CERIUM ANOMALY IN REE PATTERN OF ANTARCTIC EUCRITE

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Abstract: To examine the weathering effect, we determined abundances of rare-earth elements (REE), Ba and Sr and contents of major elements (MgO, FeO, CaO, MnO and Na_2O) for inner and outer parts of the ALH-78132 Antarctic eucrite. It was observed that the inner part of this eucrite (ALH-78132,78) showed a negative Ce anomaly, while all of the outer part specimens (ALH-78132,71a, b, c and 79) displayed positive Ce anomalies. On the other hand, contents of MgO, FeO and CaO for the outer part of the eucrite were similar to those for the inner part of the eucrite. Ce and Nd isotopic ratios were also determined for ALH-78132,71c, 79 and 78. In the $^{143}Nd/^{144}Nd$ *vs.* $^{147}Sm/^{144}Nd$ diagram, all points of ALH-78132,71c, 79 and 78 appeared to fall in the chondritic evolution field within the experimental errors. Meanwhile, in the $^{138}Ce/^{142}Ce$ *vs.* $^{138}La/^{142}Ce$ diagram, it was observed that the points of the outer part specimens, ALH-78132,71c and 79, deviated from the chondritic lines, while the point of inner part sample of ALH-78132,78 lied in the chondritic range within the experimental uncertainty. These results suggest strongly that the positive Ce anomaly of the Antarctic eucrite is a result of terrestrial weathering.

1. Introduction

It is considered that Ce is more volatile than other rare-earth elements (REE) at higher oxygen partial pressures. Therefore, Ce anomaly can be one of indicators of oxidizing conditions for meteorite formation in gaseous phase. Only a few non-Antarctic meteorites show the Ce anomaly; Khohar and Barwise chondrites, the Melrose-b howardite and giant olivine chondrule and hibonite inclusion from the Allende meteorite (NAKAMURA and MASUDA, 1973a, b; MASUDA and TANAKA, 1980; TANAKA *et al.*, 1975; DAVIS *et al.*, 1982). (It is added that all chips from these meteorites do not always show the Ce anomaly.) On the other hand, the Ce anomaly is observed for all of six Antarctic eucrites analyzed by isotope dilution method (NAKAMURA and MASUDA, 1980; FUKUOKA and NAKAMURA, 1981; SHIMIZU and MASUDA, 1981, 1982). REE abundances for 27 Antarctic meteorites have been determined by the method (MASUDA and TANAKA, 1978; MASUDA *et al.*, 1977, 1979; NAKAMURA and MASUDA, 1980; SHIMIZU and MASUDA, 1981, 1982; SHIMIZU *et al.*, 1979; FUKUOKA and NAKAMURA, 1981).

Among them, the Ce anomaly is observed for six eucrites (all cases studied), two diogenites and a unique achondrite ALH-77005. Further, it has been pointed out that Yb and Lu deviated from smooth lines for other REE in REE patterns of Antarctic eucrites (SHIMIZU and MASUDA, 1982).

There remains a question whether the Ce anomaly of Antarctic eucrites was caused by a pre-terrestrial process or by a terrestrial effect. To examine the effect of weathering, we have determined REE abundances for an inner part of ALH-78132 eucrite in the present study, in contrast to the previous studies in which REE abundances were determined for outer parts of the eucrite specimen. Further, we determined contents of MgO, FeO, CaO, MnO and Na_2O in these specimens, including both of outer and inner parts.

Recently, TANAKA and MASUDA (1982) have succeeded in developing a new geochronological method using ^{138}La-^{138}Ce system. This ^{138}La-^{138}Ce system as well as ^{147}Sm-^{143}Nd and ^{87}Rb-^{87}Sr systems will be used as a useful geo- and cosmo-chemical tracer. The ^{138}La-^{138}Ce method is especially useful in judging the nature and cause of Ce anomaly in the REE patterns. In this study, Ce isotopic abundance data as well as Nd isotopic abundance have been newly added for the ALH-78132 eucrite.

2. Samples and Experimentals

In this study, the ALH-78132 polymict eucrite has been analyzed for REE abundances, Ce and Nd isotope ratios and contents of MgO, FeO, CaO, MnO and Na_2O. ALH-78132,78 is a specimen from an inner part of this meteorite and ALH-78132,71 and 79 are from an outer part of the eucrite. ALH-78132,78 and 79 have been taken from the same slice. ALH-78132,71a, b and c are different chips from the ALH-78132,71. REE abundances were determined by the isotope dilution method using a JEOL JMS-05RB mass spectrometer at the University of Tokyo and isotopic compositions of Ce and Nd were measured by a Micromass 30–54R mass spectrometer at the Geological Survey of Japan. Ions of cerium isotopes were measured as CeO^+ by means of Re triple filaments and the measured $^{138}Ce/^{142}Ce$ ratios were normalized to $^{138}Ce/^{142}Ce=0.01720$. Neodymium was measured as NdO^+ by a Re single filament and the measured isotope ratios were normalized against $^{146}Nd/^{144}Nd=0.7219$. Contents of MgO, FeO, CaO, MnO and Na_2O were determined by the atomic absorption method.

3. Results and Discussion

REE, Ba and Sr abundances and major element contents are shown in Table 1. Figure 1 shows the chondrite-normalized REE-Ba-Sr patterns. These results obtained in this study are summarized as follows. (1) The inner part of this eucrite (ALH-78132, 78) shows a negative Ce anomaly, while all of the outer part specimens (ALH-78132,79 and 71a, b and c) display a positive Ce anomaly. Here, let us define "degree of Ce anomaly" as the ratio of observed Ce abundance to that which would fall on the La-Nd join in the Masuda-Coryell plot. The degree of Ce anomaly is as follows: 0.85 for ALH-78132,78; 1.88 for ALH-78132,71a; 2.36 for ALH-78132,71b; 1.29 for ALH-78132,71c; 1.31 for ALH-78132,79. (2) Even among the same ALH-78132,71 samples,

Table 1. REE, Ba and Sr abundances (ppm) and MgO, FeO, CaO, MnO and Na_2O contents (wt %), with abundance range and abundance ratio between ALH-78132,71b and 78.

	71a*	71b	71c	78-1#	78-2#	79-1#	79-2#	Abundance range	Abundance ratio (71b/78)
La	1.225	0.959	2.86	4.29	4.31	2.91	3.01	0.959-4.31	0.223
Ce	6.23	6.19	9.90	9.53	9.60	10.44	10.63	6.19-10.63	0.645
Nd	2.65	2.15	6.13	8.43	8.44	6.45	6.63	2.15-8.44	0.255
Sm	0.978	0.804	1.983	2.61	2.62	2.10	2.16	0.804-2.62	0.307
Eu	0.543	0.522	0.605	0.685	0.686	0.668	0.670	0.522-0.686	0.761
Gd	1.446	1.235	2.62	3.66	3.67	2.81	2.85	1.235-3.67	0.337
Dy	2.02	1.773	3.23	4.22	4.25	3.51	3.55	1.773-4.25	0.417
Er	1.365	1.213	1.967	2.56	2.58	2.15	2.16	1.213-2.58	0.470
Yb	1.509	1.391	1.945	2.43	2.39	2.17	2.18	1.391-2.43	0.582
Lu	0.236	0.215	0.287	0.359	0.368	0.320	0.321	0.215-0.368	0.584
Ba	36.6	38.7	34.7	—	35.6	—	38.1	34.7-38.7	1.087
Sr	68.2	64.4	68.5	—	76.7	—	72.2	64.4-76.7	0.840
MgO	7.19	6.93	6.86	7.24		6.90		6.86-7.24	0.957
FeO	18.38	18.86	18.69	19.64		18.40		18.38-19.64	0.960
CaO	8.69	8.40	8.58	9.60		9.00		8.40-9.60	0.875
MnO	0.37	0.43	0.50	0.44		0.54		0.37-0.54	0.977
Na_2O	0.53	0.48	0.30	0.39		0.30		0.30-0.53	1.23

* SHIMIZU and MASUDA (1982).

\# REE in ALH-78132,78 and 79 were determined twice for the same specimen.

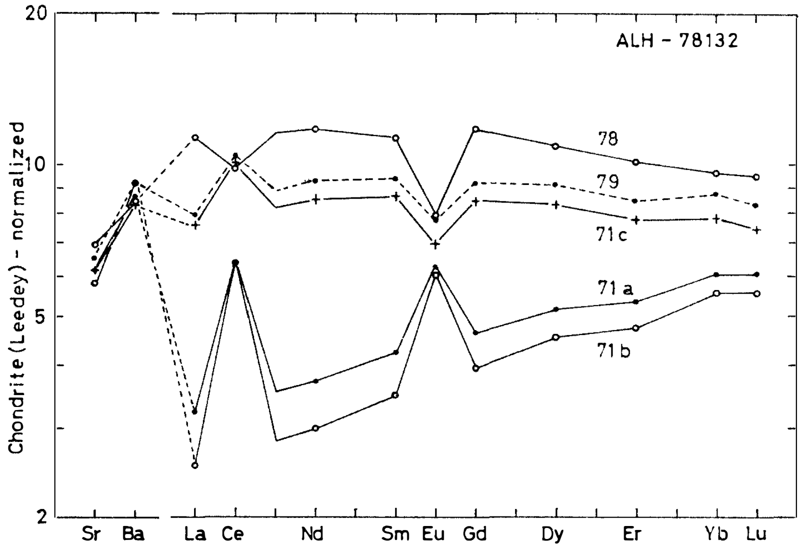

Fig. 1. Chondrite-normalized REE plus Ba-Sr patterns of some chips of the ALH-78132 eucrite. The normalizing values for REE and Ba are from abundances of these elements in the Leedey chondrite (MASUDA et al., 1973; NAKAMURA and MASUDA, 1973b). The normalizing value, 11.1 ppm, for Sr is from GOPALAN and WETHERILL (1971).

the chip 71c is different from 71a and b. The latter two chips show light REE depletion, excepting Ce. (3) The outer part of the ALH-78132 eucrite has a major element composition (MgO, FeO, CaO, MnO and Na_2O) similar to that of the inner part of the eucrite, while the former shows a positive Ce anomaly and the latter does a negative Ce anomaly. However, FeO, MgO and CaO contents appear to be higher in the inner part specimen (ALH-78132,78) than in the outer part specimens (ALH-78132,71a. b, c and 79). ALH-78132,71a and b with light REE depletion show a relatively high Na_2O content compared with other specimens.

Heterogeneous distribution of Ce anomaly, positive at the outside and negative at the inside, suggests that Ce anomaly observed for Antarctic eucrites has been produced by the terrestrial processes rather than by the pre-terrestrial processes. Table 1 shows also the abundance range for each element and the abundance ratio between ALH-78132,71b and 78 for each element. This abundance ratio is also shown in Fig. 2. As shown in Table 1 and Fig. 2, the abundance ratios between ALH-78132,71b and 78 are 1.0–0.7 for MgO, FeO, CaO, MnO, Sr and Eu. The corresponding ratios are 0.7–0.4 for Ce, Dy, Er, Yb and Lu and 0.2–0.4 for La, Nd, Sm and Gd. Further, the ratios of Ba and Na_2O are 1.09 and 1.23, respectively. These data indicate that REE, especially La, Nd, Sm and Gd, were mobile elements in terrestrial weathering of Antarctic eucrites, which apparently resulted in a positive Ce anomaly in them. In submarine alteration of abyssal basalt, it was shown that REE were the most immobile elements (SHIMIZU *et al.*, 1980). This can be interpreted as suggesting that alteration mechanism during burial in ice is different from that in submarine environment. It may be considered that REE were enriched in grain boundary of Antarctic eucrites and that these REE were leached selectively by weathering of the eucrites within the ice. Generally, it is considered that the physical weathering is intense at such low temperatures as within the ice. Here, we have no conclusive words about whether the burial of eucrites in ice at low temperatures for a considerably long time urged the segrega-

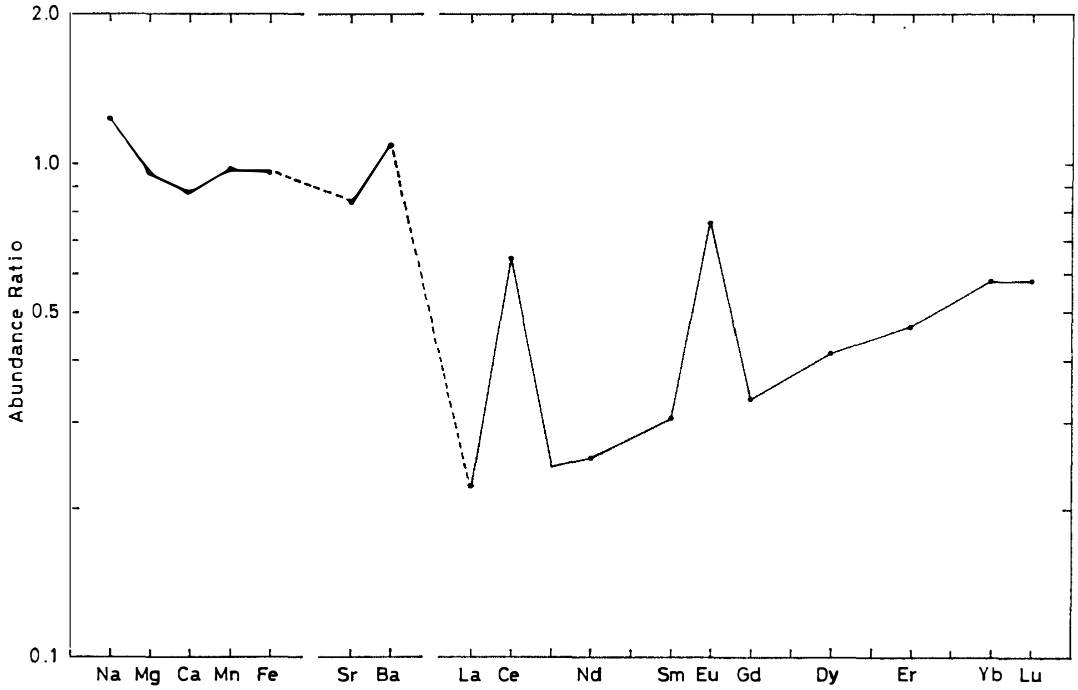

Fig. 2. Abundance ratios of REE, Ba, Sr, Na, Mg, Ca, Mn and Fe between ALH-78132,71b and ALH-78132,78.

Table 2. ^{138}Ce/^{142}Ce *and* ^{143}Nd/^{144}Nd *data.*

	^{138}Ce/^{142}Ce	^{143}Nd/^{144}Nd
ALH-78132,71c	0.0228489± 22	0.512543±24
ALH-78132,78	0.0228547±118	0.512440±30
ALH-78132,79	0.0228525± 62	0.512587±32
Pasamonte	0.0228518± 26	—
Juvinas	0.0228533± 26	—
Jilin (1)	0.0228538± 58	0.512587±66
Jilin (2)	0.0228521±114	0.512547±42

Errors are 2σ mean and correspond to the last significant figures. In this study, ^{138}Ce/^{142}Ce value for Johnson Matthey Ce reagent, JMC 304, was 0.0228559±11 and ^{143}Nd/^{144}Nd value for La Jolla Nd isotope standard was 0.51183±3.

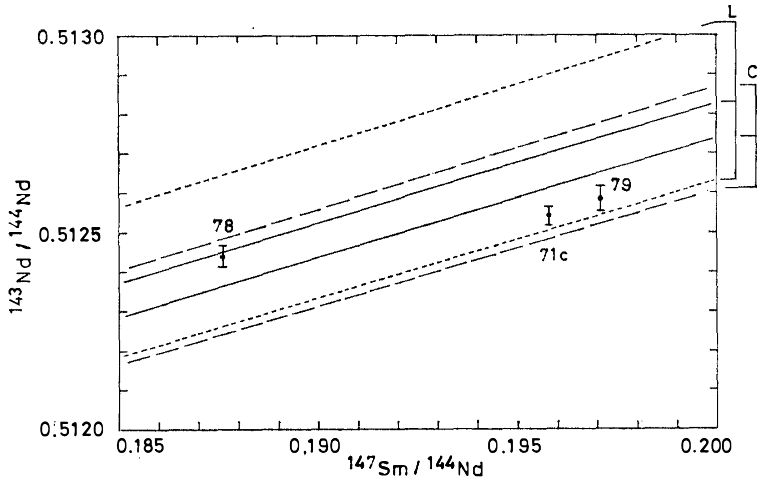

Fig. 3. A plot of ^{143}*Nd*/^{144}*Nd vs.* ^{147}*Sm*/^{144}*Nd. The lines labelled (C) and (L) are drawn by using the initial* ^{143}*Nd*/^{144}*Nd value of 0.50668±0.00003 by* W*ASSERBURG et al. (1981) and of 0.50677 ±0.00010 by* L*UGMAIR et al. (1975), respectively.*

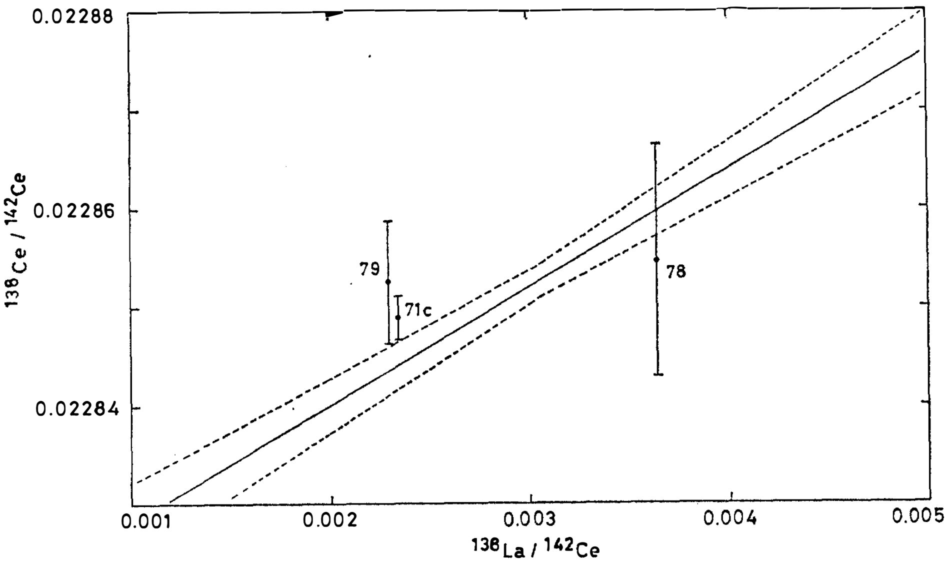

Fig. 4. A plot of ^{138}*Ce*/^{142}*Ce vs.* ^{138}*La*/^{142}*Ce. (See text for drawn lines).*

tion of light REE into the grain boundaries. Anyway, it is worth noting that the changes observed for such major elements as Mg, Fe and Ca are rather slight.

Table 2 shows ^{138}Ce/^{142}Ce ratio and ^{143}Nd/^{144}Nd ratio observed for three specimens of ALH-78132, with the corresponding data for three non-Antarctic meteorites. Figure 3 is a plot of ^{143}Nd/^{144}Nd *vs.* ^{147}Sm/^{144}Nd and Fig. 4 is a plot of ^{138}Ce/^{142}Ce *vs.* ^{138}La/^{142}Ce. The line in Fig. 3 is drawn by the following equation,

$$({}^{143}\mathrm{Nd}/{}^{144}\mathrm{Nd})_p = ({}^{143}\mathrm{Nd}/{}^{144}\mathrm{Nd})_0 + (e^{\lambda t} - 1)({}^{147}\mathrm{Sm}/{}^{144}\mathrm{Nd})_p\,,$$

where subscript p refers to the present value; decay constant λ is assumed to be $6.54 \times 10^{-12}\mathrm{yr}^{-1}$ (LUGMAIR and MARTI, 1978, summarized half-life data of ^{147}Sm and obtained a value of $(1.06 \pm 0.016\ (2\sigma)) \times 10^{11}$ yr). As for initial value 4.56 Ga ago, $({}^{143}\mathrm{Nd}/{}^{144}\mathrm{Nd})_0$, LUGMAIR *et al.* (1975) reported a value of 0.50667±0.00010, and later, WASSERBURG *et al.* (1981) adopted the initial value of 0.50668±0.00003 (this value is a recalculated one normalized to ^{143}Nd/^{144}Nd$=0.7219$ and, in this calculation, the age t is assumed to be 4.56×10^9 yr). In Fig. 3, corresponding to the two initial values, two sets of lines are drawn. In the meantime, the line in Fig. 4 is drawn based on the following equation,

$$\begin{aligned}({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_p &= ({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_0 + \frac{\lambda_\beta}{\lambda_\beta + \lambda_{EC}}[e^{(\lambda_\beta + \lambda_{EC})t} - 1]({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_p \\ &= ({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}} + \frac{\lambda_\beta}{\lambda_\beta + \lambda_{EC}}[e^{(\lambda_\beta + \lambda_{EC})t} - 1] \\ &\quad \times [({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_p - ({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}}],\end{aligned}$$

where $({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_0$ is initial ratio 4.56 Ga ago, which is calculated to be 0.0228162± 0.0000014 (SHIMIZU *et al.*, 1984); λ_β and λ_{EC} are partial decay constants and are taken to be $2.58 \times 10^{-12}\,\mathrm{yr}^{-1}$ and $4.59 \times 10^{-12}\,\mathrm{yr}^{-1}$, respectively; t is the age (4.56 Ga) of eucrite formation. (TANAKA and MASUDA (1982) have reviewed the partial and total half-life data of ^{138}La decay system and they have adopted the partial half-life values of $(2.69 \pm 0.24) \times 10^{11}$yr for β decay and $(1.51 \pm 0.10) \times 10^{11}$yr for electron capture decay.) Further, in this equation, $({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}}$ and $({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}}$ are presently observed ratios for meteorites which have chondritic La/Ce abundance ratio; here, these ratios of $({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}}$ and $({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}}$ have been evaluated from those values of Jilin, Pasamonte and Juvinas meteorites in Table 2, that is, $({}^{138}\mathrm{Ce}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}} =$ 0.0228527±0.0000009 and $({}^{138}\mathrm{La}/{}^{142}\mathrm{Ce})_{p,\ \mathrm{chond}} = 0.00306 \pm 0.00005$ (SHIMIZU *et al.*, 1984). In Figs. 3 and 4, the broken lines are drawn on the assumption that errors associated with the calculation of present isotope ratios for ^{138}Ce/^{142}Ce and ^{143}Nd/^{144}Nd involve the errors in primordial isotope ratios and decay constants and in abundance ratios presently observed for ^{138}La/^{142}Ce and ^{147}Sm/^{144}Nd, respectively; in this case, errors in abundance ratios are estimated to be 0.3%.

In Fig. 3 (the plot of ^{143} Nd/^{144}Nd *vs.* ^{147}Sm/^{144}Nd), all points of ALH-78132,71c, 78 and 79 appear to fall in the chondritic evolution field within the experimental uncertainties, although the deviation of measured points from the calculated values changes depending on the value of the initial ^{143}Nd/^{144}Nd ratio. (In this discussion, the conclusion remains valid even if the effect of the instrumental bias on the measured ratios is considered. In our study, ^{143}Nd/^{144}Nd was 0.51183±0.00003 for the La Jolla

Nd standard, as stated by TANAKA and MASUDA, 1982; the value is lower by a factor of 1.00006 than that of WASSERBURG *et al.*, 1981.) Also, in REE patterns of these samples, remarkable fractionation is not observed between Nd and Sm. However, some minor disturbances in the Sm-Nd system might be suggested from the ^{143}Nd/^{144}Nd-^{147}Sm/^{144}Nd plot (Fig. 3), where the direction of deviation of the points for ALH-78132, 71c and 79 against the theoretical line is opposite to that for ALH-78132,78. On the other hand, Fig. 4 (the plot of ^{138}Ce/^{142}Ce *vs.* ^{138}La/^{142}Ce) shows that the points for ALH-78132,71c and 79 deviate from the lines drawn theoretically, while ALH-78132,78 falls on the theoretical line within the experimental uncertainty. The results shown in Fig. 4 mean that the presently observed positive Ce anomaly of ALH-78132,71c and 79 was not produced 4.56 Ga ago. This suggests strongly that the positive Ce anomaly of these eucrite specimens was produced by the terrestrial weathering. In this connection, it is added here that the ALHA-77302 eucrite deviated from the isochron for other non-Antarctic eucrites in the Lu-Hf systematics (PATCHETT and TATSUMOTO, 1980). They suggested that ALHA77302 lost Lu in the Antarctic ice. As for negative Ce anomaly observed for ALH-78132,78, it would be needed to mention that analytical error in isotope measurement of this sample happened to be relatively large. Therefore, more precise data of Ce isotope ratio for ALH-78132,78 are needed to decide whether the negative Ce anomaly of the specimen was caused by the terrestrial weathering.

While most of Antarctic eucrites have a Ce anomaly in REE patterns, Antarctic chondrites do not show the Ce anomaly. This difference would mean the relatively high resistance of chondrites against weathering compared with eucrites. The difference of resistance against chemical weathering may be related with the difference of physical properties (*e.g.*, porosity) between chondrite and eucrite. Also it may be conceivable that this difference reflects the difference in the state of presence of REE between the chondritic and eucritic meteorites.

As discussed above, heterogeneous distribution of Ce anomaly and Ce isotope ratio data indicate that a positive Ce anomaly of Antarctic eucrites was caused by terrestrial weathering. The degree of Ce anomaly would be used as an indicator for the degree of chemical weathering. It should be noted that one cannot obtain such information from major elements. The degree of Ce anomaly would be useful in considerations on other trace element or nuclide abundances in Antarctic eucrites.

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