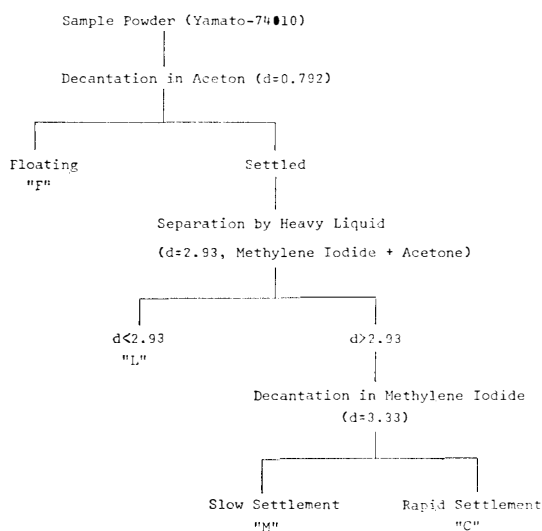

Fig. 1. Scheme of separation employed.

Table 1. Fractions of Yamato-74010B separated by the experimental procedure shown in Fig. 1.

Notation	wt. %	Grain size (mm)
"F" (floating)	12.68	0.01~0.1
"L" (light)	0.20	
"M" (slow settlement)	31.75	*ca.* 0.1
"C" (rapid settlement)	55.37	0.1~0.5

MgO, CaO, Na$_2$O and Cr$_2$O$_3$ were determined by atomic absorption spectrophotometry in addition to REE.

Novelty of the procedure of separation mentioned above consists in collection of floating fine particle fraction, F, after rather gentle crushing. One cannot rule out a possibility that part of this fraction was produced by pulverization of originally coarse grains. Nevertheless, we have employed this procedure with expectation to selectively recover the originally ultrafine-grained and/or heterogeneous thin-film portion presumably filling the boundaries between well-developed "major" grains. According to the mineralogical description by TAKEDA et al. (1978), the structure with coarse-grained orthopyroxene includes islands of fine-grained crystals of pyroxene with numerous minute inclusions. The inclusions resemble dust and their shape is droplet-like. We cannot say any words about whether our "floating fine particle fraction" represents fine-grained portion with droplet-like inclusions described by TAKEDA et al. (1978). It is not necessarily unlikely that the "F" fraction in question differs from fine-grained portion or droplet-like inclusions mentioned by those authors. This problem remains to be studied.

After crushing a chip (B) of diogenite Yamato-74010, we applied the above procedure of separation to most of Yamato-74010B and the remainder was used for the whole rock analysis. (Another chip (A) of Yamato-74010 was analyzed for REE.) The data on results of separation of Yamato-74010B are given in Table 1.

Besides, coarse orthopyroxene grains were handpicked from Yamato-74013.

3. Results and Discussion

In Fig. 2 and Table 2 are shown the REE abundances in diogenite samples, Yamato-74010A, -74010B, -74013, -74037 and -74136, and separated fractions Yamato-74010B–F and Yamato-74010B–C. In this paper, REE abundances obtained were all normalized by the Leedey chondrite values (MASUDA et al., 1973) in preparing Masuda-Coryell plot (MC plot).

3.1. Whole-rock REE pattern

As seen in Fig. 2, diogenite REE patterns have similar features in a very rough sense, but it might be said at the same time that the differences among individual patterns are considerably large. In particular, notable differences are recognized for light REE span and Eu. The sample Yamato-74013 shows a positive Eu anomaly, whereas all other whole-rock samples studied have negative Eu anomalies, extent of which is variable. Differences in "tail", namely the lightest REE range here, are also remarkable. When starting from Lu, the chondrite-normalized value in MC plot decreases linearly with the decrease of atomic number for heavy REE range from Lu through Dy with frequent, small
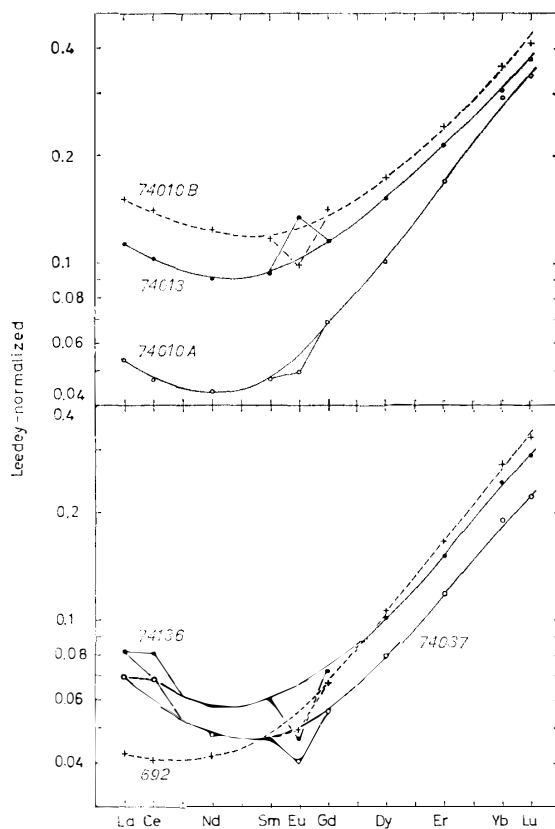
Fig. 2. Leedey-normalized REE patterns of Antarctic diogenites studied (cf. Table 2). For Yamato-74010B (calculated) and -74010A, see text.

irregularities at Yb; a *very* slight concave curvature may be felt sometimes. (It will be seen below that this almost insensible concave curvature for heavy REE can be related with appearance of obvious concave curvature for light REE span.) The curve of the pattern for light REE span is turned up to varying extent toward the lightest REE, and, accordingly, the position of minimum appears to differ from sample to sample analyzed. Analyses of Yamato-74010A and -74010B reveal the noticeable heterogeneity even in the same sample of the size less than 2 g. The REE pattern for whole-rock sample of Yamato-74010B was calculated from REE patterns for its fractions, F and C, assuming the REE abundances in M to be the same as in C; appropriateness of this assumption will be proved by the chemical data presented below. (Influence of fraction L is negligible, although in the present calculation we took the REE abundances in L as equal to those in F.)

Diogenites Yamato-74136 and -74037 are peculiar in showing positive Ce anomalies; extents of positive deviations are 17 and 14% for 74136 and 74047, respectively, relative to smooth curve values. Also these two diogenites are distinct

Table 2. Abundances (ppm) of REE in Yamato diogenites and their normalized values by Leedey chondrite.

	Yamato-74010A	Yamato-74013	Yamato-74037	Yamato-74136	Yamato-74010B "fine"	Yamato-74010B "coarse"	Yamato-74010B calculated	Yamato-74013 ortho-pyroxene	Yamato-692*	Leedey chon-drite**
REE abundances (ppm)										
La	0.0204	0.0427	0.0264	0.0311	0.0741	0.0548	0.0572	0.0164	0.0160	0.378
Ce	0.0459	0.1001	0.0663	0.0789	0.1628	0.1343	0.1379	0.0421	0.0397	0.976
Nd	0.0315	0.0646	0.0342	0.0411	0.0963	0.0887	0.0897	0.0347	0.0297	0.716
Sm	0.01092	0.0214	0.0106	0.01381	0.0271	0.0270	0.0270	0.0127	0.0107	0.230
Eu	0.00431	0.01171	0.00351	0.00401	0.0285	0.00570	0.00860	0.00484	0.00429	0.0866
Gd	0.0212	0.0362	0.0172	0.0223	0.0403	0.0442	0.0437	0.0251	0.0206	0.311
Dy	0.0397	0.0590	0.0310	0.0397	0.0650	0.0687	0.0682	0.0437	0.0417	0.390
Er	0.0434	0.0553	0.0302	0.0390	0.0574	0.0622	0.0616	0.0451	0.0429	0.255
Yb	0.0725	0.0768	0.0477	0.0603	0.0843	0.0901	0.0893	0.0718	0.0681	0.249
Lu	0.01314	0.01445	0.00860	0.0112	0.01429	0.01624	0.01599	0.0133	0.0127	0.0387
Leedey-normalized values										
La	0.0539	0.1130	0.0698	0.0822	0.1960	0.1449	0.1514	0.0434	0.0423	
Ce	0.0470	0.1026	0.0680	0.0808	0.1668	0.1376	0.1413	0.0431	0.0407	
Nd	0.0439	0.0902	0.0477	0.0574	0.1345	0.1239	0.1252	0.0485	0.0415	
Sm	0.0475	0.0930	0.0461	0.0600	0.1177	0.1173	0.1174	0.0552	0.0465	
Eu	0.0498	0.1351	0.0405	0.0463	0.330	0.0658	0.0993	0.0559	0.0495	
Gd	0.0681	0.1164	0.0555	0.0718	0.1296	0.1422	0.1406	0.0807	0.0662	
Dy	0.1018	0.1513	0.0795	0.1018	0.1667	0.1761	0.1749	0.1121	0.1069	
Er	0.1700	0.217	0.1184	0.1529	0.225	0.244	0.2416	0.1769	0.1682	
Yb	0.291	0.308	0.1916	0.242	0.338	0.362	0.3588	0.288	0.273	
Lu	0.340	0.373	0.222	0.290	0.369	0.420	0.4132	0.344	0.328	
Amount taken (mg)	503.4	505.1	988.5	1017.4	94.2	110.7		86.1	380.2	

* MASUDA and TANAKA (1978), ** MASUDA et al. (1973).

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from other Antarctic diogenites studied here in that their Lu contents are lowest.

The Lu contents in Antarctic diogenites investigated by us are lower than those reported by SCHMITT et al. (1963) and FUKUOKA et al. (1977) for their diogenites, except Shalka. That the REE patterns obtained by these authors do not display the rolling-up toward the lightest REE as disclosed by the present work would also be worth pointing out. It has been reported that Yamato-692 (TAKEDA et al., 1975) and -74 diogenites (TAKEDA et al., 1978) are unique in having non-brecciated granoblastic texture. Both geochemical and mineralogical investigations demonstrate that Antarctic diogenites are different generally from diogenites studied thus far. It should not be considered that such characteristics of REE geochemistry as low Lu content and rolling-up of REE pattern are not always associated intrinsically with findings of mineralogical texture. This can be understood as indicating a great difference in origin.

3.2. Separated fractions

FUKUOKA et al. (1977) made geochemical investigations about two fractions, i.e., fine-grained fraction (<100 mesh) and handpicked pyroxene crystals, of Johnstown. As mentioned above (see Fig. 1), we attempted a new type of separation with the aim at collecting "floating" fines. (It is questionable whether the fine-grained fraction obtained by FUKUOKA et al. is similar in quality to our fines.) Fig. 3 shows that the heavy REE abundances in fraction C are a little higher than in fraction F, while the abundances of La, Ce, and Nd in fraction C are somewhat lower than in fraction F. At any rate a great difference in Eu abundance between the two fractions would draw our keen attention. Compared with the "normal" value estimated from the relevant smooth curve, Eu in fraction F
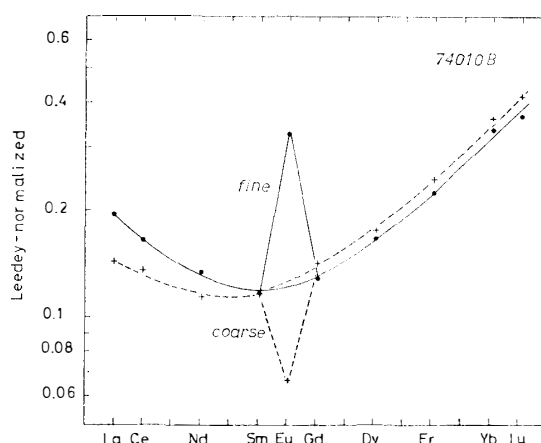

Fig. 3.   Leedey-normalized REE patterns of fine (floating) and coarse (rapid settlement) fractions (cf. Fig. 1).

is *enriched* by a factor of 2.69, whereas Eu in fraction C is *depleted* by a factor of 1.94. It should be noted that any whole rock samples do not exhibit either positive or negative Eu anomalies as observed in fractions F and C. Remarkable peculiarity of Eu is demonstrated in Fig. 4.

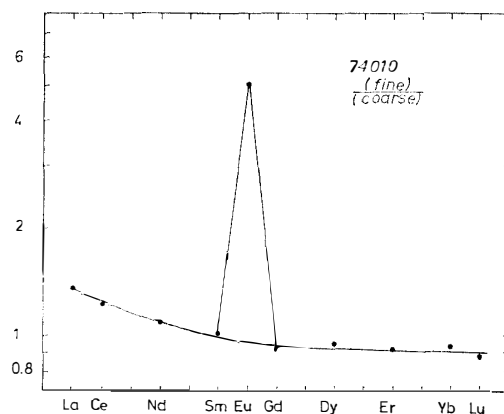Analyses of fractions F, M and C and whole rock of Yamato-74010B were

Fig. 4. REE abundance ratios between fine and coarse fractions (cf. Fig. 3) of Yamato-74010 B.

Table 3. Contents (wt. %) of Al_2O_3, FeO (total iron), MgO, CaO, Na_2O and Cr_2O_3 in Yamato-74010B and its separates (cf. Table 1), with concentration ratios among them and ratios of Eu to Na_2O and Al_2O_3.

	Whole rock	"F"	"M"	"C"
Al_2O_3	0.54	0.46	0.54	0.56
FeO	15.4	15.8	16.4	17.1
MgO	23.7	19.3	25.7	25.6
CaO	1.06	0.93	1.13	1.12
Na_2O	0.022	0.056	0.015	0.013
Cr_2O_3	0.62	0.57	0.58	0.58
Na_2O/CaO	0.0208	0.0602	0.0133	0.0116
Na_2O/Al_2O_3	0.0407	0.122	0.0278	0.0232
Al_2O_3/CaO	0.509	0.495	0.478	0.500
CaO/MgO	0.0447	0.0482	0.0440	0.0438
CaO/FeO	0.0688	0.0589	0.0689	0.0655
Cr_2O_3/FeO	0.0403	0.0361	0.0354	0.0339
Eu/Na_2O		0.509×10^{-5}		0.438×10^{-5}
Eu/Al_2O_3		0.620×10^{-6}		0.108×10^{-6}
Amount taken (mg)	52.51	5.96	46.52	52.14

Table 4. Comparison between observed concentrations (wt. %) and calculated
ones for Al_2O_3, FeO, MgO, CaO, Na_2O and Cr_2O_3 in Yamato-74010B.

	Al_2O_3	FeO	MgO	CaO	Na_2O	Cr_2O_3
Observed	0.54	15.4	23.7	1.06	0.022	0.62
Calculated	0.54	16.7	24.8	1.10	0.019	0.58
Calculated/observed	1.00	1.09	1.05	1.04	0.873	0.934

carried out for Al_2O_3, FeO, MgO, CaO, Na_2O and Cr_2O_3 (see Table 3). Re-
liabilities of these chemical analyses would be endorsed by the rather good agree-
ment (see Table 4) between calculated and observed values for whole rock.
(Note that powder sample used for whole rock analysis belongs to a portion
different from that spared for fractional separation. A fact that the values for
FeO and Cr_2O_3 in whole rock sample fall a little outside the corresponding ranges
covered by the separated fractions would be ascribed to possible high heterogeneity
of distribution of these elements in meteorites.) One would notice easily that the
Na_2O content in "F" is markedly higher than in "M" and "C", in contrast with
little if any differences in contents of other elements analyzed. This relatively
high content of Na_2O in "F" is considered to be of much significance in relation
with remarkable positive Eu anomaly. Intriguingly, the abundance ratio of Eu
to Na_2O appears to be mutually similar between F and C, while there is a great
difference in Eu/Al_2O_3 between them. Taking into account the possibility that
the F fraction involves the powders derived from originally coarse-grained material,
chemical peculiarity of the phase reflected by the F fraction would be enhanced.
Someone might tend to attribute such a peculiarity to the presence of plagioclase.
However, contents of Al_2O_3 and CaO and ratios, Al_2O_3/CaO, Na_2O/CaO, and
Na_2O/Al_2O_3, argue against such an interpretation. Note that the Al_2O_3 and CaO
contents are lower in "F" than in "M" and "C". At the same time high constancy
of the Al_2O_3/CaO ratios for those three fractions should be noted. Presence of
intercumulus material representing the melt coexisting with orthopyroxene crystals
might be conceived as an explanation of observed facts. But quantitative exami-
nation of data on REE and major elements would lead one to a conclusion that
such an explanation is also implausible. Anyway we cannot deny the presence of
peculiar material, whose effect is clearly reflected by the F fraction. We suggest
that this material in question is not an intrinsically primary one, but a product of
secondary elemental redistribution or recrystallization provoked presumably by
thermal metamorphism. According to this suggestion, the F fraction may represent
at large the material phase enriched in elements which are subject to sweeping

out. Based on mineralogical investigations, TAKEDA *et al.* (1975, 1978) maintain the recrystallization of the pyroxene with minor change in composition.

3.3. Pattern analysis

We have found that the chondrite-normalized REE patterns of Antarctic diogenites appear turned or rolled up toward the lightest REE. On the other hand, REE patterns for a few diogenites (FUKUOKA *et al.*, 1977) appear to decline straightforwards. REE partition coefficient function for an orthopyroxene, GSFC 271, investigated by SCHNETZLER and PHILPOTTS (1970), can also be considered to be a logarithmically linear function of difference in atomic number (cf. Fig. 6).

Here let us assume that, in ideally the simplest case, the REE partition coefficient function for orthopyroxene is a logarithmically linear function of difference
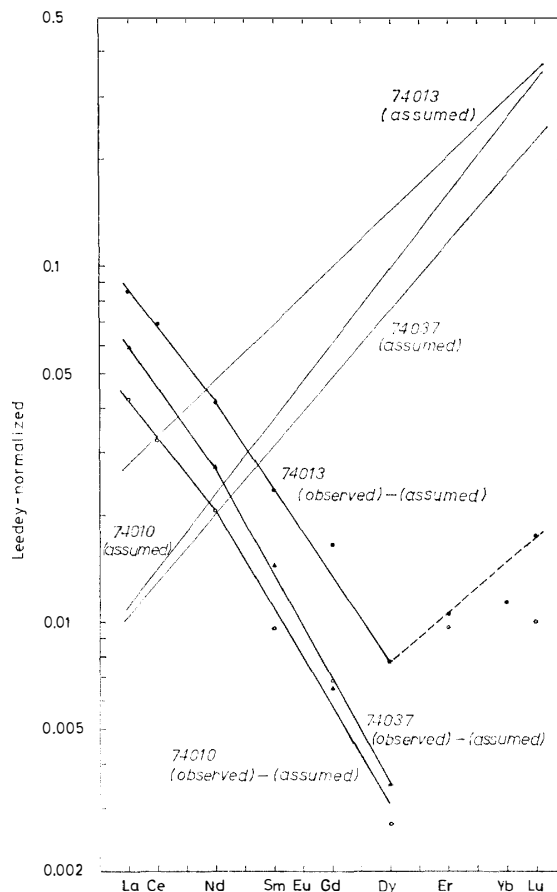

Fig. 5. Estimation of light-REE preference effect, on the basis of observed value minus assumed one; solid circles, open circles and solid triangles refer to Yamato-74013, -74010 and -74037, respectively.

in atomic number. Then it follows that the turning-up or rolling-up effect observed for Yamato recrystallized diogenites is due to another factor (factor L) favoring the entry of lighter REE with larger ionic radii. Employing the above assumption as a working hypothesis, pattern analysis was tried for Yamato-74037, -74013 and -74010. The curves eventually assumed for Yamato-74037, -74013 and -74010 are given, respectively, by $\log R = -1.97697 + 0.095309n$, $\log R = -1.55284 + 0.078854n$ and $\log R = -1.99457 + 0.104506n$, where R is the Leedey-normalized value assumed and n is the difference in atomic number starting with La, *i.e.*, $n = 0$ for La. Differences between observed and assumed values are plotted in Fig. 5. Needless to say, the ambiguities of resultant values become greater for heavier REE with larger integers of n. That is, the influences of both the assumed curve and the experimental error in determination become greater for heavier REE. Therefore, less certainties could be given to heavy REE, while increasing reliability is devoted to light REE.

Fig. 5 indicates that the curve representing factor L (large REE preference effect) is an almost linear function of atomic number. It would intrigue us that, in spite of opposite relationship in direction, the absolute value of inclination for the curve obtained here is analogous to that for the assumed function, and, in addition, that the inclinations under consideration run parallel with the inclinations for light REE span observed for olivine phase of two pallasites, Brenham (Masuda, 1968) and Thiel Mountains (Schmitt *et al.*, 1963). The latter observation concerning parallelism with the pallasite olivine may be interpreted as suggesting that the turning-up effect recognized in Yamato recrystallized diogenites is due to essentially the same effect that gives rise to the trend as seen in light REE span for pallasite olivine.

The large REE preference effect may be accounted for in three ways. (For Brenham pallasite, two sorts of interpretation were presented by Masuda (1968).) The first possibility would be contamination by plagioclase. Most of whole-rock REE patterns with marked turning-up features do not have positive Eu anomalies. The diogenites studied by Fukuoka *et al.* (1977) and Schmitt *et al.* (1963) show little if any turning-up features, but the Al_2O_3 contents in them are higher than in recrystallized diogenite Yamato-74010. These facts are not favorable for plagioclase contamination. (Presence of quenched liquid in equilibrium with diogenitic orthopyroxene is judged to be unfavorable as an explanation, in view of data on REE and major elements secured by us and those by Fukuoka *et al.* (1977).) The second interpretation is that there happens to be a site in orthopyroxene favoring entry of larger cations. Thirdly, assumption of transitory partial formation of mafic mineral with large site or vacancy available for cations may give a possible explanation to factor L. The second and third thoughts can form a continuum.

Someone might think of terrestrial contamination in connection with the turning-up feature. However, the observations that the REE abundances in "F" are nearly the same as those in "C" and that the F fraction has positive Eu anomaly in marked contrast with the C fraction speak against the terrestrial contamination. Apart from this, it is considered unlikely that the terrestrial contamination of REE takes place for meteorites buried in ice.

3.4. Handpicked orthopyroxene

Orthopyroxene crystals were handpicked from Yamato-74013. As shown in Fig. 6, the turning-up effect for this handpicked orthopyroxene is much less marked than for whole-rock sample Yamato-74013 (cf. Fig. 2). This difference is worth mentioning, but also one should bear in mind that there can be considerable difference even for the same whole-rock specimen as shown by Yamato-74010A and -74010B (cf. Fig. 2). The REE pattern for whole-rock sample of diogenite Yamato-692 (MASUDA and TANAKA, 1978) resembles that of orthopyroxene shown in Fig. 6. (The data presented for handpicked orthopyroxene could be considered
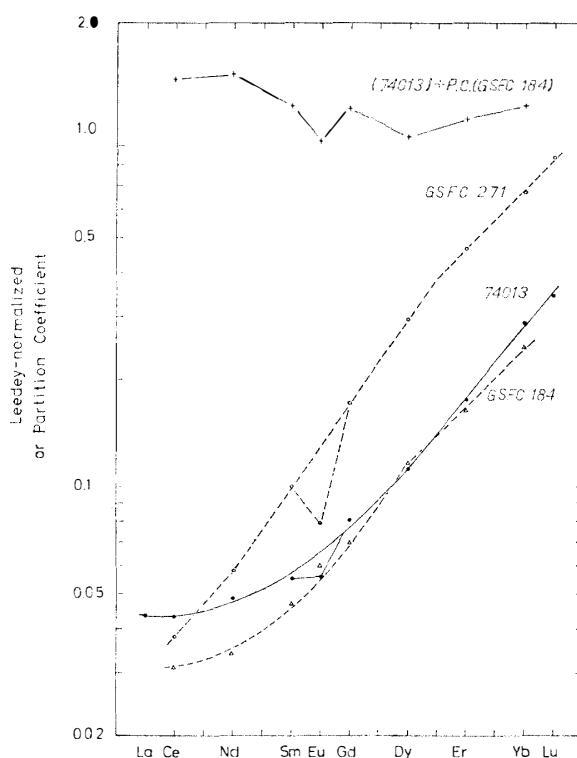

Fig. 6.   Comparison of Leedey-normalized REE pattern of hand-picked orthopyroxene from Yamato-74013, with partition coefficients (P.C.) of terrestrial orthopyroxenes, GSFC 271 and GSFC 184, presented by SCHNETZLER and PHILPOTTS (1970).

to lack in high accuracies with respect to a few elements; as compared with a smooth pattern curve, Nd and Gd abundances are 2.3 and 5.1% too high, respectively, and Sm is 4.0% too low.) Anyway, it would intrigue us that the Leedey-normalized pattern of handpicked Yamato-74013 orthopyroxene appears quite similar to partition coefficient function for GSFC-184 hypersthene (Schnetzler and Philpotts, 1970).

Acknowledgments

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