NEUTRON ACTIVATION ANALYSIS OF RARE EARTH ELEMENTS IN METEORITE SAMPLES INCLUDING ANTARCTIC METEORITES

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Abstract: Ten rare earth elements (REE) (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu) were determined by neutron activation analysis for 7 Antarctic meteorites (Yamato-74001, -74082, -74094, -74155, -74191, -74371 and Allan Hills-78084) and for three non-Antarctic enstatite chondrites (Abee, Indarch and Qingzhen). The Antarctic meteorites studied in this work show similar REE abundance patterns to those in C1 chondrite. Their absolute REE abundances are about 1.2 to 2.1 times higher than the C1's, but no systematic variations were confirmed in the REE abundances of bulk chondrites with petrologic types 3 to 6. Smooth patterns and uniform abundances of the C1-normalized REE's suggest that most of these Antarctic meteorites are free from alteration due to terrestrial weathering as for bulk abundances of the REE's.

1. Introduction

The rare earth elements (REE) have been recognized as the most informative trace elements in geochemical and cosmochemical samples. After the pioneering work by SCHMITT *et al.* (1963), neutron activation analysis (NAA) has been extensively applied for determination of the trace amounts of REE's. Though precision of this method is thought to be relatively poor compared with mass spectrometric isotope dilution (MSID), NAA has an advantage that mono-isotopic elements whose determination is not feasible by MSID can be determined.

The Antarctic meteorites made it possible to study a wide variety of specimens for their chemistry and petrology. As for ordinary chondrites, the least altered meteorites classified as type 3 are not so scarce in the Antarctic meteorite collections and are much more accesible than before. Being different from the case of the falls, however, effects of terrestrial weathering and alteration should always be taken into consideration in evaluating the analytical results of the Antarctic meteorites.

In this work, ten REE's (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu) were determined by NAA for 7 Antarctic meteorites along with three non-Antarctic enstatite chondrites. Radiochemical separation of REE's was applied after irradiation. In addition to a conventional coaxial-type pure Ge detector, a planar-type pure Ge detector was used for gamma-ray spectrometry to achieve a high resolution for the peaks of radionuclides emitting low energy gamma-rays. Based on these data, the following problems are discussed: (i) whether systematic variations in REE abundances are present among bulk meteorite samples with petrologic types ranging from 3 to 6, and (ii) whether any weathering effect is detectable in REE compositions.

2. Experimental

Meteorite specimens, which were originally received in chips, were carefully ground in a clean agate mortar. A portion (about 50 mg) of each powdered sample was weighed and wrapped with clean aluminum foil. All samples were stacked and sealed in a silica tube. The samples were activated in the JRR-4 reactor of the Japan Atomic Energy Research Institute (JAERI) for 6 h in a thermal neutron flux of 5.5×10^{13} n cm^{-2} s^{-1}. After an appropriate cooling interval, the samples were subjected to group separation of gross REE's as a group. The meteorites were first fused with alkali fluxes of sodium peroxide and sodium hydroxide in Zr crucibles, in which the known amounts of REE carriers had been taken and dried up. Fused cakes were dissolved in H_2O. Hydroxide precipitates were separated from the supernatant, dissolved in HBr and loaded on anion exchange columns to separate the REE's from ^{46}Sc (EBIHARA, 1984). The gross REE's were then purified through a cycle of fluoride-hydroxide precipitation, and finally precipitated in an oxalate form for gamma-ray spectrometry.

Standard samples were prepared by drying a proper amount of REE mixture solution on the Al foil under a heat lamp, and were activated together with the meteorite samples. After activation the Al foil was opened carefully, placed in a beaker containing 5–10 ml of 1 M HNO_3 and REE carriers, and heated gently on a hot plate for a few minutes. After washed with H_2O, the Al foil was checked by means of gamma-spectrometry. More than 99% of the REE activities were confirmed to have been transferred into solution. The REE's were once precipitated in a fluoride form and finally prepared in an oxalate form just the same as the case for the samples.

Normally each sample was counted three times repeatedly. Both coaxial-type pure Ge and planar-type pure Ge detectors were used. Low energy photon spectrometry (LEPS) using the latter detector was proved to be highly effective for NAA of the REE's, especially of Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu. After completion of all the measurements both meteorite samples and standards were reactivated to obtain chemical yields of the REE's. Chemical yields were found to change monotonically among the REE's, those of light and heavy REE's being low with the maximum at middle REE's, ranging from 0.48 to 0.65 (0.56) for La, 0.63 to 0.82 (0.72) for Sm, and 0.56 to 0.76 (0.66) for Lu (values in parentheses are mean values). The detailed procedures will be reported elsewhere (EBIHARA in preparation).

3. Samples

The samples analyzed in this work are listed in Table 1. For the Antarctic meteorites the weathering grade listed in the meteorite catalogs supplied by the National Institute of Polar Research as well as the petrological and chemical classifications according to VAN SCHMUS and WOOD (1967) are quoted in this table.

4. Results and Discussion

Analytical results of the REE's are summarized in Table 2. Their relative abundances are shown in Figs. 1 and 2 for the Antarctic meteorites and the enstatite chon-

Table 1. Description of samples used in this work.

Meteorites	Type	Class	Weath.*	Weight** (mg)	Remarks
Antarctic					
Y-74191,107	L	3	A	49.2	
ALH-78084,91	H	3		47.6	
Y-74082,83	H	4	A	53.8	
Y-74155,100	H	4	B	56.4	
Y-74001,99	H	5	C	49.9	
Y-74371,93	H	5	A	48.5	
Y-74094,95	H	6	C	51.9	
Non-Antarctic, enstatite					
Qingzhen	E	3–4		12.0	Fell 1976, China
Abee	E	4		12.5	Fell 1952, Canada
Indarch	E	4		13.2	Fell 1891, USSR

*Degree of weathering.
**Sample size used for analysis.

Table 2. Rare earth elements in Antarctic and enstatite meteorites (in ppm).

Meteorites	La	Ce	Nd	Sm	Eu	Gd	Tb	Tm	Yb	Lu
Antarctic										
Y-74191	0.436	1.12	0.809	0.272	0.110	0.401	0.0667	0.0470	0.285	0.0473
ALH-78084	0.371	0.958	0.648	0.217	0.0774	0.327	0.0538	0.0386	0.232	0.0382
Y-74082	0.401	1.08	0.758	0.251	0.0918	0.405	0.0587	0.0427	0.264	0.0429
Y-74155	0.419	1.10	0.758	0.238	0.0902	0.330	0.0577	0.0450	0.260	0.0420
Y-74001	0.347	1.16	0.608	0.204	0.0880	0.308	0.0505	0.0350	0.232	0.0379
Y-74371	0.295	0.746	0.554	0.180	0.0837	0.242	0.0428	0.0352	0.205	0.0336
Y-74094	0.506	1.25	0.877	0.273	0.0989	0.406	0.0639	0.0442	0.275	0.0439
Enstatite										
Qingzhen	0.273	0.740	0.578	0.186	0.0634	0.239	0.0371	0.0310	0.194	0.0309
Abee	0.285	0.863	0.588	0.206	0.0675	0.247	0.0460	0.0313	0.209	0.0328
Indarch	0.198	0.503	0.403	0.138	0.0458	0.188	0.0264	0.0231	0.145	0.0230

drites, respectively. Cl chondritic abundances proposed by ANDERS and EBIHARA (1982) were taken for normalizing values. Analytical precisions (1σ) due to mainly counting statistics are estimated at 20 and 10% for Gd and Tm, respectively, 8% for Nd and Ce, and less than 5% for the rest of the REE's (EBIHARA in preparation). Analytical results for enstatite meteorites are slightly less precise than these estimates because of experimental problems. Gd values are above the smooth lines of REE abundance patterns for some cases.

4.1. General features in REE patterns

Antarctic meteorites: As observed in Fig. 1, the Antarctic meteorites studied in this work show similar REE abundance patterns to those of Cl chondrites, and their absolute abundances of the REE's are about 1.2 to 2.1 times larger than the Cl's. Small Eu anomalies could be confirmed in Y-74001 and -74371. Their Eu abundances are 25 and 16% higher than the interpolated values. These values are slightly higher than

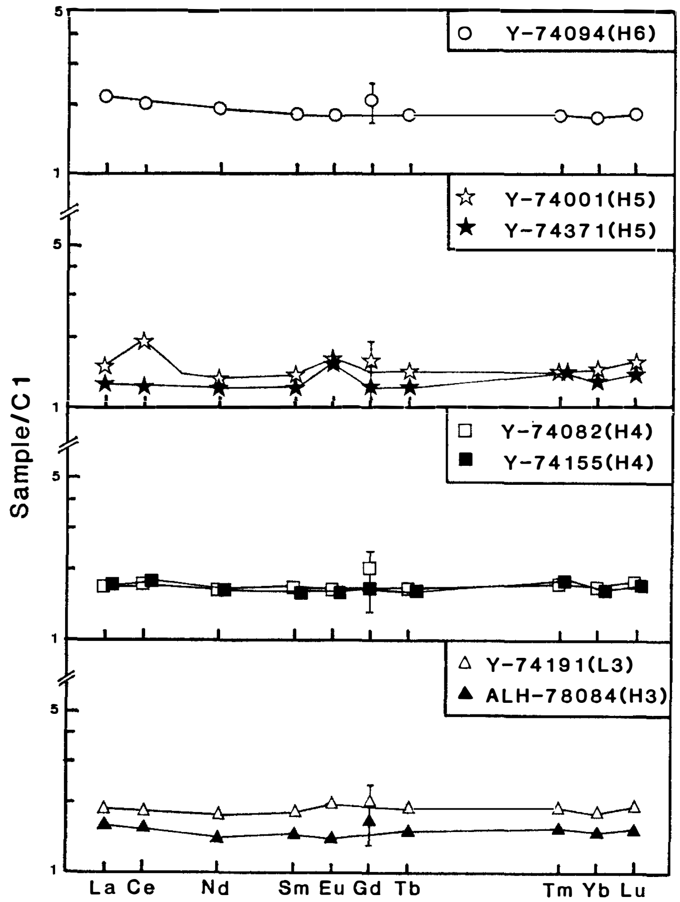

Fig. 1. C1 chondrite-normalized REE abundance patterns for 7 Antarctic meteorites. Antarctic meteorites analyzed in this work show the similar REE abundance patterns to those in C1. Small Eu anomalies could be observed in Y-74001 and -74371. Y-74371 possesses a possible Ce anomaly, which may have been caused by terrestrial weathering. No systematic variations were confirmed in the REE abundances of bulk chondrites with petrologic types ranging from 3 to 6.

the estimated error based on analytical errors of Eu and neighboring elements. No difference was confirmed in the REE patterns of Y-74082 and -74155.

Rare earths abundances in two meteorites (Y-7411 5 and -74371) can be compared with those determined by MSID (Nakamura, private communication, 1984), although locations of the specimens analyzed are different from each other. An Eu anomaly which was detected in Y-74371,93 by NAA was not confirmed in Y-74371,91, which was analyzed by MSID. For Y-74115, the NAA values are about 30% higher than the MSID ones, but their relative abundance patterns are essentially identical, suggesting that the host phase(s) of the REE's disperse heterogeneously in the spacimens to the extent of sample scales of 10–50 mg.

Enstatite meteorites: Although being quite similar to those in the Antarctic meteorites and C1 chondrites, the relative REE abundances in the enstatite chondrites studied in this work are somewhat fractionated (Fig. 2) and their absolute abundances vary from meteorite to meteorite. Indarch gives the lowest REE concentrations, whereas Abee

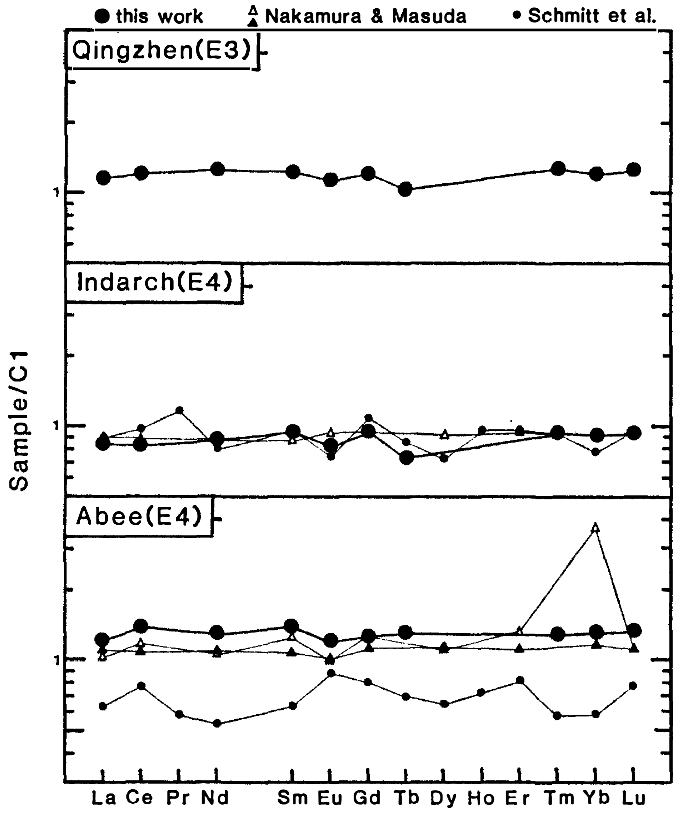

Fig. 2. C1 chondrite-normalized REE abundance patterns for 3 non-Antarctic enstatite chondrites. Indarch is depleted in REE by a factor of 1.5 compared with the others. The REE data for Indarch and Abee by SCHMITT *et al. (1963) and* NAKAMURA *and* MASUDA *(1973) also are shown for comparison. For Abee the zigzag patterns pointed out by* NAKAMURA *and* MASUDA *(1973) were observed, whereas no Yb anomaly was confirmed in the specimen studied in this work.*

shows the highest.

Abee and Indarch were analyzed for their bulk REE contents by SCHMITT *et al.* (1963) and NAKAMURA and MASUDA (1973). Their analytical results also are shown in Fig. 2 for comparison. By means of mass spectrometric isotope dilution technique, the latter authors determined the REE abundances in two different specimens, fragments 1 and 2, for Abee, and found a large Yb anomaly (positive) in fragment 1. Zigzag features also were pointed out for this fragment. Apparently such a zigzag pattern can be also confirmed in the REE abundance pattern of the sample studied in this work, although no anomaly is present for Yb. For Indarch the REE abundances obtained in this work are essentially identical with those by NAKAMURA and MASUDA (1973), having been depleted by a factor of 0.89 (mean) compared with those in C1 chondrite.

It is well known that the REE's in ordinary chondrites are highly concentrated in Ca-phosphates, apatite and merrillite (MASON and GRAHAM, 1970; ALLEN and MASON, 1973; CURTIS and SCHMITT, 1979; EBIHARA and HONDA, 1983a, 1984). EBIHARA and HONDA (1984) found that more than 80% of the total La and Sm reside in Ca-phosphates for Kesen (H4), Richardton (H5), Bruderheim (L6) and St. Séverin (LL6). The host phase(s) of the REE's in the enstatite chondrites, however, have remained unknown and are in dispute. SEARS *et al.* (1983) speculated the host phase of REE's in Abee to be Ca-sulfide, oldhamite, which was questioned by EBIHARA and HONDA (1983b). As mentioned earlier, Indarch is depleted in REE by a factor of 1.5 compared with Abee and Qingzhen. Calcium abundance in the Indarch specimen studied in this work is 0.137% (EBIHARA, unpublished work), which is depleted as low as a factor of 6.9 compared with the rest of the three. Although the material balances of Ca and REE's in various phases need to be known for more precise discussion, the present data suggest that Ca-sulfide is not the only host phase for REE's in the enstatite chondrites.

4.2. *Systematic variations in REE patterns*

GOODING *et al.* (1983) found that the REE's are more concentrated in chondrules of type 3 ordinary chondrites than in those of ordinary chondrites with higher petrologic types. There seem to be no systematic differences in distribution of the REE's among ordinary chondrites with petrologic types of 4 to 6 (EBIHARA and HONDA, 1984), suggesting that the REE's are largely redistributed during a metamorphic sequence from types 3 to 4. No systematic variations were confirmed in the REE abundances of bulk chondrites with petrologic types ranging from 3 to 6.

Only the Y-74094 (H6) chondrite shows a slightly fractionated REE pattern, with the light REE's being enriched compared with the heavy ones. Cl chondrite-normalized La/Lu ratio is 1.19 for this meteorite, whereas the rest of the meteorites take essentially the same ratio as Cl's.

4.3. *Weathering effects on REE composition*

As shown in Table 1, meteorites studied in this work suffered a wide variety of terrestrial weathering. Cerium may be one of the most mobile REE's under the presence of liquid water (NAGASAWA *et al.*, 1979; SHIMIZU and MASUDA, 1982). Although Ce has a large statistic error, no apparent anomaly was confirmed among the Antarctic meteorites analyzed. The only possible exception is Y-74001, which shows a slightly high Ce abundance. Considering that this meteorite is listed in degree C of weathering, this Ce anomaly may suggest the alteration effect. Smooth patterns and uniform abundances of the Cl-normalized REE suggest that the other Antarctic meteorites analyzed in this work are almost free from alteration due to terrestrial weathering as for bulk abundances of the REE's.

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