# Sm-Nd ISOTOPIC SYSTEMATICS AND REE ABUNDANCE STUDIES OF THE ALH-765 EUCRITE

Noboru Nakamura<sup>1,2,3</sup>,

<sup>1</sup>Department of Earth Sciences, Faculty of Science, Kobe University, Rokkodai-cho, Nada-ku, Kobe 657

Mitsunobu TATSUMOTO<sup>2</sup> and Denis COFFRANT<sup>1,2,4</sup>

<sup>2</sup>U.S. Geological Survey, Mail Stop 963, Box 25046, Denver, Colorado 80225, U.S.A.

**Abstract:** Analyses of Sm-Nd systematics and REE concentrations were carried out for the whole rock and mineral separates from the ALH-765 meteorite. A Sm-Nd age of  $4.52\pm0.09$  (2  $\sigma$ ) b.y. and an initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio of 0.50675  $\pm 0.00011$  (2  $\sigma$ ) have been obtained. The previously reported Ce irregularities have been re-examined in this work. The large Ce anomalies and some minor Sm-Nd system disturbances observed for the meteorite may be interpreted as results of terrestrial weathering effects.

## 1. Introduction

The ALH-765 meteorite is a polymict brecciated eucrite as described by MIYA-MOTO et al. (1979a) and OLSEN et al. (1978). We have undertaken Sm-Nd isotopic studies and precise REE analyses of the constituent minerals of the meteorite as well as the whole rock to examine Sm-Nd isotopic and REE elemental abundances in Antarctic meteorite "finds". Our preliminary results for the ALH-765 eucrite were reported by NAKAMURA et al. (1979).

The main purposes of this work are to present Sm-Nd isotopic data and additional REE analyses, and to discuss the chronological significance of the Sm-Nd systematics and the interpretation of REE abundances for this Antarctic eucrite. Based on isotope dilution analyses, NAKAMURA *et al.* (1979) and NAKAMURA and MASUDA (1980) first reported a significantly large positive Ce anomaly in the whole rock and positive and negative anomalies in pyroxenes for the meteorite. However, this observation was not confirmed by the INAA analyses of GROSSMAN *et al.* (1981). In view of the cosmochemical importance of a Ce anomaly in early solar system materials, we have analyzed REE in the mineral separates which were used for Sm-Nd isotopic analyses and re-examined the REE patterns.

# 2. Sample Preparation and Experimental Techniques

Heavy-liquid mineral separations were carried out for the residual sample after

<sup>&</sup>lt;sup>3</sup> Also Colorado School of Mines, Golden, Colorado 80401, U.S.A.

<sup>&</sup>lt;sup>4</sup> Present address : Department des Sciences de la Terre, Universite Claude Bernard-Lyon, Lyon, France.

hand-picking coarser mineral grains which were used for REE analyses (NAKAMURA and MASUDA, 1980). Sm-Nd concentration and isotopic analyses were performed at the U.S.G.S., Denver, using a NBS type 12-inch mass spectrometer. The mineral separation and analytical procedures are in a manner similar to that described by NAKA-MURA et al. (1976). Four samples, whole-rock (1), a low density (d=2.6-2.85 g/cm<sup>3</sup>) fraction ("L"; purity >95%), a medium density (d=2.85-3.3 g/cm<sup>3</sup>) fraction ("M(1)"), and a heavy density  $(d > 3.3 \text{ g/cm}^3)$  fraction ("H(1)") were analyzed during the early phase of this study and the Nd isotopic measurements were carried out using the mass spectrometer with a CARY model 31 electrometer, but the rest of the samples were analyzed with a CARY model 401 at a later time. It was found that a bias exists between the old and the new CARY Vibrating Reed Electrometers. During the two periods of this work the mean  $^{143}$ Nd/ $^{144}$ Nd ratios of 0.511071  $\pm$  0.000016 (2  $\sigma_m$ ) and  $0.510935 \pm 0.000025$  (2  $\sigma_m$ ) were obtained for the USGS (originally designed as "NBS") Nd standard at a 300 mv scale by the old and new CARY electrometers, respectively. Thus the <sup>143</sup>Nd/<sup>144</sup>Nd ratios obtained for the later three samples were corrected for the bias by multiplying the factor of 1.00027.

The heavy-liquid mineral separates were analyzed for REE by our normal method at Kobe University (NAKAMURA, 1974a). Sample sizes of 50 to 150 mg were used for Sm-Nd work and 10–30 mg for REE analyses. Blank contributions were negligible for all analyses in this work (*c. f.* NAKAMURA *et al.*, 1982). Uncertainties for REE analyses are considered to be 1-2%.

## 3. Results and Discussion

## 3.1. REE abundances

Results of REE analyses for the heavy-liquid separates are given in Table 1 and Fig. 1. The REE abundances in the L fraction are typical for eucritic plagioclase such as that of the Juvinas meteorite (SCHNETZLER and PHILPOTTS, 1969) except for a minor positive Ce anomaly. Therefore, we concluded that this fraction consists mainly of plagioclase. The REE abundances in the H fraction are less fractionated than those of the Juvinas pyroxene (SCHNETZLER and PHILPOTTS, 1969), and the negative Eu anomaly of our analyses is not so large as that in the Juvinas pyroxene. One explanation for these observations could be a result of mixing of pyroxenes that crystalized at various stages and/or mixing with foreign pyroxenes as suggested from REE analyses of individual grains (NAKAMURA and MASUDA, 1980). However, impure mineral separation would also cause a similar trend.

The M fraction has the highest REE abundances and a flat pattern. Such a REE pattern has not been found among mineral grains of the ALH-765 meteorite (NAKA-MURA and MASUDA, 1980). A binocular microscope observation suggests that this fraction is composed mainly of plagioclase and different colored pyroxenes (*cf.* NAKAMURA and MASUDA, 1980), though the high REE abundances are not expected from mixing of these two minerals. Therefore, we suggest that REE abundances in this fraction are controlled by minor mineral components such as phosphate. This suggestion is also supported by Nd isotopic data (see Fig. 2).

Element	Plagioclase density=2.6-2.85 (g/cm <sup>3</sup> )	Intermediate 2.85–3.3	Pyroxene >3.3	Whole rock*	Chondrite**
La	1.712	3.86	2.11	2.21	0.329
Ce	4.97	12.95	8.70	9.39	0.865
Nd	2.68	7.82	5.03	4.97	0.630
Sm	0.756	2.37	1.799	1.648	0.203
Eu	1.647	0.790	0.324	0.671	0.0770
Gd	0.921	3.14	2.50	2.20	0.276
Dy	0.922	3.77	3.21	2.63	0.343
Er	0.574	2.41	2.22	1.728	0.225
Yb	0.558		2.29	1.797	0.220
Lu	0.0782		0.363	0.271	0.0339

Table 1. REE abundances (ppm) in separated phases of the ALH-765 meteorite and chondrite.

\* Data are from NAKAMURA and MASUDA (1980).

\*\* Average of ten ordinary chondrites (NAKAMURA, 1974).

Sawing oil Ce $\leq$ 0.002 ppm.

Red coating Ce  $\leq 0.05$  ppm.

As discussed by NAKAMURA and MASUDA (1980), the most problematic observation with the REE abundances in the ALH-765 meteorite is the significantly large positive and negative Ce anomalies which are typically found in pyroxenes (NAKAMURA and MASUDA, 1980). As far as we know, such large Ce anomalies have not yet been reported for differentiated meteoritic materials or lunar samples, although some less prominent positive Ce irregularities were reported for lunar highland samples (NAKA-MURA, 1974b). It is, thus, a quite serious problem that only some Antarctic meteorites show these anomalies (SHIMIZU and MASUDA, 1982).

In order to examine possible Ce contamination during sample processing, we analyzed Ce in sawing materials (sawing oil and red coating material on the saw blade) which were provided by Dr. K. YANAI. As shown in Table 1, Ce concentrations in these materials are too low to explain the positive Ce anomaly by contamination with these materials. Although we do not have detailed knowledge about other parts of sample processing, it seems improbable that the observed positive Ce anomaly in Antarctic meteorites has been caused by simple addition of artificial Ce-enriched material(s).

Another possible mechanism of Ce enrichment may be terrestrial weathering effects. It is worth mentioning that the deep sea sediments and alteration products of basalt debris in contact with sea water have large positive and negative Ce anomalies (PIPER, 1974) indicating that Ce can behave differently from other REE. The positive and negative Ce anomalies could be explaind if we consider an extreme case of weathering; for example, if the meteorite under consideration was in sea water for a long time. However, this is probably not the case because the meteorite specimen examined in this work appeared sufficiently fresh. Therefore, if the Ce irregularities under consideration were caused by weathering, the mechanism of weathering in the Antarctic ice must be quite different, particularly for the major chemical and petrological characteristics, from that in sea water (cf. PIPER, 1974).



Fig. 1. REE abundance patterns for the whole rock (NAKAMURA and MASUDA, 1980) and mineral separates from the ALH-765 meteorite.

NAKAMURA et al. (1979) and NAKAMURA and MASUDA (1980) discussed a possibility which might have caused the Ce irregularities. An early impact-metamorphic event was thought to be responsible for the relatively small Ce irregularities in lunar and meteoritic samples (NAKAMURA, 1974a, b). Discoveries of even larger Ce anomalies in other Antarctic meteorites (SHIMIZU and MASUDA, 1982) now pose more harder questions.

In this connection, it is interesting that GROSSMAN *et al.* (1981) did not observe a Ce anomaly for the whole rock sample of the ALH-765 meteorite. Their whole rock data are systematically higher than those of NAKAMURA and MASUDA (1980) except that Ce and Eu abundances are quite similar. The similarity of Eu abundance and systematic fractionation of other REE except Ce suggest that the differences in REE abundances between the two analyses were the result of sample heterogeneity since GROSS-MAN *et al.* (1981) analyzed much a smaller sample than NAKAMURA and MASUDA (1980). It should be added here that our sample was partly covered with fusion crust and thus may represent a relatively surface part to  $\sim 3$  cm inside of the whole stone. (All analyses in this work were carried out for the samples without fusion crust.)

From the above discussion it is suggested that the Ce irregularities found in our sample may not be a general feature but only a local one, and that there must have existed some later or recent events which yielded the severe Ce fractionation from other REE. However, it should be noted that even a strongly-shocked young meteorite, for example; the Shergotty meteorite (SHIH *et al.*, 1982), does show no such a Ce anomaly in its REE pattern. Thus, an impact metamorphism in the early or later history of the meteorite parent body (NAKAMURA and MASUDA, 1980) does not seem to be a main factor in creating the large Ce anomalies in the ALH-765 meteorite. Finally, we suggest that some unkown terrestrial weathering mechanism related to the Antarctic ice dynamics was the most conceivable factor responsible for the observed Ce anomalies.

#### 3.2. Sm-Nd systematics

Results of the Sm-Nd isotopic analyses are given in Table 2. As inferred from REE abundances, three main REE host phases are suggested; plagioclase, pyroxene and possibly phosphate. Such a feature is more clearly observed in the Nd concentration *vs.* <sup>143</sup>Nd/<sup>144</sup>Nd diagram as shown in Fig. 2.

Sam	Sm (ppm)	Nd (ppm)	<sup>147</sup> Sm <sup>144</sup> Nd	<sup>143</sup> Nd* <sup>144</sup> Nd	
Plagioclase (L)	$(d=2.6-2.85 \text{ g/cm}^3)$	0.7253	2.661	$0.16475 \pm 8$	$0.511689 \pm 18$
M(1) fraction	$(d=2.85-3.3 \text{ g/cm}^3)$	2.308	7.310	$0.19085 \pm 18$	$0.512451 \pm 38$
M(2) fraction	$(d=2.85-3.3 \text{ g/cm}^3)$	2.373	7.637	$0.18775 \pm 14$	$0.512393 \pm 38$
Whole rock (1)**		1.6678	4.978	$0.20316 \pm 8$	$0.512834 \pm 18$
Whole rock (2)		1.5974	4.793	$0.20138 \pm 10$	$0.512829 \pm 25$
Pyroxene (H (1))	$(d > 3.3 \text{ g/cm}^3)$	1.7056	4.751	$0.21697 \pm 13$	$0.513269 \pm 35$
Pyroxene (H (2))	$(d > 3.3 \text{ g/cm}^3)$	1.7344	4.882	$0.21468 \pm 13$	$0.513226 \pm 19$

Table 2. Sm-Nd results for the ALH-765 meteorite.

\* Ratios are nomalized to  $^{150}Nd/^{144}Nd=0.236433$ . Errors correspond to last digits and are  $2\sigma$  mean.

\*\* Ratios of non-radiogenic Nd isotopes are:  $142/144=1.14173\pm4$ ;  $145/144=0.348349\pm13$ ;  $146/144=0.72184\pm3$ ;  $148/144=0.241603\pm14$ .

As mentioned above, three mineral separates (medium density fraction-2, whole rock-2, pyroxene fraction-2) were analyzed in the later part of this work using a new CARY 401. The results for these samples are generally consistent with the earlier analyses on the other four samples after bias correction, but the Nd isotopic ratios for these three samples appear to be slightly higher than those of the other four. The minor isotopic differences between the earlier and later analyses may be results of sample heterogeneity and/or improper bias corrections though this would not influence too much the later discussions. The data are plotted on a <sup>147</sup>Sm/<sup>144</sup>Nd to <sup>143</sup>Nd/<sup>144</sup>Nd diagram in Fig. 3. The total span of isotopic ratio variation is only 30% in the <sup>147</sup>Sm/<sup>144</sup>Nd and 0.3% in the <sup>143</sup>Nd/<sup>144</sup>Nd ratios. Including all data, the slope of the linear array yields an age of  $4.60 \pm 0.06 (2\sigma)$  b.y. and an initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio of  $0.50666 \pm 0.00008$ (2  $\sigma$ ) using  $\lambda = 6.54 \times 10^{-12}$  yr<sup>-1</sup>. On the other hand, if only four data points, which were obtained by the old CARY model 31 and thus more consistent with each other, are used, the  ${}^{147}$ Sm/ ${}^{144}$ Nd- ${}^{143}$ Nd/ ${}^{144}$ Nd regression line gives an age of  $4.52 \pm 0.09$  (2  $\sigma$ ) b.y. (The age of  $4.47 \pm 0.09$  b.y. reported by NAKAMURA et al. (1979) has been recalculated using the same data set) and initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio of  $0.50675 \pm 0.00011$  (2  $\sigma$ ). Although both the age and initial Nd ratios agree within the analytical errors for the two data sets, the later values are more consistent with our recent Sm-Nd data; which were revised using the newly calibrated tracer concentrations (NAKAMURA et al., 1982).

Our revised Sm-Nd isochron age for the Pasamonte eucrite (UNRUH *et al.*, 1977) is  $4.50 \pm 0.09$  (2  $\sigma$ ) b.y. and the initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio is  $0.50683 \pm 0.00008$  (2  $\sigma$ ). The age and the initial Nd ratio obtained for the ALH-765 meteorite are in good agreement with those of the Pasamonte meteorite, and are also in agreement with most Sm-Nd internal isochron ages obtained for eucrites and the Angra Dos Reis meteorite (LUG-MAIR *et al.*, 1976; LUGMAIR and MARTI, 1977; JACOBSEN and WASSERBURG, 1980; NY-



Fig. 2. Nd concentration vs. <sup>143</sup>Nd/<sup>144</sup>Nd diagram. Three major host phases of REE (plagioclase, pyroxene and possibly phosphate) are suggested from the diagram.

QUIST *et al.*, 1979) within the experimental errors. Close examination of the Nd isotopic data for the BCR-1 standard rock and the initial Nd ratio for the achondrites obtained in different institutes suggest that machine biases exist between laboratories. The <sup>143</sup>Nd/<sup>144</sup>Nd ratio for the BCR-1 at USGS (NAKAMURA *et al.*, 1982) is higher than that by WASSERBURG *et al.* (1981) by the  $\varepsilon$  value of  $0.7 \pm 0.5$  when the normalization is adjusted. The initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio at 4.55 b.y. ago for meteorites (JACOBSEN and WASSERBURG, 1980, 1981) is calculated to be 0.50669 when normalized to our value (<sup>150</sup>Nd/<sup>144</sup>Nd=0.236433) which is originally calculated from the data by LUGMAIR *et al.* (1976). Therefore the initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio for the ALH-765 is ~1 higher in  $\varepsilon$  units than the former value.

The Sm-Nd age obtained here is in sufficient agreement with the meteorite formation age of 4.55 b.y. within the experimental error. However, as seen in the inserted diagram of Fig. 3, the slight younger age is controlled mainly by the lowest data point of the low density mineral fraction enriched in plagioclase, which is considered to be more sensitive to impact metamorphism for the Sm-Nd system (LUGMAIR and SCHEININ, 1975; SHIH *et al.*, 1982). Therefore, it is possible that the Sm-Nd system of the meteorite was reset to some degree by impact metamorphism just after its formation. Except for the plagioclase, the array of other 6 data points corresponds to an age of  $4.68 \pm$ 0.15 (2  $\sigma$ ) b.y. and initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio of  $0.50655 \pm 0.00021$  (2  $\sigma$ ). Similar high model ages were also reported for the meteorite by WOODEN *et al.* (1981). So far, the Sm-Nd age obtained in this study were treated as the true age of the meteorite. How-



Fig. 3. Sm-Nd evolution diagram for the ALH-765 meteorite. Four data points (●) obtained in the early part of this work (see text) define an array corresponding to an age of 4.52±0.09 (2σ) b.y. and an initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio of 0.50675±0.00011 (2σ). This age is interpreted as a time of formation and/or impact metamorphism. Except for the lowest data point (plagioclase) the data array corresponds to an age of 4.68±0.15 (2σ). This apparent old age may be the result of isotopic disturbances by later impacts or more probably terrestrial weathering.

ever, the somewhat lower value of 4.52 b.y. compared to the meteorite formation age and the high age value of the 6 data points may be probably due to the disturbance from multiple impacts as inferred from the <sup>39</sup>Ar release pattern (KANEOKA, 1981) or by other factors which might have affected the REE distributions in the meteorite in more recent time.

As suggested from REE abundances of constituent minerals of the meteorite, REE in this meteorite are unusual in respect to Ce abundances. This observation leads us to be more conscious of terrestrial weathering effects on the Sm-Nd system of the meteorite. Because REE in meteorites are generally considered to be most resistant elements in terrestrial weathering conditions, it seems rather difficult to envision how REE can be removed from portion to portion in a meteorite by weathering without apparent effects on the major chemical and petrological features of the meteorite.

In this connection, it is worth noting that the Lu-Hf systematics of the ALH-77302 eucrite appear to be affected by terrestrial weathering effect (PATCHETT and TA-TSUMOTO, 1980). The ALH-765 meteorite is rather similar to the ALH-77302 meteorite chemically (FUKUOKA and NAKAMURA, 1981) and petrologically (MIYAMOTO *et al.*, 1979b), and the sample is described as "fresh". Our sample also appeared quite "fresh" (MARVIN and MASON, 1980). Hence, it seems probable that some of the unusual behaviors of the REE and Sm-Nd system found in this work and of Lu-Hf systems 330

(PATCHETT and TATSUMOTO, 1980) in the Antarctic meteorites are partly attributed to weathering effects in the Antarctic ice. In order to understand these effects on minor and trace chemical components in meteorites, more refined chemical and petrological examinations would be required.

In conclusion, our results suggest that the REE and Sm-Nd system in the ALH-765 meteorite have substantially preserved the chemical and isotopic characteristics of the early solar system in which the meteorite formed: If the Sm-Nd age of  $4.52 \pm 0.09$ b.y. obtained for the meteorite is accepted as the true age, a clear evidence of early igneous formation and/or impact metamorphism on the parent body of the meteorite.

The Ce irregularities and some minor disturbances of the Sm-Nd system found for the constituent minerals of the meteorite are not fully understood in the present work. However, the large Ce anomalies found for the Antarctic "finds' seem to be best understood by assuming that this unusual feature is a result of weathering effects. On the other hand, the same effects appear to be minor on the Sm-Nd system for the same meteorite. Nevertheless, we must be cautious in evaluating the Sm-Nd ages of the Antarctic meteorites.

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