



Comparison of PGAA and wet chemical analysis for determining major element contents in eucritic meteorites

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Abstract

Prompt gamma-ray activation analysis (PGAA) was applied to well homogenized meteorite samples initially prepared for the wet chemical analysis. By comparing the PGAA data with wet chemical analysis data in literatures, it was confirmed that PGAA can be alternative or even advantageous to wet chemical analysis in terms of the data reliability. Because the same sample can be analyzed by INAA followed by PGAA, data obtained by a combination of PGAA and INAA were proved to enable us to discuss the detailed chemical characteristics of meteorite samples represented by eucritic meteorites (eucrites).

Keywords Prompt gamma-ray activation analysis (PGAA) · Instrumental neutron activation analysis (INAA) · Wet chemical analysis · Eucrites · Meteorites

Introduction

In 1969, nine meteorites were accidentally found on Antarctica by the Japanese Antarctic expedition team. Since then, about 50,000 meteorites have been collected from Antarctica so far. Meteorites are precious materials from which the formation and early differentiation of our solar system can be elucidated. Antarctic meteorites cannot be personal properties, but are shared by the public. When those samples are needed for scientific purposes, users are to submit sample requests to appropriate agencies such as the National Institute of Polar Research (NIPR), Tokyo, Japan. For such processing, the agencies are required to supply sufficient information regarding meteoritic materials. As for such information, classification is the most fundamental and important. Meteorites are classified based on several characteristics such as petrological and mineralogical features,

elemental compositions and isotopic abundances. Among them, major element compositions can be key information.

In order to determine major element contents, so-called wet chemical analysis has been extensively used for many years [1, 2]. A major advantage of this method is being capable of determining almost all major elements. In addition, for iron, individual values of different chemical states (Fe^{0+} , Fe^{2+} and Fe^{3+}) can be separately determined. For H_2O , H_2O (+) (constitution water) and H_2O (–) (absorbed water) can be also separately determined. Disadvantages of this method are that the samples need to be physically destroyed and that gram-sized mass of the individual samples are consumed. Considering that some meteorite specimens are in such sizes, the wet chemical analysis cannot be a practical choice for those samples. Non-destructive neutron activation analysis is exempted from those disadvantages and could be a substitute for wet chemical analysis. Particularly, prompt gamma-ray activation analysis (hereafter, PGAA) can be an alternative to wet chemical analysis of meteorite samples.

By PGAA, most major elements can be non-destructively determined for their elemental contents of meteorite samples either in powder or in chunk. These samples are normally less than a few hundred milligrams in mass, but larger samples can also be analyzed [3]. As the neutron flux for PGAA is much lower than that for conventional instrumental neutron activation analysis (INAA), the induced radioactivity even in large samples analyzed by PGAA is kept minimal and decreased down to the natural background level after a

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proper cooling. Thus, the samples once analyzed by PGAA can be reused for other analytical procedure. By utilizing this advantage of PGAA, an analytical scheme consisted of nuclear analytical methods of PGAA, INAA and instrumental photon activation analysis (IPAA) was proposed to determine as many elements as possible [4]. In the proposed analytical scheme, the sample is firstly analyzed by PGAA, which is followed by INAA and IPAA. This study was conducted, following a part of the proposed analytical scheme; the three eucrites were analyzed by PGAA followed by INAA. Significant merits of the combination of different analytical methods are that a larger number of elements can be determined for their contents in a limited amount of spacious samples and that these elemental abundance data can be obtained in excluding the sample heterogeneity by analyzing the same specimens by different analytical methods.

In this study, analytical capability of PGAA is evaluated by comparing the major element contents data with those obtained by wet chemical analysis. Considering a possible variation of analytical data due to compositional heterogeneity of the meteorite samples, aliquants of the powder samples used for wet chemical analysis were used so that the dispersion caused by the sampling bias can be minimized. Besides PGAA, INAA was also conducted by using the same powder samples as used for PGAA as well as wet chemical analysis and the data obtained by INAA were also compared with those by PGAA and wet chemical analysis.

Experimental

Samples

In this study, three eucritic meteorites (eucrites) recovered on Antarctica were analyzed; Y-792510 (monomict eucrite), Y-793547 (polymict eucrite) and Y-82082 (polymict eucrite). Because eucrites mostly consist of silicate with no metallic iron, they can be easily pulverized into fine and homogenized powder samples. Lump specimens of individual eucrites weighing several grams were carefully ground in clean agate mortars for wet chemical analysis at NIPR [5]. Portions of the powder samples thus prepared (102 mg for Y-792510, 120 mg for Y-793547 and 316 mg for Y-82082) were allocated to us for PGAA and INAA from NIPR.

PGAA

Each eucrite powder samples weighing 78 to 115 mg was heat-sealed into a thin fluorinated ethylene-propylene resin film bag and was irradiated for two hours with thermal neutrons (neutron flux: $2.4 \times 10^7 \text{ n cm}^{-2} \text{ s}^{-1}$) guided out of the JRR-3M research reactor of the Japan Atomic Energy Agency (JAEA). Elemental contents of the eucrite samples

were determined by a comparison method using JB-1 (a geological standard rock sample issued by the Geological Survey of Japan) for Al, Si, Ca, Ti, Mn, Fe, Sm and Gd. Literature values for JB-1 were taken from Imai et al. [6]. In addition to JB-1, chemical reagent samples of Na_2SO_4 , MgO and NH_4Cl , and metal powder of Cr were used for the determination of Na, S, Mg and Cl, and Cr, respectively. A reference sample for B was prepared by dropping a proper amount of concentration-known B solution onto filter paper. The analytical procedure of PGAA is essentially the same as that described by Oura et al. [7]. Gamma-ray energies used are shown in Table 1.

INAA

In INAA, samples were irradiated two times with different irradiation periods in consideration of half-lives of the nuclides used for elemental quantification. For the determination of Mg, Al, Ca, Ti, V and Mn, samples weighing about 45 to 65 mg were irradiated for 10 s at a thermal neutron flux of $1.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in the JRR-3 reactor of JAEA and were immediately measured for their emitting gamma rays. The same samples were reirradiated for 20 min at a neutron flux $4.3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in the JRR-4 reactor of JAEA. After the irradiation, the samples were measured for gamma rays several times with different cooling intervals at the RI Research Center of Tokyo Metropolitan University. The JB-1 powder sample was used as a reference material for determining elemental contents for Na, K, Sc, Cr, Fe, Co, Ga, La, Ce, Sm, Eu, Yb, Lu, Hf, Ta and Th. As a reference value of Cr for JB-1, a literature value from Kong and Ebihara [8] was used, whereas literature values of Imai et al. [6] were used for the remaining elements. Gamma-ray energies used in INAA are shown in Table 1. The analytical procedure of INAA is the same as that described by Shirai and Ebihara [9].

Results and discussion

Comparisons of analytical data for major elements in eucrites between NAA (PGAA and INAA) and wet chemical analysis

PGAA versus wet chemical analysis

Our analytical data of PGAA for the three eucritic meteorites are summarized in Table 1, where wet chemical analysis data [5] are also shown for comparison. In this study, a total of fourteen elements (B, Na, Mg, Al, Si, S, Cl, Ca, Ti, Cr, Mn, Fe, Sm and Gd) were determined for their contents by PGAA. Potassium, Co and Ni could not be detected due to their lower contents. These three elements were quantified

Table 1 Elemental mass fraction in the three euries (Y-792510, Y-793547 and Y-82082)

Elements	Unit	Y-792510			Y-793547			Y-82082		
		Gamma-ray energy (keV)	INAA	PGA ^a	Wet chemistry ^b	PGA ^a	INAA ^a	Wet chemistry ^b	PGA ^a	INAA ^a
B	ppm	477.595		30.3±0.5		12.5±0.3		46.2±0.7		
Na	%	869.210	1368.60	0.427±0.058	0.377±0.002	0.385±0.055	0.383±0.002	0.418±0.069	0.349±0.002	0.33
Mg	%	2828.172	1014.43	3.09±0.81	3.82±0.25	4.42±0.79	5.03±0.28	3.84±0.98	4.56±0.32	4.32
Al	%	1778.92	1778.92	6.60±0.27	5.88±0.07	5.90±0.24	5.29±0.06	6.56±0.32	6.26±0.07	6.192
Si	%	3538.966		23.1±0.7		22.7±0.7		23.0±0.8		22.41
S	%	840.993		0.311±0.067				0.250±0.054		0.21
Cl	ppm	1164.8650						127±27		
K	%	770.3050	1524.58		0.0468±0.0038		0.0657±0.0045		0.0405±0.0031	0.03
Ca	%	1942.67	3084.54	6.81±0.21	7.38±0.50	6.63±0.20	7.04±0.45	6.55±0.24	7.52±0.49	6.95
Sc	ppm		889.25		32.2±0.1		30.9±0.1		32.8±0.1	
Ti	%	1381.745	320.08	0.437±0.013	0.498±0.050	0.529±0.014	0.520±0.043	0.433±0.016	0.444±0.046	0.25
V	ppm		1434.08		78.9±4.5		75.8±5.2		84.8±5.0	
Cr	%	749.09	320.08	0.297±0.055	0.230±0.001	0.274±0.050	0.312±0.001	0.305±0.059	0.246±0.001	0.075
Mn	%	212.039	1810.77	0.465±0.044	0.413±0.007	0.408±0.038	0.381±0.006	0.466±0.046	0.433±0.007	0.23
Fe	%	1725.288	1099.25	15.7±0.6	16.6±0.1	14.4±0.6	15.3±0.1	16.5±0.7	16.2±0.1	15.92
Co	ppm	277.161	1332.50		5.11±0.10		10.3±0.1		7.45±0.09	
Ga	ppm		630.01		2.18±0.18		2.70±0.23		2.63±0.22	
La	ppm		1596.54		2.36±0.06		5.27±0.07		1.42±0.04	
Ce	ppm		145.44		7.77±0.26		12.9±0.3		8.59±0.21	
Sm	ppm	333.97	103.18	1.55±0.14	1.17±0.03	3.04±0.15	2.99±0.08	1.07±0.17	1.03±0.03	
Eu	ppm		1408.00		0.634±0.024		0.700±0.023		0.656±0.022	
Gd	ppm	181.931		1.77±0.10		3.93±0.12		1.42±0.10		
Yb	ppm		197.96		1.77±0.10		2.74±0.13		1.68±0.09	
Lu	ppm		208.36		0.244±0.009		0.356±0.013		0.233±0.009	
Hf	ppm		482.00		1.07±0.07		2.04±0.06		1.62±0.05	
Ta	ppm		1221.41		0.256±0.046		0.395±0.050		0.413±0.041	
Th	ppm		312.01		0.318±0.030		0.532±0.024		0.373±0.024	

^aMeasurement precision for individual values are due to counting statistics (1 s) in gamma-ray counting^bYanai and Kojima [5]

by PGAA for chondritic meteorite samples [3]. As for Na, although its 472.202 keV peak may be overlapped with a 477.598 keV peak of B for rock samples in gamma-ray spectrometry [10], the contribution from B could be spectrometrically decoupled when the degree of overlapping is not too large. For the three eucrites analyzed in this study, however, Na peaks were completely covered with B peaks because of low Na and high B contents. Karouji and Ebihara [11] examined the reliability of Na contents in geological and cosmochemical rock samples determined by using eight prompt gamma ray peaks in PGAA and found that the 869.210 keV was appropriate for terrestrial samples with no spectral interference. As the three eucritic meteorites analyzed in this study have similar chemical compositions to those of terrestrial geological samples such as basalt and high B contents compared with Na contents, 869.210 keV peak was used for the determination of Na contents.

Among the 14 elements determined by PGAA in this study, ten elements (Na, Mg, Al, Si, S, Ca, Ti, Cr, Mn and Fe) can be compared for their contents with those by wet chemical analysis [5]. The agreement between our PGAA data and wet chemical analysis data are evaluated by using zeta-scores. A zeta-score is calculated using the following formula [12],

$$\text{zeta-score} = \frac{x - c}{\sqrt{u_x^2 + u_c^2}} \quad (1)$$

where x and c are the our PGAA data and wet chemical analysis data, respectively and u_x and u_c are standard uncertainties (1 s) in PGAA (due to counting statistics) and in wet chemical analysis, respectively. For wet chemical analysis, a standard deviation (σ_R) was used in place of u_c to estimate a minimum value of the zeta-score. σ_R values are estimated by the following modified Horwitz function [13],

$$\sigma_R = 0.22^c \quad (2)$$

where c is concentration obtained from the wet chemical analysis. Zeta-scores of the PGAA data are summarized in Table 2 and shown in Fig. 1. As seen in Fig. 1, zeta-scores for most elements fall in the range from 2 to -2 , indicating that our PGAA data are mostly consistent with wet chemical analysis data. Exceptions are for Ti (3.2), Cr (3.7) and Mn (3.4) in Y-82082, implying that these three elements could not be reliability determined for Y-82082 by either our PGAA procedure or wet chemical analysis. This issue will be further discussed later.

It is worthy to notice that our S values obtained by PGAA are in excellent agreement with wet chemical data as shown in Fig. 1. Although analytical procedures such as ion chromatography, thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry (ICP-MS)

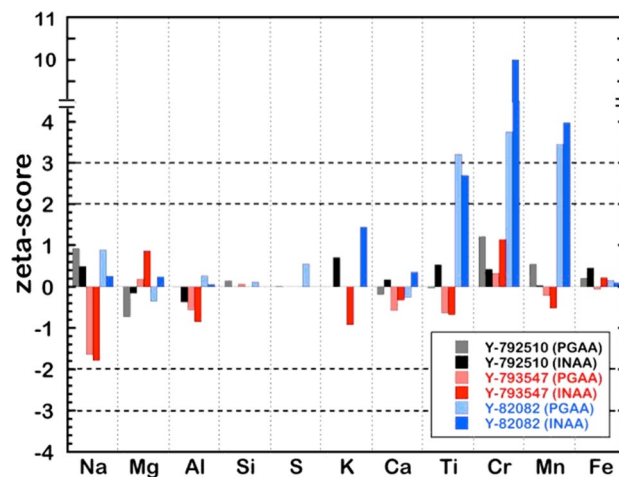


Fig. 1 Zeta-scores for PGAA and INAA data of the three eucritic meteorites (Y-792510, Y-793547 and Y-82082) with respect to wet chemistry values [5]

Table 2 Zeta-scores for PGAA and INAA data of the three eucrites (Y-792510, Y-793547 and Y-82082) obtained in this study with respect to wet chemistry values

Elements	Y-792510		Y-793547		Y-82082	
	PGAA	INAA	PGAA	INAA	PGAA	INAA
Na	0.92	0.49	-1.6	-1.8	0.88	0.26
Mg	-0.73	-0.15	0.18	0.86	-0.35	0.24
Al	-0.0012	-0.37	-0.56	-0.85	0.26	0.052
Si	0.14		0.070		0.11	
S	0.0078				0.55	
K		0.71		-0.92		1.4
Ca	-0.18	0.17	-0.57	-0.32	-0.26	0.36
Ti	-0.031	0.53	-0.64	-0.68	3.2	2.7
Cr	1.2	0.42	0.32	1.1	3.7	10
Mn	0.54	0.028	-0.21	-0.52	3.4	4.0
Fe	0.21	0.46	-0.06	0.22	0.15	0.093

were developed for the determination of S in solid samples [14–16], these analytical procedures seem to be less practical for routine analysis of S in such samples, considering that fairly large amounts of samples are needed and that rather complicated chemical separation procedures are required. Besides, these analytical procedures are specialized in the determination of S. In contrast, PGAA can non-destructively determine S together with other major elements.

INAA versus wet chemical analysis

INAA data of this work also are given in Table 1. Twenty-two elements (Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ga, La, Ce, Sm, Eu, Yb, Lu, Hf, Ta and Th) were determined for their contents. Among them, eight elements (Na, Mg, Al, Ca, Ti, Cr, Mn, Fe and Sm) were determined by both INAA and PGAA. Consistency between our PGAA and INAA data were statistically evaluated by using zeta-scores. Zeta-score values of PGAA data are calculated by using Eq. (1) and summarized in Table 3. As shown in Table 3, zeta-score of PGAA data except for Al in Y-792510 and Y-793547, and Sm in Y-792510 fall within an acceptable range of ± 2 , indicating that our PGAA data are in good agreement with

our INAA data. Zeta-scores of our values for INAA data against wet chemical values [5] were also calculated by using Eq. (1) and shown in Table 2 and Fig. 1. Among the eleven elements shown in Fig. 1, Na, Mg, Al, K, Ca, Ti, Cr, Mn and Fe were determined by INAA. Zeta-scores of our INAA data are within -2.0 and 2.0 except for Ti (2.7), Cr (10) and Mn (4.0) in Y-82082. Disagreements with wet chemical data for these three elements in Y-82082 are also confirmed as already pointed. Considering that our PGAA and INAA data of Ti, Cr and Mn contents in Y-82082 are consistent with each other (Table 3), it is likely that the Ti, Cr and Mn values for Y-82082 obtained by wet chemical analysis are incorrect. Because the sample heterogeneity cannot be invoked for their inconsistency, there must have been involved an analytical defect in wet chemical procedure. From these comparisons, it is reasonably concluded that our PGAA procedure is able to provide major element abundances in cosmochemical samples with an accuracy equivalent to or even better than those for wet chemical data.

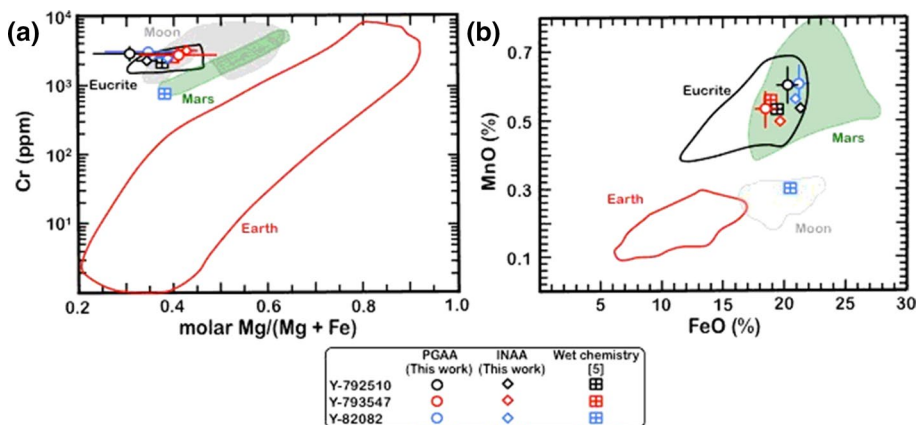
Chemical classifications of the three eucrites

Each differentiated planetary body, such as Earth, Moon and Mars, have undergone distinct differentiation processes, and thus have different chemical compositions from each other. For example, an FeO/MnO ratio has been used for identification of the origin and classification of planetary materials [17]. Similarly, a Cr/mg number (= molar Mg/(Fe + Mg) ratio) ratio has also been used for the classification of terrestrial and extraterrestrial materials [e.g., 18]. Figure 2a, b show correlations of Cr contents versus mg numbers and FeO contents versus MnO contents, respectively, obtained by PGAA (this work), INAA (this work) and wet chemical analysis [5] for the three eucritic meteorites. Obviously, our PGAA and INAA data for the three eucritic meteorites are plotted in the area of eucrites, confirming their classifications as eucrites. These observations are consistent with mineralogical and petrological features [5]. In contrast, Cr/

Table 3 Zeta-scores for PGAA data of the three eucrites (Y-792510, Y-793547 and Y-82082) with respect to INAA data

Elements	Y-792510	Y-793547	Y-82082
Na	0.86	0.046	1.0
Mg	-0.86	-0.72	-0.70
Al	2.6	2.5	0.92
Ca	-1.0	-0.83	-1.8
Ti	-1.2	0.20	-0.21
Cr	1.2	-0.78	1.0
Mn	1.2	0.71	0.71
Fe	-1.3	-1.5	0.29
Sm	2.6	0.32	0.18

Fig. 2 Correlation of molar Mg/(Mg + Fe) ratios versus Cr contents (a) and FeO contents versus MnO contents (b) for four differentiated planetary materials (Earth, Moon, Mars and eucrite)



mg number and FeO/MnO ratios for Y-82082 obtained by wet chemical analysis [5] are plotted in the area for Mars and Moon, respectively, apparently being inconsistent with mineralogical and petrological observations [5]. Such an inconsistency must be caused by incorrect data obtained by wet chemical analysis of Y-82082. From a viewpoint for classification of Y-82082, it is again confirmed that our PGAA and INAA data of this meteorite are more reliable than its wet chemical analysis data [5].

Analytical merit of PGAA in quantification of B and Cl in meteoritic samples

Besides the nine elements (Mg, Al, Si, S, Ca, Ti, Cr, Mn and Fe) shown in Fig. 1, B, Cl, Sm and Gd also could be determined for their contents in the three eucrite samples by PGAA. Among these four elements, B and Cl have been hardly determined for cosmochemical and geological samples due to the analytical difficulty [e.g., 19, 20]. Even now, the situation does not seem to be improved for B. In fact, it is difficult to obtain reliable content data of B in rock samples by analytical methods accompanying acid digestion such as ICP-MS, because B is prone to contamination from the laboratory environment and evaporation loss during analytical procedure [20]. Being a non-destructive method, PGAA is exempted from these analytical defects. Hence, with its high sensitivity [21], PGAA has been acknowledged to be the most reliable analytical method for determining B contents in solid samples [e.g., 22]. Boron contents determined for the three eucrites in this study range from 12.5 to 46.2 $\mu\text{g/g}$. These values are several times to an order of magnitude higher than those for non-Antarctica eucrites (0.965 to 3.39 $\mu\text{g/g}$) [23]. Previously, high B contents in Antarctic meteorites were also reported [24]. Considering that B is susceptible to terrestrial contamination, its high contents in Antarctic meteorites cannot be indigenous to the meteorites.

Like B, Cl can be reliably determined its contents in solid samples by PGAA. Chlorine has relatively high analytical sensitivity in PGAA and can be non-destructively determined when the content is in a few hundreds $\mu\text{g/g}$ [3]. The detection limit of Cl can be lowered by PGAA using multiple Ge detectors (multiple γ -ray analysis; MPGAA) [25]. Chlorine has been determined by neutron activation analysis involving separation procedure of Cl either by pyrohydrolysis extraction [e.g., 26, 27] or by alkaline fusion–precipitation, which is a conventional procedure in radiochemical NAA (RNAA) of three halogens (Cl, Br, I) [e.g., 28, 29]. Comparing analytical data obtained by these neutron activation methods, it was found that Cl data for the Allende meteorite determined by PGAA (including MPGAA) and by RNAA are consistent, while the data by NAA with pyrohydrolysis are systematically lower than PGAA and RNAA values, suggesting that Cl

cannot be quantitatively extracted by pyrohydrolysis [19, 26, 27, 29]. In this study, a Cl content was determined only for one sample ($127 \pm 27 \mu\text{g/g}$ for Y-82082). This value is considerably higher than those for non-Antarctica eucrites (12 to 34.5 $\mu\text{g/g}$) [23]. Like B, Cl and I were observed to be overabundant in some Antarctic meteorites [30], highly probably caused by terrestrial contamination on Antarctica. Among the three eucrites analyzed in this study, Y-82082 has the highest B content and a Cl content was determined solely for Y-82082, implying that Y-82082 suffered from terrestrial contamination on Antarctica to the highest extent.

Significance of PGAA for elemental characterization of geo- and cosmochemical samples

Among the 27 elements determined by PGAA and INAA, seven rare earth elements (REEs) could be quantified (Table 1). It is well acknowledged that REEs are particularly informative in discussing geochemical and cosmochemical processes [e.g., 31], where REE contents are expressed in relative abundances normalized to their solar system abundances represented by those in CI chondrite [e.g., 32]. Because ionic radii of the trivalent REEs (REE^{3+}) smoothly decrease with the increase of the atomic number, CI chondrite-normalized REE abundances in geochemical and cosmochemical samples change smoothly except for Ce and Eu, which could be partly present as Ce^{4+} and Eu^{2+} , respectively, depending upon the redox condition in the environment where those samples are evolved. Irregularities from the smooth change in CI chondrite-normalized REE abundances appearing at Ce and Eu (called Ce and Eu anomalies) can be numerically expressed as follows;

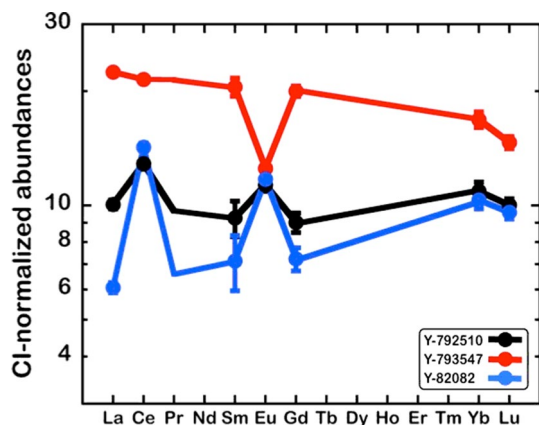
$$\text{Ce}/\text{Ce}_* = \text{Ce}_N / 10^{[(\log \text{La} + \log \text{Pr})/2]}, \quad (3)$$

$$\text{Eu}/\text{Eu}_* = \text{Eu}_N / 10^{[(\log \text{Sm} + \log \text{Gd})/2]}, \quad (4)$$

where the left side denotes the degree of anomaly, the symbol of an element of the right side represents a content of the corresponding element (e.g., in ppm) and an element content with a subscript N indicates a determined value of a given element by NAA. Denominators of the right side correspond to interpolated values for Ce and Eu calculated from observed values of neighboring elements, La and Pr, and Sm and Gd, respectively. For the Ce anomaly (Ce/Ce_*) calculation, a Pr value is to be used as a neighboring element together with that of La. In INAA, however, Pr is hard to be quantified. Therefore, a Sm value can be used as a proxy of that of Pr. In this case, the above, first equation can be rewritten as follows;

Table 4 Ce/Ce* and Eu/Eu* ratios for the three eucrites (Y-792510, Y-793547 and Y-82082)

	Ce/Ce*	Eu/Eu*
Y-792510	1.31 ± 0.11	1.24 ± 0.18
Y-793547	0.979 ± 0.044	0.618 ± 0.048
Y-82082	2.253 ± 0.299	1.63 ± 0.33

**Fig. 3** REEs contents of the three eucrites obtained in this study. Data are normalized to CI chondrite contents [32]

$$Ce/Ce_* = Ce_N / 10^{[(4 \log La + \log Sm)/5]} \quad (5)$$

For the Eu anomaly (Eu/Eu*), both neighboring elements (Sm and Gd) can be determined for their contents by PGAA. Considering a low sensitivity of Gd in INAA, PGAA contributes greatly in this matter. Anomalies of Ce (Ce/Ce*) and Eu (Eu/Eu*) for the three eucrites calculated by the above equations are given in Table 4. Anomalies of Ce and Eu could be determined within 13% and 20% uncertainties (propagated values; 1 s), respectively.

CI-normalized REE abundances in the three eucrite samples are shown in Fig. 3, where mean values calculated from PGAA and INAA data are plotted for Sm. As shown in Fig. 3, both Y-792510 and Y-82082 have positive Ce and Eu anomalies, whereas Y-793547 has a negative Eu anomaly with no anomaly of Ce. In eucrites, Eu is mostly partitioned into plagioclase, while light REEs and heavy REEs are distributed into Ca-phosphates and clinopyroxene, respectively [33]. Regardless of the anomaly, CI chondrite-normalized Eu abundances are similar for the three eucrites as shown in Fig. 3, which is consistent with their similar contents of Al. Relatively high contents of REEs in Y-793547 suggests that this eucrite has high modal abundance of Ca-phosphates. In contrast, Ca-phosphates must be depleted in Y-82082. Thus, it is likely that plagioclase is quite homogeneously present in the eucrite

parent material, whereas Ca-phosphates are heterogeneously present.

Some Antarctic eucrites have been reported to have Ce anomalies, which is contrast to non-Antarctic eucrites where no Ce anomalies are observed [34]. Ce anomalies in Antarctic eucrites are explained in terms of terrestrial weathering on Antarctica [34]. As mentioned above, light REEs are mostly allocated to Ca phosphates. On Antarctica, when Ca phosphates in eucrites may contact water, a part of REEs including Ce in Ca phosphates may be dissolved as REE³⁺, which are then precipitated as REE(OH)₃. Ce³⁺ is easily oxidized to Ce⁴⁺ in fluid and then precipitated as Ce(OH)₄. As a solubility of Ce(OH)₄ is much smaller than those of other REE(OH)₃, Ce(OH)₄ tends to stay at the original position in eucritic material, where other REE(OH)₃ can be gradually mobilized and eventually leached away, yielding positive Ce anomalies. As noticed in Fig. 3, the degree of Ce anomalies is inversely correlated with the light REE abundances. This relationship does not seem to be simply explained in terms of terrestrial contamination. The detailed discussion of this issue will be done elsewhere.

Comparison of NAA (PGAA and INAA) with other analytical methods

Compared with terrestrial rock samples, meteorite samples have severe limitations of the sample amount usable for chemical analysis. Thus, such analytical methods as those with high sensitivity, and non-destructivity are suitable when meteorite samples are quantitatively analyzed. For major element content determination, wet chemical analysis [1, 2], NAA (PGAA and INAA; this study), particle-induced X-ray emission (PIXE) [35], X-ray fluorescence spectrometry (XRF) [36], ICP atomic emission spectrometry (ICP-AES) [37] and ICP-MS [38] have been applied. The laser-induced breakdown spectrometry (LIBS) was recently developed for the determination of major elements in meteorites [e.g., 39]. LIBS as well as PIXE could offer a strong potential for analysis in situ without any sample preparation. However, these two analytical methods are unsuitable for obtaining the representative elemental abundances due to the extremely small area for the analysis. In addition, poor accuracy of LIBS data [39] is suggestive of its unsuitability for representative elemental analysis. XRF is commonly used for the determination of representative elemental abundances, especially for terrestrial rock samples. However, XRF is hardly applied to meteorite samples for such a purpose, because not a small amount of powdered sample is to be fused with alkaline flux, hence, the sample once used for XRF cannot be reused for other analytical methods. In recent years, ICP-AES and ICP-MS are widely used for the determination of representative elemental abundances of rock samples including meteorites. Both ICP-methods have high sensitivity for

many elements and allow the simultaneous determination of wide range of major, minor and trace elements. In ICP-AES and ICP-MS, samples need to be completely dissolved before introduction to the instrument. During preparation of the sample solution, loss of analytes and contamination from the laboratory environment could be involved, implying that high accuracy of ICP-AES and ICP-MS data is not always guaranteed. Thus, considering several competing analytical methods for elemental abundances in meteorite samples, it may be reasonably concluded that PGAA and INAA are the most suitable.

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