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GEOCHEMISTRY OF LANTHANIDES IN BASALTS OF CENTRAL JAPAN

Akimasa Masuda

ABSTRACT

Lanthanides in six basalts from Central Japan have been determined by a stable isotope dilution method. The chondrite-normalized lanthanide patterns are discussed in terms of partition coefficients estimated by Masuda and Matsui (1). An areal relationship was found in which the uniform enrichment factor, estimated from the lanthanide pattern, appears to decrease from the Pacific Ocean side towards the Japan Sea side. Cerium in Japanese basalts is depleted sometimes by a factor of about 13% in relation to the smooth curves. To examine the heterogeneity of lanthanide distribution in rather small samples, two different portions of three rock specimens were analyzed.

INTRODUCTION

The Japanese Islands are part of the circum-Pacific orogenic zone; they are situated off the eastern margin of the Eurasian continent, and separate the Japan Sea from the Pacific Ocean. Japanese petrologists, including Tomita (2), Kuno (3, 4) and Sugimura (5) established that Japan and its surrounding area could be divided into two or three petrographic provinces. Roughly, the Japan Sea side of Japan belongs to an alkali rock province, whereas the Pacific Ocean side belongs to a tholeiitic province. Kuno (4) suggests that high-alumina basalts occur along the intermediate belt between these two provinces.

The contours of earthquake depth (3, 5), gravity isostatic anomaly (6) and heat flow (7) appear to run approximately parallel with the elongation of the island arc of Japan. Based on the parallelism between petrographic boundaries and contours of intermediate and deep seismic foci, Kuno (3) postulated that the depth of source of magmas below Japan increases from the Pacific Ocean to the Japan Sea side, namely, towards the continent. Taneda (8), Katsui (9) and Ishikawa and Katsui (10) have shown the tendency for the Quarternary volcanic rocks in Japan to be more alkaline towards the continent.

Recently, the present author (11) investigated the lanthanide abundance in seven basalts from Japan, but not much attention was directed to the areal features of lanthanide geochemistry. One of the purposes of the present work is to study possible areal variations of lanthanide geochemistry, in addition to the interpretations of the lanthanide patterns.

Six rocks were analysed in this study; three of them were analysed previously (11) with inferior precisions. The lanthanide determinations were carried out by a mass spectrometric isotope dilution method, with precisions of less than 3% (probably 1% in most cases). The results of the analyses are summarized in Table 1; sample locations are shown in Fig. 1. To examine the heterogeneity of lanthanide distribution in rather small samples, two different portions of three rock specimens were analysed. 100 to 300 mg of rock powder were used per analysis.

PATTERN ANALYSIS

The first procedure in performing a pattern analysis of lanthanides is to normalize their abundances against chondritic abundances (12, 13). For the purpose of normalizing the observed abundances in the Japanese basalts, the abundances in the Modoc chondrite (analysed by the author) are employed in order to minimize the systematic errors for chondrite-normalized values. Thus, the effect of the possible experimental errors in the calibration of spike solutions can be completely eliminated from the chondrite-normalized values so long as the comparison is made between results obtained using the same spike solutions. The difference in absolute concentrations between the average chondrite (18) and Modoc is less than 5%, on an average. A study on Norton County (unpublished) showed that the lanthanum abundance in Modoc 0.374 ppm is somewhat too high to give Norton County a very smooth chondrite-normalized pattern passing

through a point for La; a lower "chondritic" abundance of 0.325 ppm gives a smoother pattern. The ratio based on the latter value is represented by a triangle in the diagrams.

In an attempt to analyse the chondrite-normalized lanthanide pattern, the partition coefficients for fractional solidification play an important role. Inasmuch as all of the patterns considered below show no sharp inflections over the whole range of La through Lu, and appear to be smooth as a whole, excepting fine structure or minor deviations, they will be dealt with in light of the partition coefficients for non-inflectional lanthanide patterns (1) as presented in Table 2.

It would be better to note that the partition coefficients in Table 2 were estimated for a solidification process as a total effect, not for particular minerals. It is a big problem how the partition coefficient, as a total effect, is controlled in a solidification process. It is possible that partition coefficients between some definite mineral species and the coexisting melt are approximately constant, and that the partition coefficient for the total solid during solidification is given subsidiarily as a sum of the mutually independent fractional effects of constituent minerals. It is also conceivable, however, that the partition coefficient for a total solidification process under some conditions may be controlled primarily as a whole, so that the partition coefficients for constituent mineral species are not always mutually independent. (These problems are thought to be related with the atomic-scale mechanism of solidification.) Above all, in a

case where the formation of an initial solid involves an intermediate amorphous or low-crystallinity state, and the early stage plays a decisive role in fixation of minor elements from the melt, the idea of strictly defined mineral would be restricted in its applicability. No doubt the partition coefficient (19) as estimated from phenocrysts in a rock are extremely significant, and it is desirable that more such information be obtained. On the other hand, however, seeing that there can be problems, difficult to understand in terms of present knowledge, the partition coefficients estimated by a phenomenological and mathematical treatment of data on gross rocks can have its own merit, because they can represent the averaged total effect involving some factors which may not be realized or understood at the present time. Needless to say, the method by Masuda and Matsui (1) belongs to this kind of approach. The author has no intention of maintaining that the partition coefficients in Table 2 are the only reliable series of partition coefficients, but he thinks that they can be the most basic ones as an explanation of chondrite-normalized lanthanide pattern with no inflection.

A characteristic of this series of partition coefficients is that they form an arithmetical progression from La through Lu. In cases where the differential fractionation of lanthanides takes place under the control of this series of partition coefficients, if the abundances of lanthanides in earth's original oxide material were similar to those in chondrites, then the chondrite-normalized patterns of remnant liquids at various stages should have a common feature of being logarithmically linear in the type of diagram employed here. As a matter

of course, the solid phase which was separated from these liquids under the influence of the same partition coefficients should have different patterns than those in the liquids. Also, a partial remelting of quenched liquid gives rise to another type of pattern. However, these modified patterns can also be discussed very often, although not always, in connection with the logarithmic linearity and the partition coefficients underlying it.

In this paper, the chondrite-normalized values are plotted against the equi-differential scale. According to the author's interpretation, this equi-differential scale should be understood, physically, as representing the reciprocal ionic radius. An equi-differential scale of reciprocal ionic radius proposed by Masuda (14) is shown in Fig. 8. For practical use, however, an arbitrary scale (Lm scale) is more convenient, because it is affected neither by any corrective shift in the absolute magnitude of ionic radius nor by any modification in the interpretation of the function of the equi-differential scale, in the future. The Lm scale at the top of abscissa (cf. Fig. 8) is set in such a way that the position of lanthanum, which corresponds to reciprocal ionic radius = 0.820Å^{-1}, is arbitrarily taken as zero, and the unit quantity of this Lm scale could correspond to the difference in reciprocal ionic radius, of 0.0171Å^{-1} according to Masuda (14).

The classification below of rock types is after Kuno (4; private communication).

Alkali basalt, Kiso district

As seen in Fig. 2, the pattern of this rock (open symbols) is slightly concave upwards, but the pattern (solid symbols) resulting from multiplication by the

partition coefficients is logarithmically linear. This suggests that the alkali basalt, Kiso district, was produced by partial melting of a quenched liquid as represented by solid symbols.

High-alumina basalt, Mishima, a lava of Fuji Volcano

This rock has a logarithmically linear pattern as seen in Fig. 3.

Tholeiitic basalt, Tanna Basin

In contrast with the alkali basalt, Kiso district, this tholeiitic basalt (open symbols in Fig. 4) has a slightly convex upwards lanthanide pattern. Dividing the observed values by the partition coefficients, however, produces a logarithmically linear pattern (solid symbols in Fig. 4). This fact suggests that this rock could represent a solid system separated from a liquid as represented by solid symbols in Fig. 4.

Tholeiitic basalt, Ô-shima

Of a rock specimen available (8 g), outer portion a (4.7 g) and inner portion b (1.2 g) were analysed. Except La, the lanthanide abundances are substantially the same for both portions; Fig. 5 is drawn based on portion a. The characteristic of the lanthanide pattern in this rock is quite similar to that in tholeiitic basalt from Tanna Basin (cf. Fig. 4), putting aside the absolute abundances. Followingly, this pattern is not inconsistent with the interpretation that this lava was produced by body melting of solid phase system which was separated once from the equilibrated liquid phase.

High-alumina basalt, Nii-jima

Of a given rock specimen (8.3g), homogeneous-looking main portion a (6.7g) and somewhat heterogeneous-looking rim portion (1.6g) were analysed. As seen in Table 1, there are small differences between the two portions in lanthanide abundances, and the relative difference appears to become bigger for the heavier lanthanides; Fig. 6 is drawn based on the data on portion a. The wide deviation of lanthanum from the general smooth trend is apparent; a similar deviation is seen for the tholeiitic basalt from Ô-shima. This deviation is not thought to be due to experimental error, because the redetermination of La for the same rock powder showed good agreement with the previous one. It is difficult to account for this peculiarity in terms of partition coefficients in fractional solidification. Secondary local mobilization of lanthanum may be a cause of this peculiarity, and a relatively big difference in La between portions a and b may endorse this speculation. In this connection, the especially high value of the solubility product of lanthanide hydroxide (15) may be worth pointing out.

Tholeiitic basalt, Hachijô-jima

Two portions of a specimen (10 g) of Hachijô-jima tholeiite were analysed (a, 7g, and b, 1 g). As seen in Fig. 7, there is a considerable difference between their lanthanide concentrations. The curvature of the convex upwards lanthanide pattern for portion a (represented by open symbols with vertical bars atop in Fig. 7) is similar to those for tholeiitic basalts from Tanna Basin and Ô-shima, whereas the curvature for portion b (represented by open symbols with vertical

bars beneath) is bigger than the others. It appears that portion b happens to represent some peculiar phase or phase system. The lanthanide pattern for this portion can be interpreted in three ways as mentioned below.

As seen in Fig. 7, division of the chondrite-normalized values for portion b by squares of the partition coefficients happens to produce a logarithmically, almost linear pattern (half-solid symbols in Fig. 7). Apparently, this result is not inconsistent with an interpretation that the genetic history of this portion involved two stages of separation as solid phase systems. If the co-existence of portions a and b is understood not to be a fortuitous one, however, the above interpretation would be judged not to be very reasonable.

A second interpretation of portion b is that both of portions a and b were separated from the same liquid at a certain stage of development history, and that the portion b reflects variants of partition coefficients, whereas the portion a reflects "the commonest" partition coefficients k_p as presented in Table 2. If so, the varied partition coefficients k_p' for portion b are estimated to be k_p times the concentration ratio of portion b to a. The result of the calculation is shown in Fig. 8. (If this calculation is significant, the limit size (16) pertinent to k_p' is estimated to be Lm = -1.3, i.e., reciprocal ionic radius = 0.798 (= 1/1.25) A^{-1}. Needless to say, the different limit size means the different curvature for chondrite-normalized lanthanide pattern for solid phase system.)

A third interpretation is that the portion b under question happens to involve a selective aggregate of crystals formed in the lava.

AREAL FEATURES

As shown above, the lanthanide pattern varies from rock to rock, reflecting different genetic settings or history. Nevertheless, obvious characteristics pertaining to locality are revealed by the basalts investigated.

According to an extrapolation, the series of partition coefficients in Table 2 reaches a value of 1.00 on a Lm scale = 24.5. This means that fractional solidification controlled by this series of partition coefficients does not cause either enrichment or depletion for the hypothetical element corresponding to Lm = 24.5. In other words, if the lanthanide abundances in the initial liquid were similar to those in chondrites and their differentiation was developed under the control of the partition coefficients employed here, then extrapolation of a logarithmically linear pattern, whether it is directly observed or indirectly estimated, should reach unity at Lm = 24.5. However, the study by Schmitt et al. (18) on calcium-rich achondrites showed that there is an effect which gives rise to substantially uniform enrichment of all the lanthanides. This is interpreted as indicating that the partition coefficients for lanthanides are very small under certain conditions of crystallization. It is considered likely that a similar effect was operating inside the earth. If so, the extrapolation of a logarithmically linear line does not pass unity near Lm = 24.5. Anyway it would be interesting to see the chondrite-normalized value reached by an extrapolated, logarithmically linear line at Lm = 24.5. The value thus obtained will be called uniform enrichment factor. (This factor can also be calculated without extrapolation.)

The results of such extrapolation, that is, the uniform enrichment factor is presented in Fig. 1. For rocks, two portions of which were analysed, the estimation was made based on their portions a, because these represent the major portions of the samples studied. It is shown here that the uniform enrichment factor is greater than unity for all the basalts studied. Aside from the mechanism responsible for uniform enrichment, we can realize an intriguing fact that the uniform enrichment factors are close to each other for basalts from close localities, in spite of differences in type of pattern. This fact indicates strongly that the process of uniform enrichment preceded the differentiation process which occurred under the control of the partition coefficients presented in Table 2.

Attention should be also drawn to the fact that, as far as the samples studied are concerned, the uniform enrichment factor appears to decrease (see Fig. 1) steadily from the Pacific Ocean side, 15, towards the Japan Sea coast, 3.2. It would be worth mentioning that the similar enrichment factors for two alkali olivine basalts occurring near the Japan Sea coast of western Japan were between 1 and 2 (11). (The same factor for alkali basalt from Southern Manchuria (unpublished) is also close to unity.) Although the data obtained here is more or less open to prudent skepticism about whether each of the rock specimens studied can represent the enormous mass of relevant basalt, this tendency of steady decrease of the uniform enrichment factor from the Pacific Ocean side towards the Japan Sea side (perhaps towards the continent) is thought to be

closely associated with a change in the nature of mantle material below Japan. Naturally, this fact is regarded as being related with the geophysical and petrological observations described in the introduction.

ADDITIONAL COMMENTS

Four of six basalts studied show apparent depletion of cerium compared with the smoothed curved defined by the abundances of most of the other lanthanides, and the extent of the cerium depletion is about 13% on an average for four basalts. This corroborates the previous observation (11).

The author has attempted to employ a liquid fraction value f_w to estimate the depth of a magma source (17). He thinks that, if the calculation is applied to less fractionated, common rocks, the results can be significant so long as they are dealt with statistically. In the previous paper (11) about lanthanides in Japanese basalts, however, only the effect (namely, the diminution of liquid volume) having accompanied the differential enrichment of lanthanides was taken into account in such calculations. The results of the present study suggest that the effect accompanying the uniform enrichment should also be taken into account. Suppose that the rate of diminution of liquid volume having accompanied the differential enrichment is f_w and the uniform enrichment factor is ϕ, then the diminution of liquid volume should be nearly f_w/ϕ, because the partition coefficients responsible for uniform enrichment are inferred to be much less than 0.1.

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Table 1
Lanthanide concentration (ppm) in Japanese basalts and in the Modoc chondrite

	Kiso	Mt. Fuji	Tanna Basin	Ô-shima (a)	Ô-shima (b)
La	23.6	9.05	1.46	2.99	3.63
Ce	42.1	19.2	3.74	6.81	6.46
Nd	25.9	16.3	4.35	7.24	7.19
Sm	5.50	4.16	1.53	2.46	2.47
Eu	1.87	1.28	0.583	0.810	0.762
Gd	5.20	4.34	2.12	3.28	3.28
Dy	4.71	4.24	2.58	4.02	4.04
Er	2.33	2.36	1.64	2.51	2.53
Yb	2.09	2.14	1.62	2.63	2.56
Lu	0.300	-----	0.259	0.410	0.400

	Nii-jima (a)	Nii-jima (b)	Hachijô-jima (a)	Hachijô-jima (b)	MODOC
La	6.52	5.20	5.90	2.74	0.374
Ce	10.3	10.1	13.8	9.05	0.835
Nd	9.14	8.95	16.2	13.1	0.702
Sm	2.72	2.42	5.60	5.12	0.216
Eu	0.991	0.865	1.72	1.60	0.070
Gd	3.18	2.96	7.34	7.13	0.277
Dy	3.66	3.32	8.71	8.70	0.329
Er	2.24	2.05	5.24	5.12	0.208
Yb	2.36	2.02	5.45	5.15	0.222
Lu	0.353	0.314	0.820	0.757	0.0347

Table 2
Partition coefficients k_p estimated Masuda and Matsui (1)

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
0.119	0.155	0.191	0.227	0.263	0.299	0.335	0.371
Tb	Dy	Ho	Er	Tm	Yb	Lu	
0.407	0.443	0.479	0.515	0.551	0.586	0.622	

FIGURE CAPTIONS

Fig. 1. Locations of basalts studied; numerals in parentheses indicate uniform enrichment factors (cf. text)..

Fig. 2. Lanthanide pattern for alkali basalt, Kiso district.

Fig. 3. Lanthanide pattern for high-alumina basalt, Mishima, a lava of Fuji Volcano.

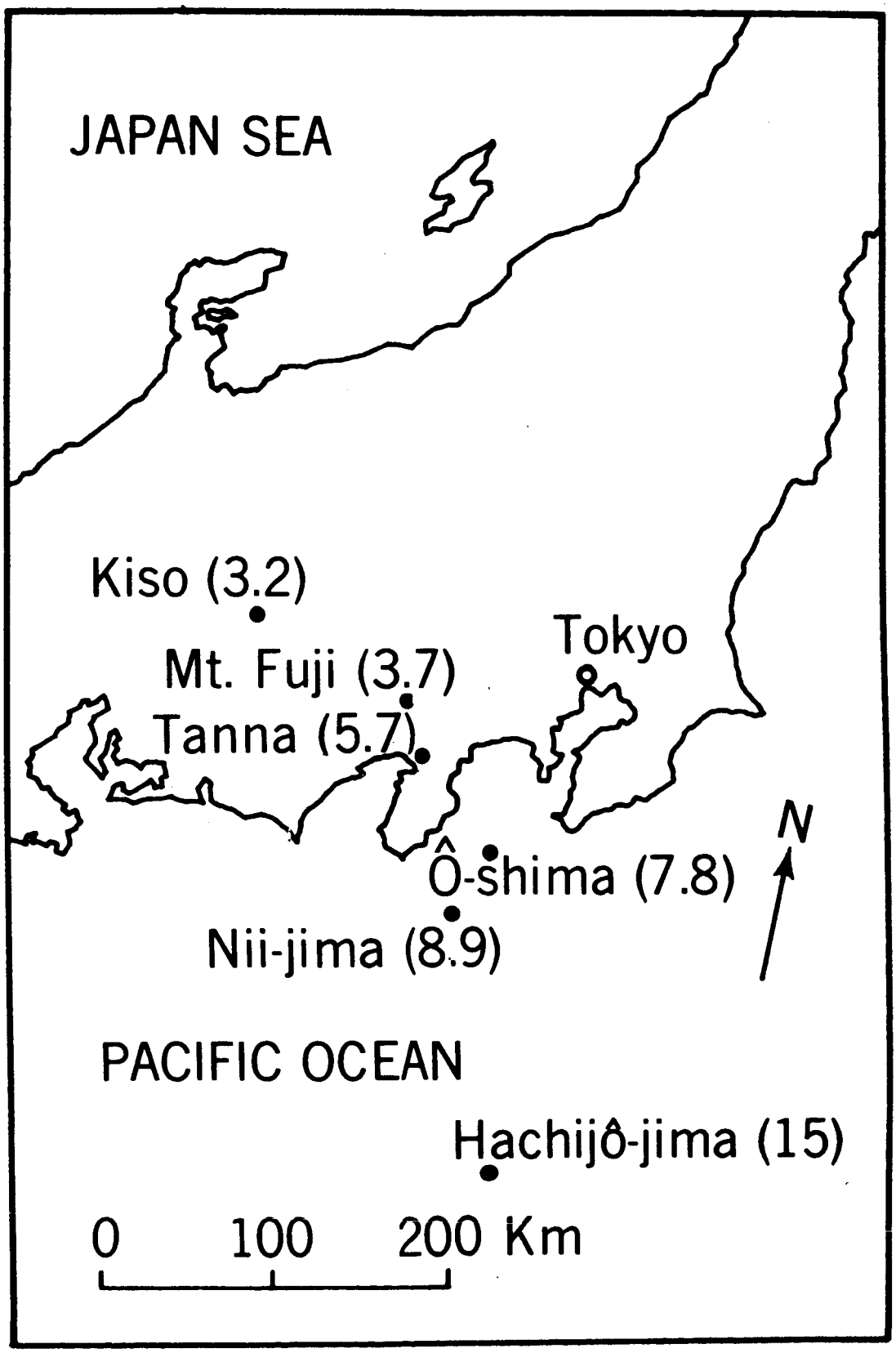
Fig. 4. Lanthanide pattern for tholeiitic basalt, Tanna basin.

Fig. 5. Lanthanide pattern for tholeiitic basalt, Ô-shima.

Fig. 6. Lanthanide pattern for high-alumina basalt, Nii-jima.

Fig. 7. Lanthanide pattern for tholeiitic basalt, Hachijô-jima; patterns for two portions a and b are presented here.

Fig. 8. Comparison of hypothetical partition coefficients k'_p with the partition coefficients, k_p, presented in Table 2; $k'_p = k_p \times (C_b/C_a)$, where C_a and C_b refer to concentrations in fractions a and b, respectively, of Hachijô-jima basalt.


JAPAN SEA
Kiso (3.2)
Mt. Fuji (3.7)
Tanna (5.7)
Tokyo
Ô-shima (7.8)
Nii-jima (8.9)
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PACIFIC OCEAN
Hachijô-jima (15)
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Figure 1

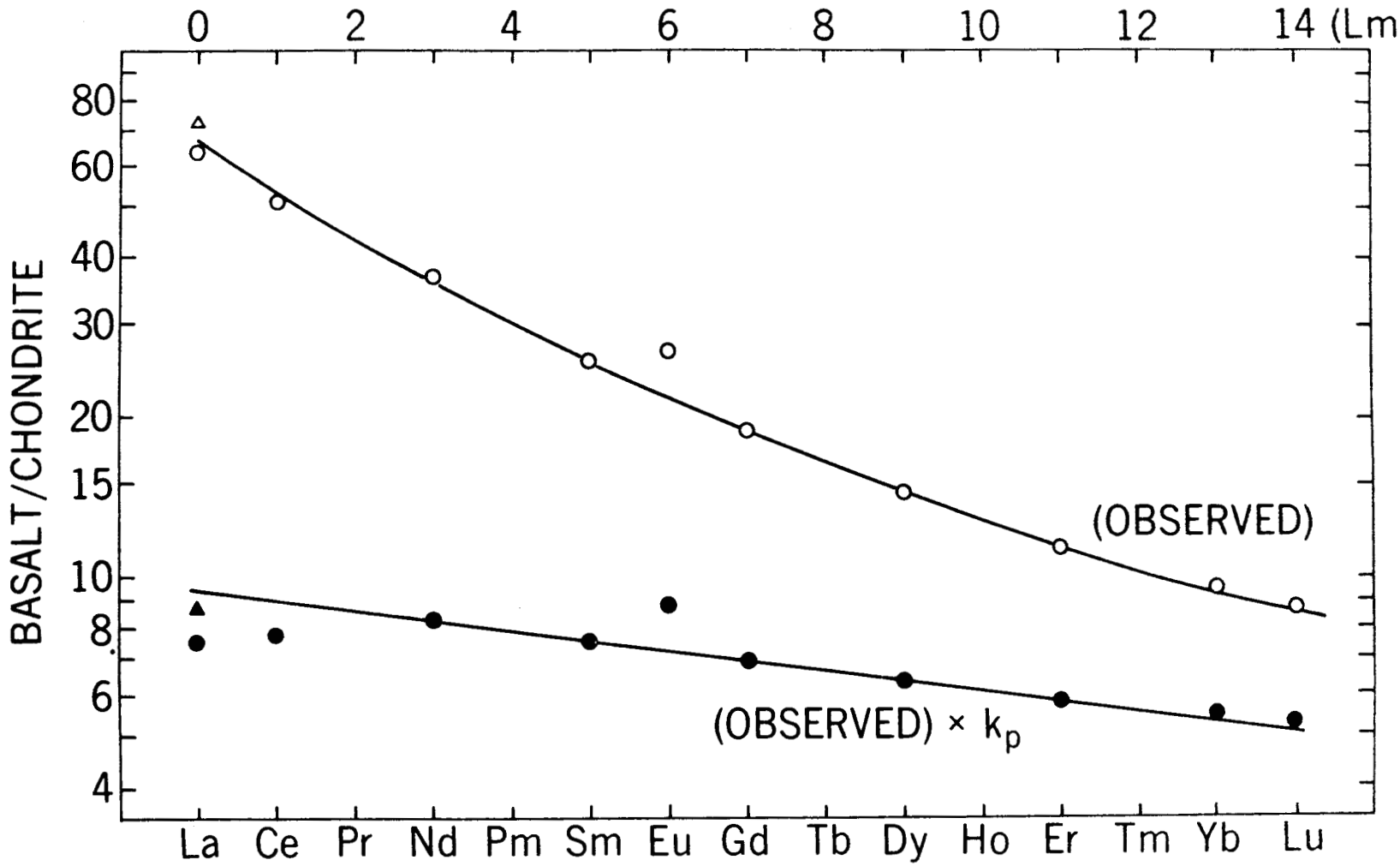
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Figure 2

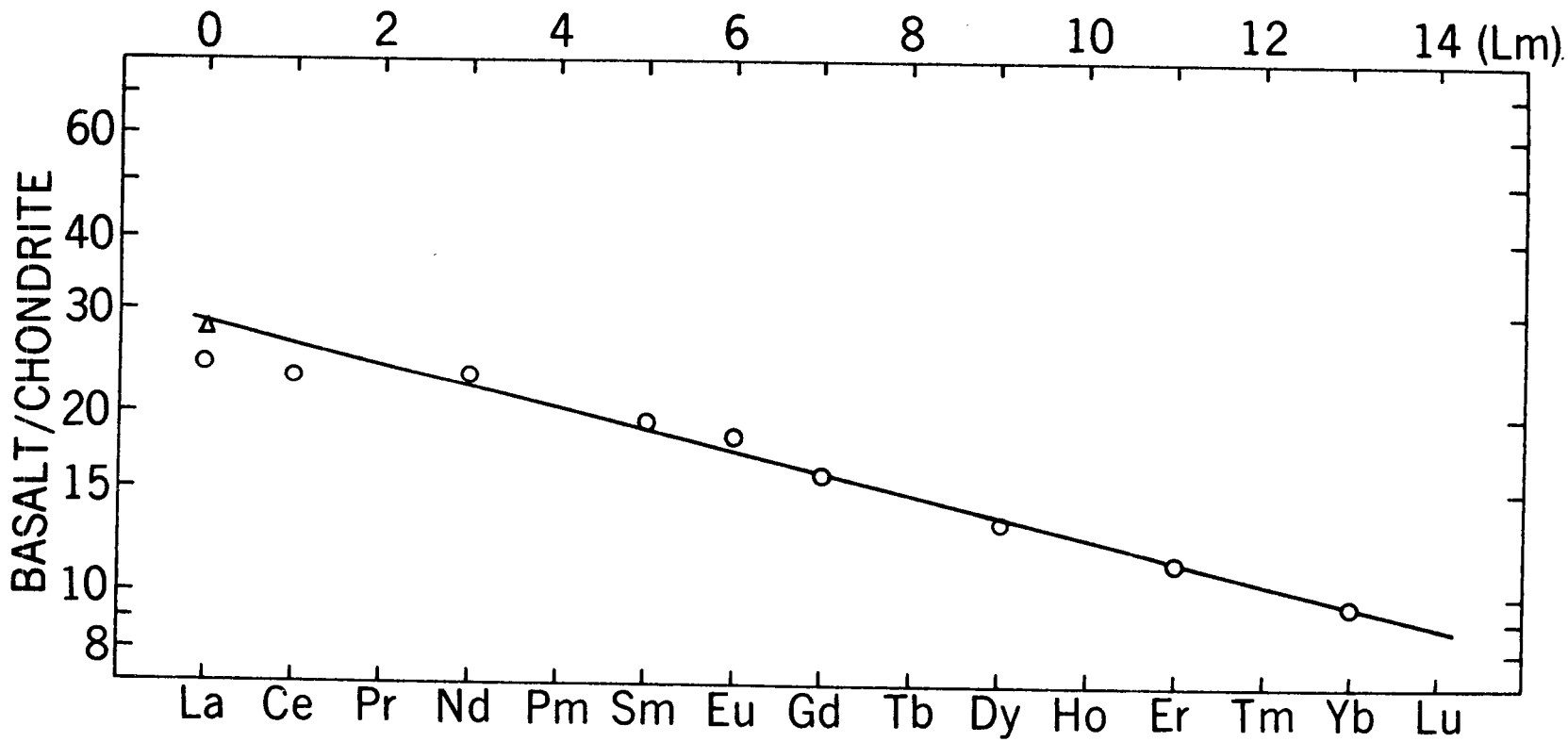
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Figure 3

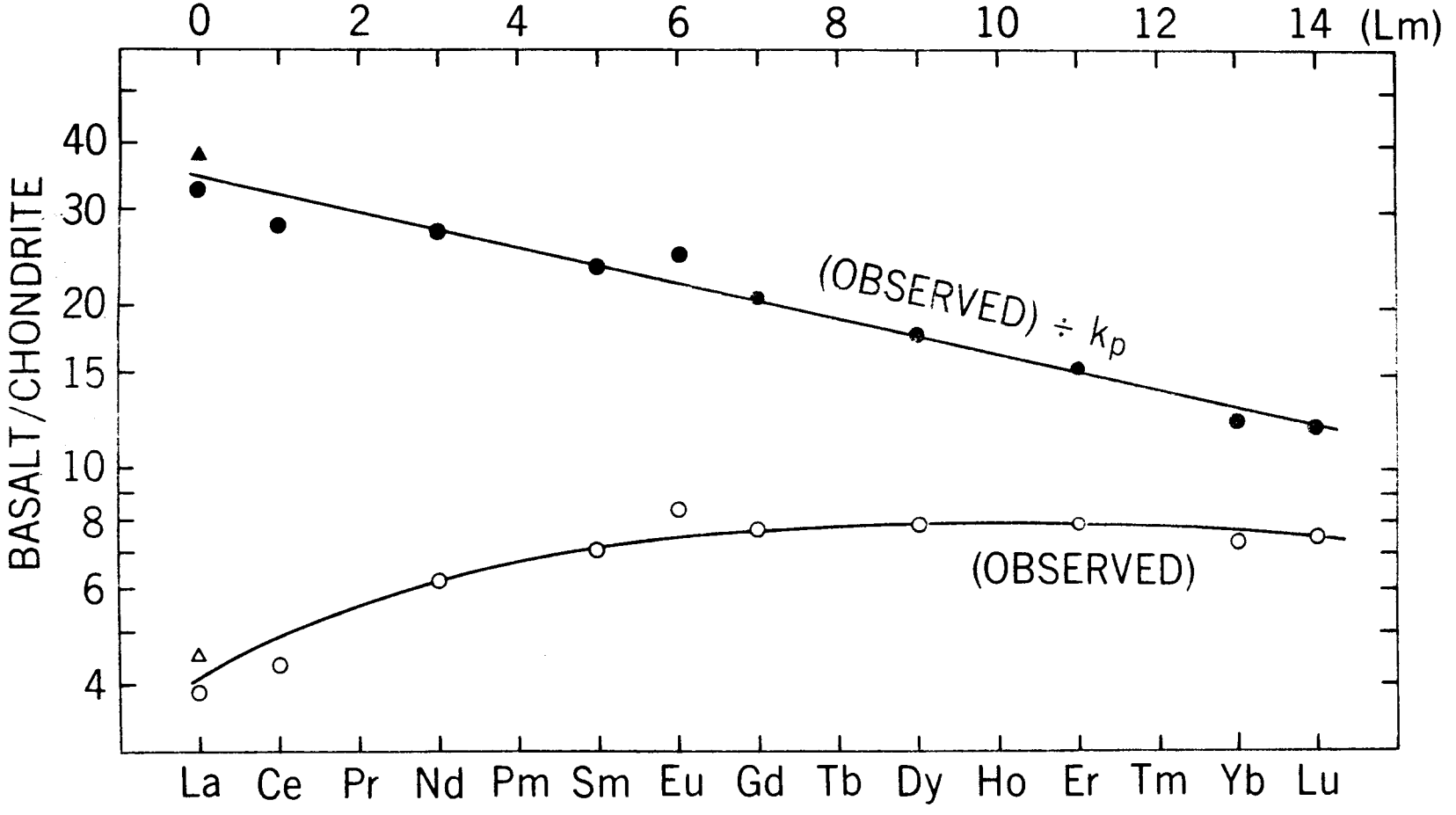
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Figure 4

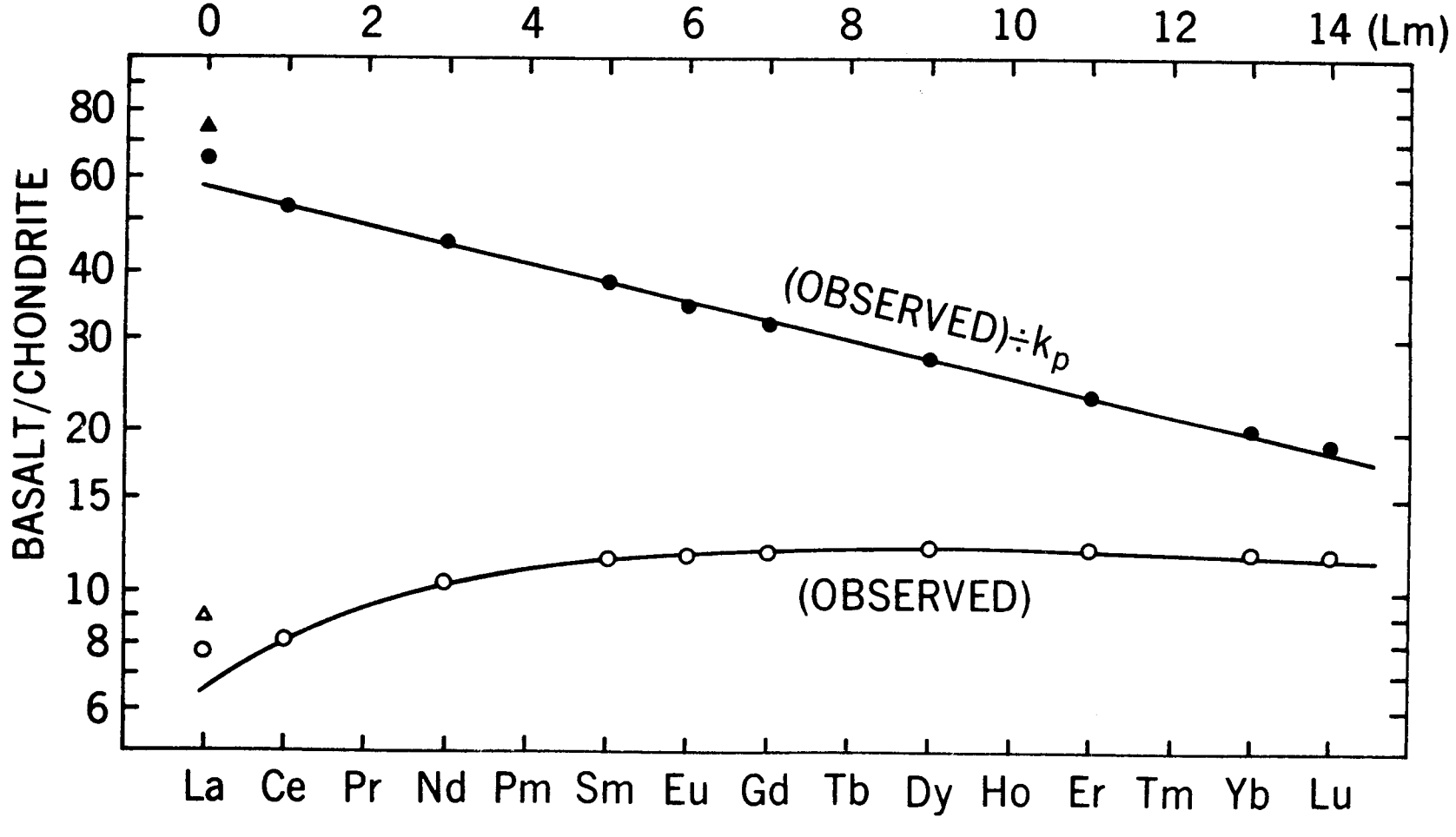
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Figure 5

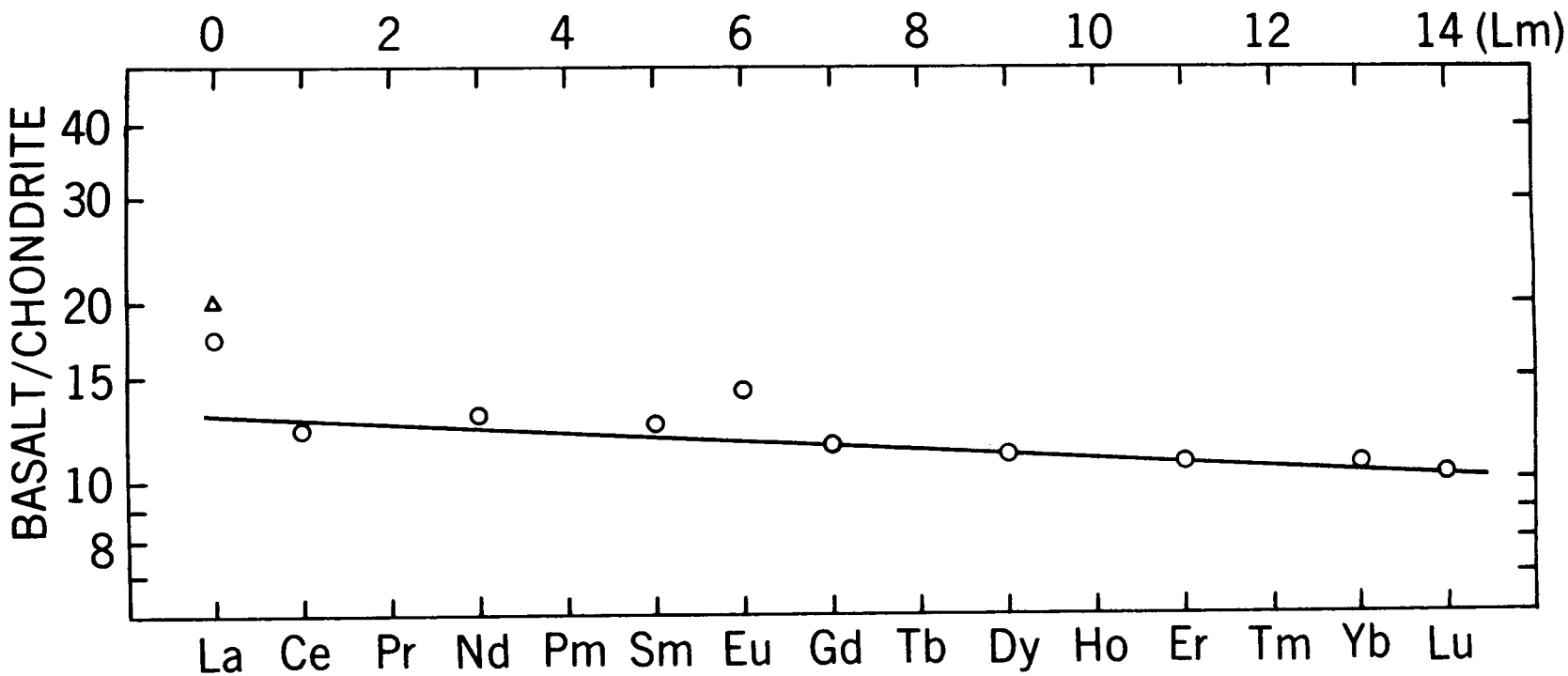
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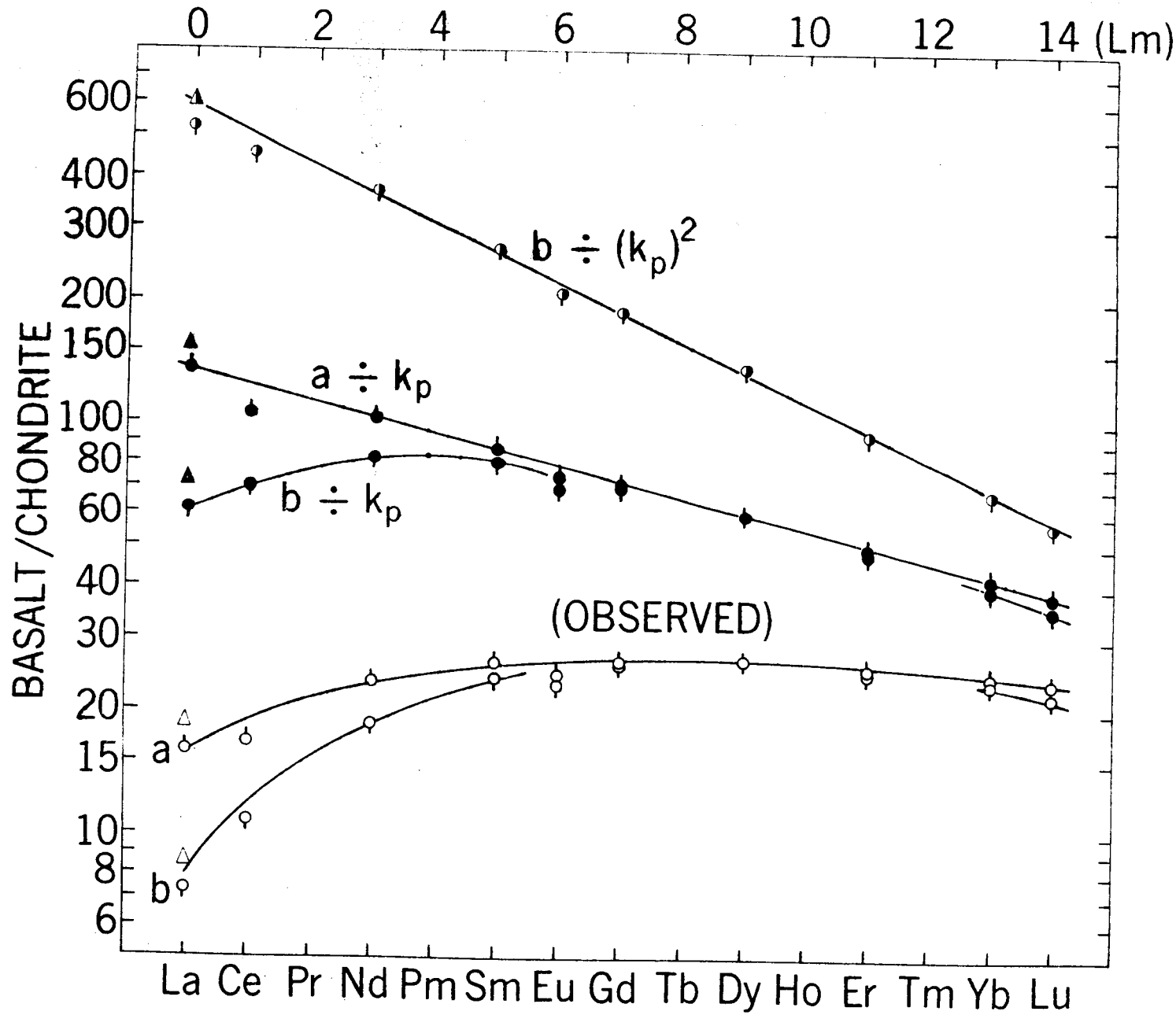
Figure 6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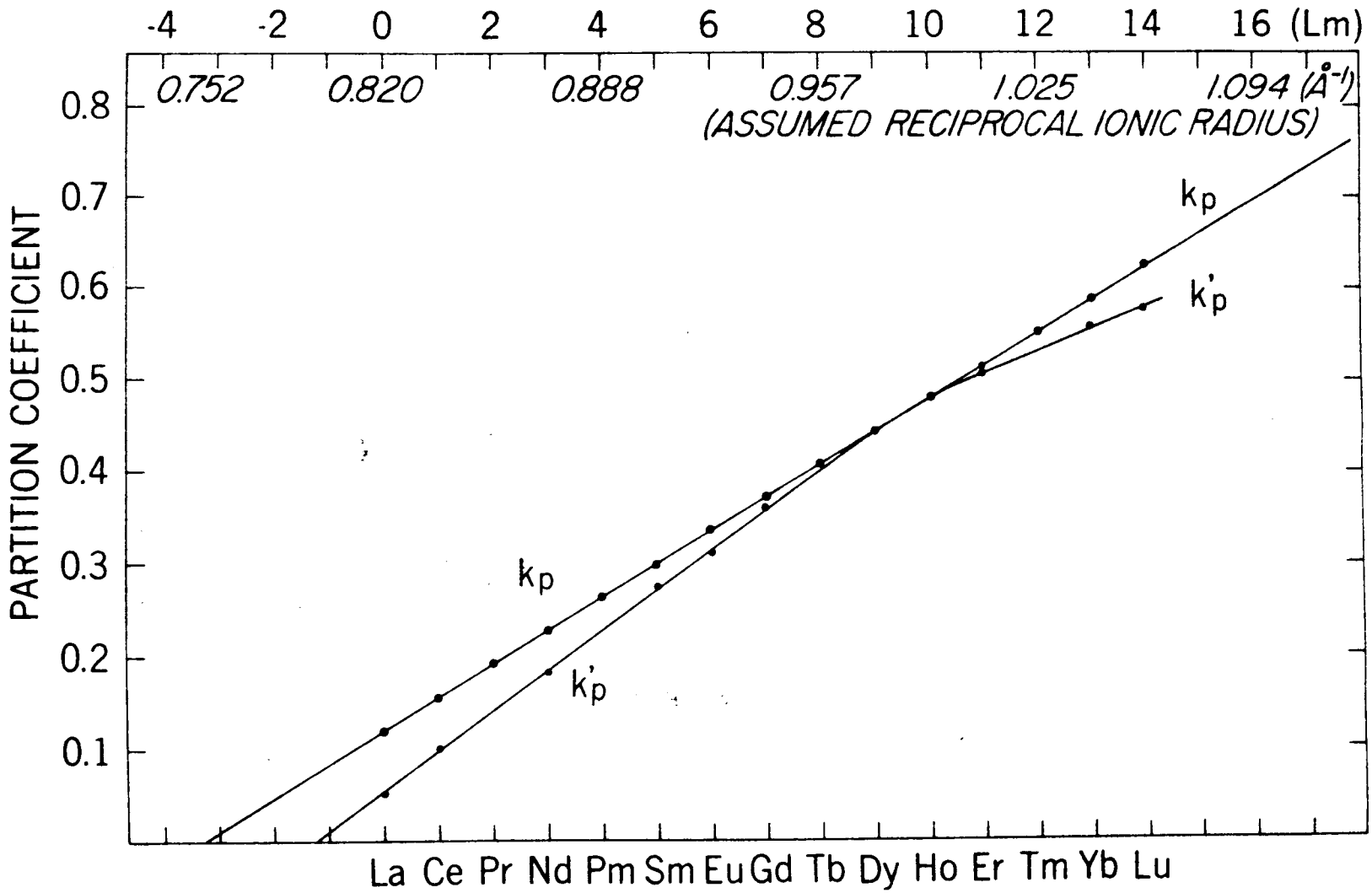
BASALT/CHONDRITE
b ÷ (k_p)^2
a ÷ k_p
b ÷ k_p
(OBSERVED)
a
b
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Figure 7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16 (Lm)
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0.820
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0.957
1.025
1.094 (Å⁻¹)
(ASSUMED RECIPROCAL IONIC RADIUS)
PARTITION COEFFICIENT
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0.7
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0.3
0.2
0.1
kp
k'p
kp
k'p
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Figure 8