REE ABUNDANCES IN THE WHOLE ROCK AND MINERAL SEPARATES OF THE ALLAN HILLS-765 METEORITE

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Abstract: The rare earth elements (REE) Ba and Sr abundances in the whole rock and mineral separates of the Allan Hills-765 meteorite and in the whole rock of the Juvinas meteorite have been determined by the mass spectrometric isotope dilution method. The REE pattern of the whole rock of the Allan Hills meteorite is similar to that of the Juvinas meteorite but is different in presence of a significantly large ($\sim +50\%$) Ce anomaly.

The hand-picked pyroxenes black clast show different REE patterns with different extents of Ce anomalies $(-40 \sim +240\%)$. On the other hand, plagioclase shows rather minor ($\sim +10\%$) Ce irregularity.

REE patterns for estimated melts in equilibrium with the minerals suggest that different pyroxenes have not been in equilibrium with each other and with plagioclase.

1. Introduction

Because of their early igneous origin, the basaltic achondrites have attracted much attention of cosmochemists regarding the age and chemical features as well as mineralogical and petrological characteristics. REE abundances in the meteorite group have been debated as to petrogenetic implications (SCHNETZLER and PHIL-POTTS, 1969; MCCARTHY *et al.*, 1973; CONSOLMAGNO and DRAKE, 1977).

In the course of our joined REE and Sm-Nd examinations of the Allan Hills-765 meteorite, we have recognized a significantly large positive Ce anomaly in the REE pattern of the whole rock of the meteorite (NAKAMURA *et al.*, 1979). In view of rare existence of Ce anomaly in differentiated meteorites and its possible cosmochemical significances, we have undertaken detailed chemical and mineralogical examinations of the meteorite.

In this work, REE analyses of whole rock and some mineral separates of the meteorite are reported.

2. Experimental

The meteorite piece (a few grams) partially covered with fusion crust was crushed to coarse-grained powder (100-150 mesh) in an agate mortar, and different

colored grains were separated by hand-picking under a binocular microscope. The rest of the sample was used for Sm-Nd work. Chemical and mass spectrometric procedures employed in this work were basically the same as our regular methods (MASUDA *et al.*, 1973; NAKAMURA, 1974a) except some modifications; because of the small sample size (1–2.5 mg for mineral separates), a micro-chemical procedure was devised for REE separation from major elements. The REE blank contributions to sample analyses were found to be negligible. The precisions of REE analyses are believed to be better than about two per cents, except some cases.

3. Results

The Allan Hills-765 meteorite is discribed as a eucritic polymict breccia by MIYAMOTO et al. (1979) and by OLSEN et al. (1978).

As shown in Table 1 and Fig. 1, the REE abundances in the whole rock are found to be typical of non-cummulate eucrites such as the Juvinas meteorite except for Ce. The whole rock of the Allan Hills-765 meteorite shows the REE pattern essentially similar to that of Juvinas determined in this work. However, the significantly large positive Ce anomaly (+50%) of the Allan Hills-765 meteorite intrigues us in relation to its origin.

Element	Allan Hills-765					Juvinas
	Whole rock 468 mg	White 1.2 mg	Yellow 0.93 mg	Brown 1.5 mg	Black 2.5 mg	Whole rock 671 mg
La	2.21	1.15		1.60	3.45	2.15
Ce	9.39	2.83	1.59	5.96	6.04	5.91
Nd	4.97	1.21	0.593	4.05	8.02	4.44
Sm	1.65		0.233	1.45	2.56	1.471
Eu	0.671	1.46	0.049	0.246	0.445	0.588
Gd	2.20	0.288	0.376	3.00	3.35	2.01
Dy	2.63	0.289	0.568	3.78	3.73	2.42
Er	1.73	0.200	0.445	2.40	2.28	1.556
Yb	1.80	0.203		2.32	2.32	1.452
Lu	0.271	0.0164	0.063		0.318	0.225
Ba		88.7	5.81		21.0	25.7
Sr		174.1	1.35		8.26	
⊿Ce/Ce* (%)	+49	+10	+240	+28	-40	-0.5

Table 1. Results of analyses of REE, Ba and Sr in the whole rock and the mineral separates of the Allan Hills-765 meteorite, and in the whole rock of the Juvinas meteorite (Abundances are given in ppm).

* Normal Ce was estimated from La, Nd and Sm, or Nd and Sm. Δ Ce indicate departure of the observed Ce from the normal Ce.

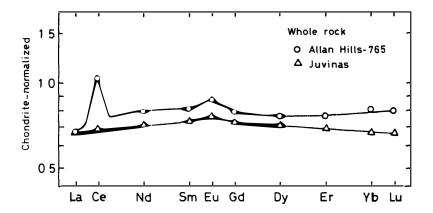


Fig. 1. Chondrite normalized REE patterns of the whole rocks of the Allan Hills-765 and the Juvinas meteorites obtained in this work.

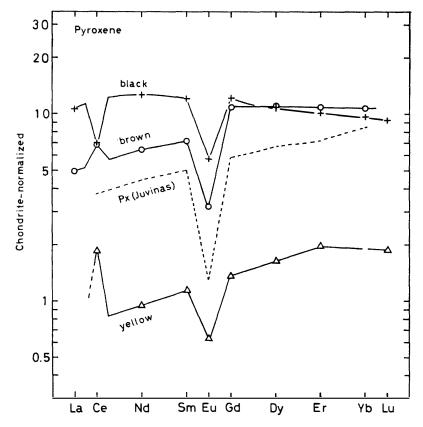


Fig. 2. REE patterns for pyroxenes from the Allan Hills-765 and the Juvinas meteorites. Data of pyroxene of Juvinas are from SCHNETZLER and PHILPOTTS (1969).

As given in Table 1, the degree of Ce anomaly was estimated from departure of the observed Ce abundance from the possible normal Ce value obtained by extrapolation from Sm and Nd, or by interpolation from the smooth curve spanning from La to Sm. As far as the REE data available for eucrite are concerned, such a clear Ce irregularity may be the first finding.

In Fig. 2, REE patterns for different colored pyroxenes separated from the meteorite are shown. The brown (to dark) pyroxene shows a light-REE-depleted and flat-heavy-REE-pattern with a relatively large negative Eu anomaly. As suggested by CONSOLMAGNO and DRAKE (1977) for non-cummulate eucrite melt, if we assume a melt with REE abundances of 30–40 times those of average chondrites, then we can expect a similar pattern for clinopyroxene which is in equilibrium with the melt. Therefore, it is suggested that the brown pyroxene has a chemical composition of clinopyroxene. This is parallel with the observation of augite in the Allan Hills-765 meteorite by OLSEN *et al.* (1978). The Ce anomaly in this mineral separate is less pronounced compared with that of the whole rock.

Although usual eucritic pyroxene shows a smooth fractionation trend from light to heavy REE except Eu, the pattern of the brown pyroxene has some stepwise structure between light and heavy REE. Because most of the previous REE analyses for minerals of eucrites have been performed for mineral concentrates obtained by

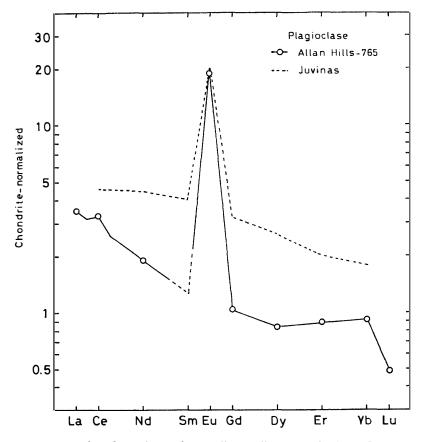


Fig. 3. REE patterns for plagioclase of the Allan Hills-765 and of the Juvinas meteorites. Data on Juvinas are from SCHNETZLER and PHILPOTTS (1969).

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heavy liquid separation, it is not clear whether the stepwise structure in REE pattern of the brown pyroxene is unique for the Allan Hills-765 meteorite or not. Anyway, in order to clarify chemical features of eucrites, it would be necessary to obtain more detailed and precise REE data for minerals of other eucrites.

The yellow pyroxene shows a relatively smooth REE pattern with a gradual increase in relative abundances from light to heavy REE except for Ce. The general trend of the pattern is typical of eucritic pigeonite. However, the Ce anomaly of +240% is extremely high. (The determination of La in the specimen was not successful.) The Fe/Fe+Mg ratio of 0.460 and CaO concentration (2.92%) in the yellow pyroxene grain suggest that the yellow pyroxene is a similar one to the type A pyroxene which was described by MIYAMOTO *et al.* (1979). (Further chemical examinations of the mineral will be published elsewhere.)

The black clasts show a relatively flat REE pattern with highest REE abundances and negative Ce anomaly. The specimen appeared to be a pyroxene under a binocular microscope and the presence of negative Eu anomaly in the pattern also supports this possibility. However, the significantly large negative Ce anomaly in the pattern is hardly explained in terms of REE distribution of pyroxene-melt in the physicochemical condition in the meteorite parent body. As demonstrated by NAGASAWA and ONUMA (1979), Ce and Eu are much more volatile at high temperature than other REE in oxidizing conditions. Thus, it is suggested that the REE in the black clasts represent a vaporization residue which was formed in the relativelyoxydizing environment.

The white mineral separate shows a REE pattern with a large positive Eu anomaly, which is typical of eucritic plagioclase (see Fig. 3). In this case, the Ce anomaly in the pattern is rather small compared to those of pyroxenes.

4. Discussion

4.1. General features of REE patterns of minerals in the Allan Hills-765 meteorite

In order to examine possible chemical relations among minerals, REE patterns for possible melts which might have been in equilibrium with the minerals were estimated by using typical solid/liquid partition coefficients of REE (SCHNETZLER and PHILPOTTS, 1970; DRAKE, 1975; GRUTZECK *et al.*, 1974) (see Fig. 4).

If we employ the REE partition coefficients obtained at 1150° C ($f_{02}=10^{-9}$ ~⁻¹⁰) for plagioclase (DRAKE, 1975), the REE abundances of the melt in equilibrium with the "white" mineral are estimated to be 20 times the chondritic abundances. The REE pattern estimated for brown pyroxene by employing the partition coefficients of clinopyroxene obtained under similar conditions (GRUTZECK *et al.*, 1974) is also generally chondritic with somewhat higher abundances compared with that for plagioclase. On the other hand, if the partition coefficients of pigeonite (SCHNETZLER and PHILPOTTS, 1970) are applied to the yellow pyroxene, then much more fraction-

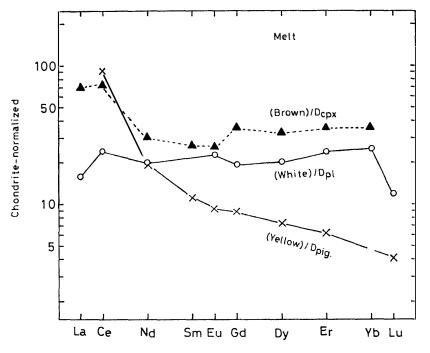


Fig. 4. REE patterns for possible melts in equilibrium with coexisting minerals in the Allan Hills-765 meteorite, which were estimated using typical solid/liquid partition coefficients of REE (see text).

ated REE pattern for the melt is obtained.

Thus, it is suggested that these two pyroxenes crystallized at different stages of the same magmatism or from different magmas in the parent body. Aside from the general REE pattern, it is interesting to note that the Eu abundances in the melts estimated by the partition coefficients obtained at oxygen fugacity of $10^{-9^{-10}}$ are normal. This oxygen fugacity is significantly higher than those estimated for other eucrites (DRAKE, 1975). If this is the case, the oxygen fugacity prevailing in the parent magma of the Allan Hills-765 meteorite might have been more oxidizing than those of typical eucrites. However, because REE partition coefficients for pigeonite, clinopyroxene and plagioclase have not been well-established regarding to their applicabilities to minerals under consideration, the above observations should be re-examined when new and more strict partition coefficients become available.

4.2. Cerium anomaly of the Allan Hills-765 meteorite

The both positive and negative Ce anomalies found in mineral separates of the Allan Hills-765 meteorite intrigue us in relation to their origin.

As far as we know, terrestrial contamination of Ce or selective Ce enrichment or depletion in the antarctic ice field may not be responsible for the observed Ce anomalies. Similar problems have been discussed in the case of the Barwise chondrite (NAKAMURA and MASUDA, 1973a) and in the work by ITO *et al.* (1980). Generally, meteorites from the antarctic ice field are found to retain their preterrestrial natures well, as has been typically demonstrated by the analyses of organic materials in a carbonaceous chondrite (CRONIN *et al.*, 1979), although such problems should be examined further with more information of the meteorite.

As mentioned below, the positive Ce anomalies of the Allan Hills-765 meteorite may be explained from a cosmochemical viewpoint.

Although irregular behavior of Ce in eucrites as well as in many other differentiated meteorites has not been known, some meteoritic specimens such as the Khohar chondrite (NAKAMURA and MASUDA, 1973b) and olivine chondrule in the Allende meteorite (TANAKA *et al.*, 1975), and certain lunar highland samples (MASUDA *et al.*, 1972; NAKAMURA, 1974b) have positive Ce anomalies. Moreover, most of chondrites show more or less small Ce irregularities (MASUDA *et al.*, 1973; NAKAMURA 1974a). Such observations suggest that there must have been some physico-chemical conditions which have produced Ce anomaly as well as negative anomaly in the early solar system.

In this connection, the positive Ce anomalies of the Allan Hills-765 meteorite are considered to be results of some specific events in the parent body (or bodies). In view of the varying extents of Ce anomalies in the meteorite minerals and the lack of Ce mass balance between the constituent minerals and the whole rock (see Table 1), it is considered that a micro component(s) enriched in Ce has been responsible for the observed Ce anomalies. As noted by NAKAMURA *et al.* (1979), the Sm-Nd isotopic system has been reset possibly by meteoritic impact(s) in the early time (~4.5 b.y. ago) of the formation of the parent body. Like the case of the lunar highland materials (except for anorthosites) (NAKAMURA, 1974b), the early severe impacts may be responsible for Ce enrichment in the surface planetary materials by unknown Ce transportation mechanism or by injection of a Ce-enriched meteoritic component. However, such speculation has not been sufficiently substantiated at the present stage by the chemical and mineralogical examinations. In order to clarify this problem, more detailed investigation of components of the meteorite such as inclusions in pyroxenes should be undertaken.

In conclusion, the variation of general REE pattern of constituent minerals of the Allan Hills-765 meteorite suggests that the meteorite represents a eucritic breccia including minerals crystallized from different magmas and/or at different crystallization stages. These results are considered to be generally consistent with the results of petrological and major chemical examinations (MIYAMOTO *et al.*, 1979; OLSEN *et al.*, 1978). However, the observed Ce irregularities in the meteorite have not been expected from any information available for this meteorite. In view of the increasing cosmochemical interest in the Ce anomaly and its possible role in order to understand chemical features of the early solar system (BOYNTON, 1978), more systematic examinations of distribution of Ce in meteoritic materials should be continuously pursued.

Acknowledgments

We are indebted to Dr. K. YANAI and to the members of the field party of the Japanese Antarctic Research Expedition in 1976 for the Allan Hills-765 meteorite, and to Dr. B. MASON for the Juvinas meteorite.

We thank Dr. M. TATSUMOTO for helpful cooperation, Prof. H. TAKEDA and Dr. M. MIYAMOTO for information on the Allan Hills-765 meteorite, and Prof. H. NAGASAWA for invaluable comments.

This work was supported in part by Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture. One of the authors (N.N.) thanks the Ito Science Foundation for the financial support in part to this work.

References

- BOYNTON, W. V. (1978): Rare-earth elements as indicators of surpernova condensation. Lunar Planet. Sci. IX. Houston, Lunar Planet. Inst., 120–122.
- CONSOLMAGNO, G. J. and DRAKE, M. J. (1977): Composition and evolution of the eucritic parent body: Evidence from rare-earth elements. Geochim. Cosmochim. Acta, 41, 1271–1282.
- CRONIN, J. R., PIZZARELLO, S. and MOORE, C. B. (1979): Amino acids in an antarctic carbonaceous chondrite. Science, 206, 335-337.
- DRAKE, M. J. (1975): The oxydation state of europium as an indicator of oxygen fugacity. Geochim. Cosmochim. Acta, 39, 55-64.
- DRAKE, M. J. and WEILL, D. F. (1975): Partition of Sr, Ba, Ca, Y, Eu⁺², Eu⁺³, and other REE between plagioclase feldspar and magmatic liquid: an experimental study. Geochim. Cosmochim. Acta, **39**, 689-713.
- GRUTZECK, M., KRIEDELBAUGH, S. and WEILL, D. (1974): The distribution of Sr and REE between diopside and silicate liquid. Geophys. Res. Lett., 1, 273–275.
- ITO, A., NAKAMURA, N. and MASUDA, A. (1980): Examination of effects of shock and weathering for the antarctic L6 chondrites, Yamato-74190 and Allan Hills-769, by the Rb-Sr method. Mem. Natl Inst. Polar Res., Spec. Issue, 17, 168–176.
- MASUDA, A., NAKAMURA, N. and TANAKA, T. (1973): Fine structures of mutually normalized rareearth patterns of chondrites. Geochim. Cosmochim. Acta, 37, 239–248.
- MASUDA, A., NAKAMURA, N., KURASAWA, H. and TANAKA, T. (1972): Precise determination of rare-earth elements in the Apollo 14 and 15 samples. Proc. Lunar Sci. Conf. 3rd., 1307–1313.
- McCARTHY, T. S., ERLANK, A. J. and WILLIS, J. P. (1973): On the origin of eucrites and diogenites. Earth Planet. Sci. Lett., 18, 433-442.
- MIYAMOTO, M., TAKEDA, H., YANAI, K. and HARAMURA, H. (1979): Mineralogical examinations of the Allan Hills No. 5 meteorite. Mem. Natl Inst. Polar Res., Spec. Issue, 12, 59–71.
- NAGASAWA, H. and ONUMA, N. (1979): High temperature heating of the Allende meteorite II. Fractionation of the rare earth elements. Lunar Planet. Sci. X. Houston, Lunar Planet. Inst., 884–886.
- NAKAMURA, N. (1974a): Determination of REE, Ba, Fe, Mg, Na and K in carbonaceous and

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ordinary chondrites. Geochim. Cosmochim. Acta, 38, 757-775.

- NAKAMURA, N. (1974b): Positive cerium anomaly and two types of lunar samples. Geochem. J., 8, 67-74.
- NAKAMURA, N. and MASUDA, A. (1973a): A detailed chemical study on the Barwise chondrite. Meteoritics, 8, 149–167.
- NAKAMURA, N. and MASUDA, A. (1973b): Chondrites with peculiar rare-earth patterns. Earth Planet. Sci. Lett., 19, 429-437.
- NAKAMURA, N., MASUDA, A., COFFRANT, D. and TATSUMOTO, M. (1979): REE abundances and Sm-Nd systematics of antarctic eucrite, Allan Hills No. 5 meteorite (Abstract). Meteoritics, 14, 492-493.
- OLSEN, E. J., NOONAN, A., FREDRICKSSON, K., JAROSEWICH, E. and MORELAND, G. (1978): Eleven new meteorites from Antarctica, 1976–1977. Meteoritics, 13, 209–226.
- SCHNETZLER, C. C. and PHILPOTTS, J. A. (1969): Genesis of the calcium-rich achondrites in light of rare-earth and barium concentrations. Meteorite Research, ed. by P. M. MILLMAN. Dordrecht, D. Reidel, 206–216.
- SCHNETZLER, C. C. and PHILPOTTS, J. A. (1970): Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts-II. Geochim. Cosmochim. Acta, 34, 331-340.
- TANAKA, T., NAKAMURA, N., MASUDA, A. and ONUMA, N. (1975): Giant olivine chondrule as a possible late-stage product in the nebula. Nature, **256**, 27–28.

(Received May 24, 1980; Revised manuscript received August 13, 1980)