View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Kyoto University Research Information Repository

KURENAI
Kyoto University Research Information Repository

KYOTO UNIVERSITY

Title	Application of neutron activation analysis to micro gram scale of solid samples
Author(s)	Sekimoto, Shun; Shirai, Naoki; Ebihara, Mitsuru
Citation	Journal of Radioanalytical and Nuclear Chemistry (2016), 307(3): 1757-1764
Issue Date	2016-03
URL	http://hdl.handle.net/2433/217404
Right	© 2015 Akadémiai Kiadó, Budapest, Hungary; The final publication is available at Springer via http://dx.doi.org/10.1007/s10967-015-4370-4; The full-text file will be made open to the public on 1 March 2017 in accordance with publisher's 'Terms and Conditions for Self-Archiving'.; This is not the published version. Please cite only the published version. この論文は出版社版でありません。引用の際には出版社版をご確認ご利用ください。
Type	Journal Article
Textversion	author

Kyoto University

Journal of Radioanalytical and Nuclear Chemistry

Special Issue (SI): MARC X

LOG NUMBER OF PAPER: 374

TITLE OF PAPER: Application of neutron activation analysis to micro gram scale of solid samples

AUTHORS: Shun Sekimoto[a,*], Naoki Shirai[b] and Mitsuru Ebihara[b]

POSTAL ADDRESS OF EACH AUTHOR:

[a] *Research Reactor Institute, Kyoto University, 2-1010 Asashiro-nishi, Kumatori, Sen-nan, Osaka 590-0494, Japan*

[b] *Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*

*CORRESPONDING AUTHOR'S

E-MAIL ADRESS: sekimoto@rri.kyoto-u.ac.jp

TELEPHONE NUMBER: +81-72-451-2480

FAX NUMBER: +81-72-451-2622

Title page

Names of the authors: Shun Sekimoto, Naoki Shirai, Mitsuru Ebihara

Title: Application of neutron activation analysis to micro gram scale of solid samples

Affiliation(s) and address(es) of the author(s):

Shun Sekimoto

at Research Reactor Institute, Kyoto University, 2-1010 Asashiro-nishi, Kumatori, Sennan, Osaka 590-0494, Japan

Naoki Shirai and Mitsuru Ebihara

at Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

E-mail address of the corresponding author: sekimoto@rri.kyoto-u.ac.jp

Application of neutron activation analysis to micro gram scale of solid samples

Shun Sekimoto[1], Naoki Shirai[2], and Mitsuru Ebihara[2]

[1]*Research Reactor Institute, Kyoto University, 2-1010 Asashiro-nishi, Kumatori, Sen-nan, Osaka 590-0494, Japan*

[2]*Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*

Abstract

An instrumental neutron activation analysis (INAA) procedure for analyzing extremely small samples was developed and applied to two kinds of extraterrestrial samples. A few mg of the Allende meteorite as well as the JB-1 basalt can work well as a reference sample for a relative method. To evaluate the applicability of this INAA procedure, detection limits are presented and compared with the elemental contents in a potential sample to be analyzed. The possibility of reuse of neutron-irradiated samples for mass spectrometry was noted by indicating degree of increase in isotopic abundance for noble gas and long-lived radioactive nuclides.

Keywords

Neutron activation analysis, relative method, magnetic spherule, Kilabo chondrite

Introduction

Neutron activation analysis (NAA) has been used in various research fields, such as geo- and cosmochemistry, environmental science, biology, archeology, *etc*. Since instrumental

NAA (INAA) is a non-destructive and multi-elemental analysis method, it is suitable for precious samples and, especially, for such specimens as those highly desired to be neither physically decomposed nor chemically dissolved. Meteorites are the best example for such samples. Chondritic meteorites (chondrites) and iron meteorites contain relatively high contents of Co and Ir compared with those in the earth crust. As Co and Ir have high sensitivity in NAA, they can be good markers for the identification of such extraterrestrial materials [1, 2]. In NAA of chondrites, a few tens mg of specimen is commonly used. For such a case, a few hundred μg kg^{-1} of Ir and a few hundred mg kg^{-1} of Co can be reliably determined. When an extremely small size (e.g., micro gram) of samples such as micrometeorites recovered on the Earth surface and tiny particles returned from extraterrestrial asteroids are to be analyzed by INAA, the conventional INAA procedure used for a few tens mg [3] is not suitable. For such tiny samples, neutron irradiation with high neutron flux and long irradiation time (namely, high neutron dose) is required. For the irradiation with high neutron dose, polyethylene bags for holding samples are not usable because they are prone to radiation damage. Polyethylene bags are also not suitable for holding tiny grain samples. It is, therefore, very important to design an appropriate sample holder for irradiating small grain samples.

In this study, we aimed to develop the INAA procedure for analyzing a single grain of down to micro and sub-micro grams in mass. At first, we present the INAA procedure applicable to such samples. As we use a relative method for quantification, the preparation of reference samples and the evaluation for their suitability are of concern and, therefore, described in detail. Then, two typical examples for the application of the proposed procedure are shown with limited scientific discussion. From those experiments, the applicability of the procedure is described from several viewpoints including detection limits and the degree of increase in isotopic abundance induced by neutron irradiation.

Experimental

Sample preparation for test samples

Two different types of small samples (a meteoritic grain and a magnetic spherule) were targeted in this study. For the meteoritic grain sample, a chunk of the Kilabo (LL6) chondrite was crushed and a single piece was picked. A magnetic spherule (6.5 μg) was separated from the Pacific Ocean sea sediment by a hand magnet. A quartz disc (9 mm ϕ x 1 mm thickness) with a small pit (1 mm ϕ x 0.3 mm depth) was used for neutron irradiation of these small samples. Each sample was carefully placed into the pit. The manner in which the spherule sample is placed into the pit in the quartz disc is shown in Supplementary Information. Then, the disc was covered with a quartz disc (9 mm ϕ x 1 mm thickness) and the sample holder assembly was wrapped tightly with high-purity aluminum foil.

Sample preparation for reference samples

Two reference samples with different elemental compositions were used; the Allende meteorite powder (1.66 mg) prepared by the Smithsonian Institution (USMN 3529; split 22 and position 6) and the basaltic rock reference sample JB-1 prepared by Geological Survey of Japan (1.12 mg). Each sample was sealed into a synthesized quartz tube (1 mm inner ϕ and 2.7 mm outer ϕ x 35 mm length), which was then wrapped with Al foil for the safety.

Neutron irradiation

The Kilabo piece and the magnetic spherule, together with the two reference monitor samples, were placed in an aluminum irradiation capsule (10 mm ϕ x 75 mm length). The neutron irradiation was performed for 45 hours at the hydro-irradiation port of Kyoto University Reactor (KUR) in Kyoto University Research Reactor Institute (KURRI) under 1MW operation, where thermal and fast neutron fluxes are 1.6×10^{13} n cm^{-2} s^{-1} and 7.8×10^{12} n cm^{-2} s^{-1}, respectively.

Gamma-ray spectrometry for test and reference samples

Gamma rays emitted from irradiated samples were measured using Ge semiconductor detectors at KURRI. After irradiation, test samples were transferred into new (non-irradiated) quartz holders of the same size as used for irradiation and subjected to

gamma-ray counting. Measurements were repeated with different cooling intervals and total of 10 and seven elements were determined for a meteorite piece and a magnetic spherule, respectively. Among the ten elements determined for the piece of the Kilabo meteorite, Na, La, Sm and Au were determined with measurement time of 110,000-120,000 sec after a few days cooling. The rest of elements (Sc, Cr, Fe, Co, Ni and Zn) were determined with measurement time of 110,000-140,000 sec after two weeks cooling. For the magnetic spherule, Na, Cr, Fe, Co, Ni, Ir and Au were determined. Gamma-ray counting for the spherule was done within a day for Na-determination and within a week for the rest. Gamma-ray spectrometry for reference samples was completed in the same manner as described in Ebihara et al. [4].

Geometry-correction in gamma-ray counting

In relative method of INAA [3], test samples and reference samples are usually prepared in the same shape and measured at the same position in gamma-ray counting for simplifying the data reduction procedure and reducing analytical uncertainty. In this study, however, both sample shape and counting position were largely different between the test samples and the reference samples. Because the sample size was different by three orders of magnitude in mass and, hence, the induced radioactivity was similarly different, the counting position was changed to keep the counting loss smaller than 10%. The piece of Kilabo and the magnetic spherule were measured as closely as possible to the Ge detector surface while the reference samples were placed at 8 cm apart from the detector surface. Although the reference samples were sealed into quartz tubes, they could be regarded as point sources just like the tiny test samples when they were place at such position. The difference in counting efficiency between the two positions was corrected by using commercially available checking sources of radioactivity.

Data reduction

Nuclear data related to this study are summarized in Supplementary Information. An (n,γ) reaction was used in NAA for all elements except Ni, for which an (n,p) reaction was used. The elemental contents were determined by a relative method. Some elements (Sc,

Cr, Fe, Co, Ni and Sm) were determined by using both reference monitors and two sets of results were consistent. Allende was used for the determination of Na, Ir and Au while Zn and La were determined by JB-1. Only upper limits were calculated for Ir in the piece of Kilabo and for Sc, Zn, La and Sm in the magnetic spherule. The definition of an upper limit has been reported elsewhere [4]. Certified values for Allende and JB-1 given by Jarosewich et al. [5] and by Imai et al. [6], respectively, were used for reference values.

Results and discussion

Consistencies in reference monitor samples

For quantification in INAA, two reference samples (the Allende meteorite and the JB-1 basalt) having different elemental contents were used. We have conducted similar INAA experiments where tiny grain samples collected by the spacecraft were analyzed by using Allende and JB-1 as reference samples. Hereafter, these experimental runs named run-2 [4] and run-3 [7] are discussed in comparison with the present study, which is named run-1. Table 1 summarizes experimental conditions of these three runs. It is meaningful to compare the activity of radioactive nuclides used in INAA for two different reference samples. Figure 1 compares the gamma rays counting rate per unit mass for each target element, hereafter gamma-ray intensity, among three runs. In runs 2 and 3, iron reagents (iron oxide (Fe_2O_3) powder or iron metal (Fe) powder) were used in addition to Allende and JB-1 as reference samples and their data are shown. The gamma rays counting rate is gamma ray counts per second and correspond to gamma ray energies designated for individual nuclides shown in Fig. 1.

Table 1 Experimental conditions in run-1, run-2 and run-3[a]

	Run-1 (This work)	Run-2[b]	Run-3[c]
Irradiation time (h)	45	28	19
Thermal neutron flux (n cm^{-2} s^{-1})	1.6×10^{13}	8.2×10^{13}	8.2×10^{13}
Fast neutron flux (n cm^{-2} s^{-1})	7.8×10^{12}	3.9×10^{13}	3.9×10^{13}
Operation power (MW)	1	5	5
Mass of reference monitors			
Allende (mg)	1.66	2.00	1.67
JB-1 (mg)	1.12	1.62	1.03
Iron oxide (Fe_2O_3) powder (mg)	-	2.23[d]	-
Iron metal (Fe) powder (mg)	-	-	3.17

[a]Neutron irradiation in runs 1-3 was performed at the hydro-irradiation port of Kyoto University Reactor (KUR). [b][6]. [c][7]. [d]1.56 mg as Iron metal.

The nine nuclides shown in Fig. 1 were determined both for Allende and JB-1. Relative gamma-ray intensities of ^{24}Na, ^{46}Sc and ^{59}Fe in both reference samples are highly consistent for the three runs. Such a consistency can also be seen for Fe reagents. Kong and Ebihara [8] evaluated the consistency in elemental contents in the mg size of JB-1 and confirmed that JB-1 is well homogenized for its use in mg. Figure 1 further confirms that Allende can also be used as a reference sample for mg scale of sample at least for Na, Sc and Fe. For the rest of elements, Allende and JB-1 show a small inconsistency, most of which may be due to poor counting statistics for either sample. For example, Allende tends to have relatively low contents of rare earth elements (La and Sm), whereas JB-1 has a low content of Ni and Zn. Depending upon elemental contents, either Allende or JB-1 may be used for a reference sample.

There appears an apparent inconsistency in Cr data between the two reference samples, with JB-1 having systematically higher gamma-ray intensity. This is undoubtedly due to an erroneous reference value (425 mg kg^{-1}) of Cr for JB-1. If a proposed value (475 mg kg^{-1}) [8] is instead used, an excellent consistency can be seen as shown in Fig. 1 for ^{51}Cr.

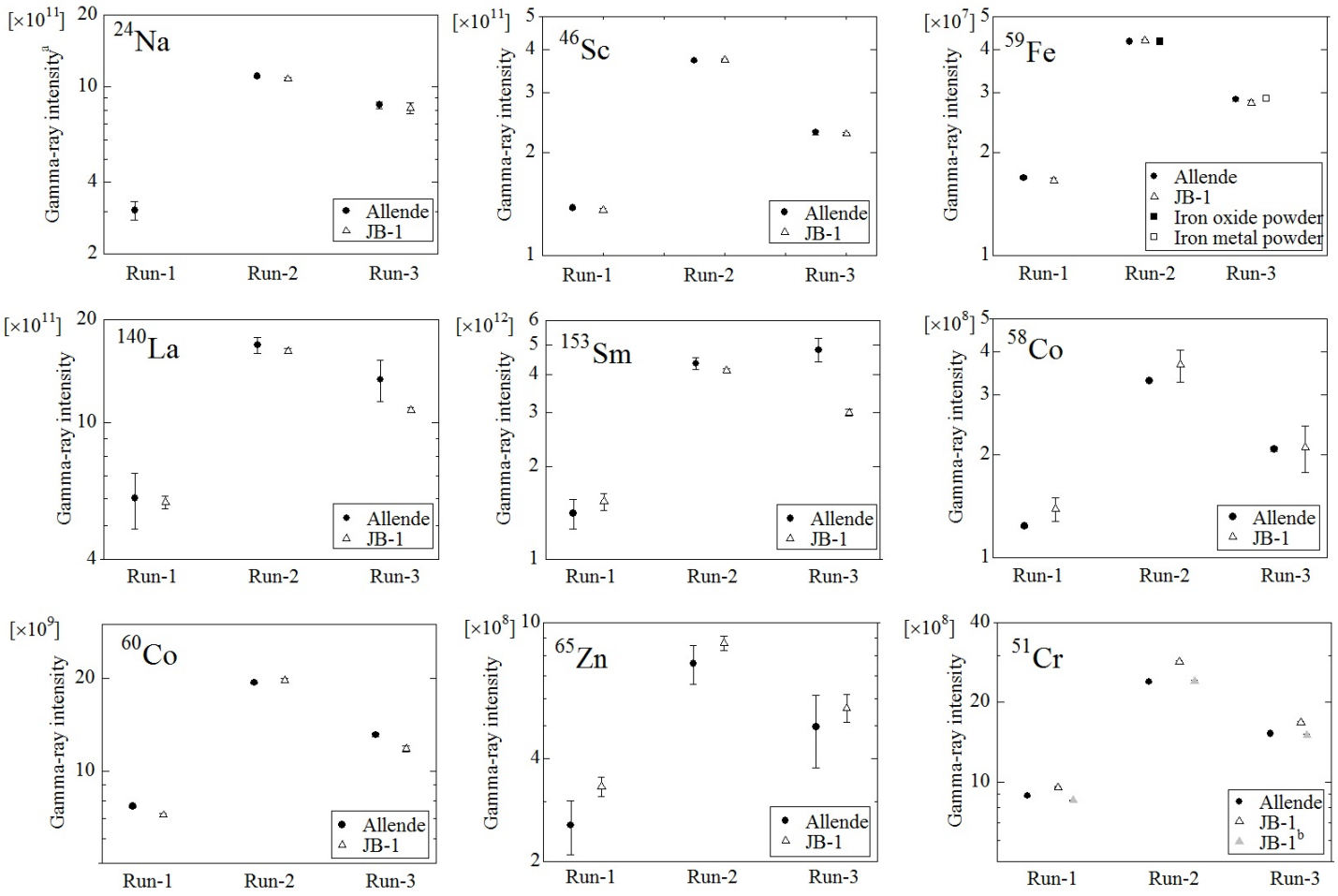


Fig. 1 Gamma-ray intensities of ^{24}Na, ^{46}Sc, ^{59}Fe, ^{140}La, ^{153}Sm, ^{58}Co, ^{60}Co, ^{65}Zn and ^{51}Cr in reference monitors for run-1, run-2 and run-3 [a]Gamma-ray intensity means the gamma rays counting rate per unit mass for each target elements. [b]Proposed value for Cr in JB-1 is 475 mg kg^{-1} [8].

Elemental abundances for Kilabo and magnetic spherule samples

Instrumental NAA results of the Kilabo piece and the magnetic spherule are summarized in Table 2. As for the spherule sample, elemental concentrations are also given. The magnetic spherule analyzed is characterized by high concentrations of iron (601 g kg^{-1}) and nickel (50 g kg^{-1}). These two elements comprise 65% of the bulk mass. Its Ir concentration (2.51 mg kg^{-1}) also is extremely high compared with terrestrial samples. Apparently, this spherule is extraterrestrial in origin. Such spherules are called cosmic spherules and often picked up from the deep sea sediment [9]. Elemental abundances of this spherule are illustrated in Fig. 2, where abundances are normalized to CI chondrite values [10]. Data for the other magnetic spherules from our previous work [11] are also indicated for comparison. Based on the elemental composition, magnetic spherules can be classified into two groups: one group have high CI-normalized abundances of Ir, Co, Ni and Fe (siderophile elements), and low abundances of Cr and Sc (lithophile elements), whereas another group have unfractionated CI-normalized abundances of both siderophile and lithophile elements. The magnetic spherule analyzed in this study apparently belongs to the former group. There has not been reported for Sc values for this group. It now becomes obvious that Sc is even lower than Cr in their CI-normalized abundances.

Table 2 Elemental contents in Kilabo and magnetic spherule analyzed by INAA in this study

	Kilabo	Spherule	
	Content	Content	Concentration
Sm	0.38 ± 0.04 pg	< 0.4 pg	< 0.06 mg kg^{-1}
La	2.6 ± 0.3 pg	< 1.6 pg	< 0.24 mg kg^{-1}
Sc	22.2 ± 0.4 pg	< 1.8 pg	< 0.27 mg kg^{-1}
Fe	0.576 ± 0.007 μg	3.90 ± 0.05 μg	601 ± 8 g kg^{-1}
Na	7.93 ± 0.12 ng	0.406 ± 0.008 ng	62.5 ± 1.3 mg kg^{-1}
Co	0.589 ± 0.008 ng	20.4 ± 0.2 ng	3140 ± 40 mg kg^{-1}
Cr	4.60 ± 0.04 ng	1.06 ± 0.06 ng	164 ± 9 mg kg^{-1}
Ni	14.5 ± 0.3 ng	328 ± 4 ng	50 ± 1 g kg^{-1}
Au	0.62 ± 0.03 pg	0.59 ± 0.05 pg	0.091 ± 0.007 mg kg^{-1}
Zn	1.4 ± 0.1 ng	< 0.98 ng	< 0.1 g kg^{-1}
Ir	< 0.068 pg	16.3 ± 0.4 pg	2.51 ± 0.06 mg kg^{-1}

The Kilabo sample analyzed in this study is a small silicate piece. Therefore, its chemical composition cannot be the same as that of the bulk Kilabo meteorite. As no mineralogical and petrological information is available for the Kilabo piece sample, the detailed cosmochemical discussion cannot be developed. Here, only Ni and Co contents are concerned. Cobalt and Ni are known to behave similarly cosmochemically [12] as well as geochemically. Both elements tend to be hosted in metals in ordinary chondrites like Kilabo. Figure 3 shows the relationship between Co/Fe and Ni/Fe ratios for the Kilabo piece. In addition, data for CI chondrite [10], LL6 chondrite (bulk) [13] and metal separate of LL6 and L6 chondrites [14] are also shown for comparison. The solid line represents the Co/Ni ratio of CI chondrite, on which the Kilabo piece sample is placed along with LL6 bulk and metal samples. This suggests that the Kilabo piece contains a tiny metal grain inside. A similar chemical characteristic was observed in tiny silicate grains recovered from the asteroid Itokawa by the Hayabusa spacecraft [7]. Their Co/Fe and Ni/Fe ratios are similar to those of the Kilabo piece, falling on the CI line as seen in Fig. 3.

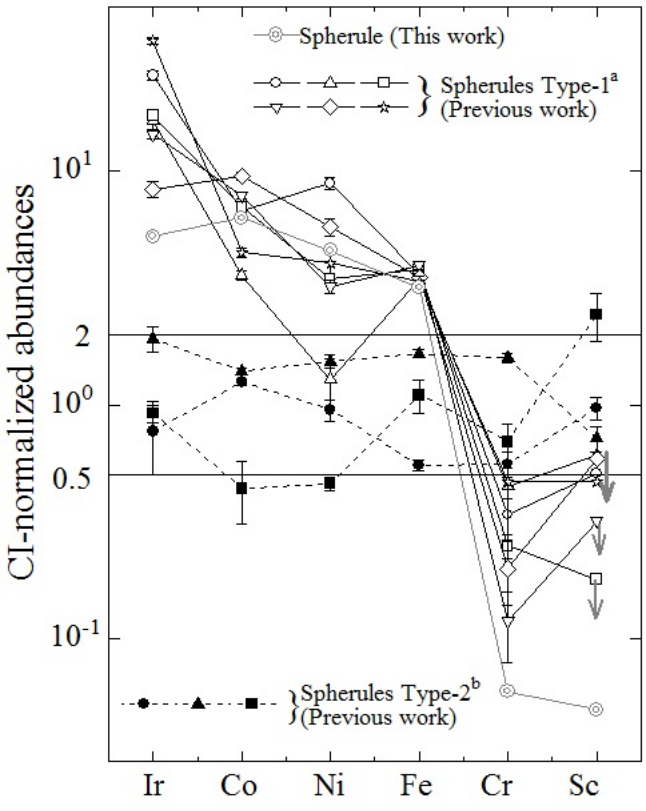


Fig. 2 CI-normalized abundances of Ir, Co, Ni, Fe, Cr and Sc in cosmic spherules

[a]Open symbols indicate spherules which have high CI-normalized abundances of Ir, Co, Ni and Fe (siderophile elements), and low abundances of Cr and Sc (lithophile abundances). [b]Solid symbols indicate spherules which have unfractionated CI-normalized abundances of both siderophile and lithophile elements.

As the Co/Ni ratio in the Kilabo piece is chondritic, the kilabo piece might contain 0.5-0.6 pg of Ir if we assume that the Ir/Co and Ir/Ni ratios in the Kilabo piece are equal to those in CI chondrite [10]. Although only an upper limit was derived for the Kilabo piece, it is clear that Ir is depleted in the tiny metal grain that the Kilabo piece contains. From the view point of Ir-depletion, Kilabo and Itokawa grains thus appear alike.

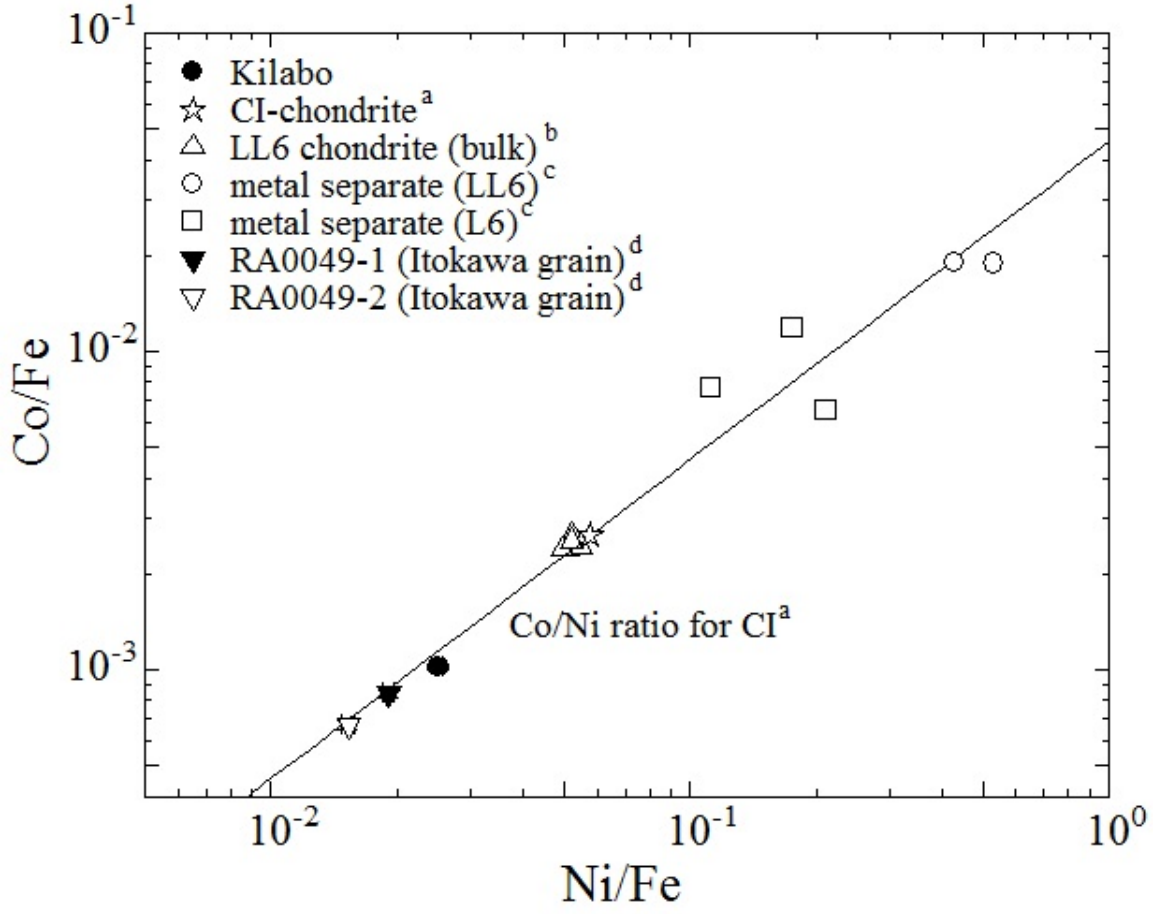


Fig. 3 Correlation between Co/Fe and Ni/Fe ratios in several astromaterials [a] [10]. [b] [13]. [c] [14]. [d] [7]

Detection limits

Detection limits of the 11 elements measured in this study are estimated under the present experimental condition. A detection limit is defined as a value corresponding to three sigma of background counts at the peak area of the gamma-ray emitted by a nuclide of interest. Calculated values are listed in Table 3, in which data for the previous experimental runs (run-2 and/or run-3) also are shown for comparison. Detection limit values were obtained based on data on either or both of the samples analyzed in individual runs. The detection limit values for run-1 (this study) are higher than those for runs-2/3 by factors of 2 to 20. Detection limits are dependent on experimental conditions such as the sample size, irradiation time, neutron flux, gamma-ray counting time and counting efficiency. In INAA, the detection limit is also largely controlled by the co-existing elements in the matrix. Therefore, detection limit values are to be regarded as information values but the values in Table 3 must be informative in the analysis of similar samples to those analyzed in this study, for example, micro meteorites, meteorite pieces and cosmic spherules.

Table 3 Detection limits for individual elements

	Detection limit (pg)		Concentration range in Chondrite [c]	Content range in Chondrite of 0.05 micro-g (pg)
	This work [a] 45 h irradiation (1MW)	Previous work [b] 28 h irradiation (5MW)		
Na	20	1	1800 - 6900 mg kg^{-1}	90 - 345
Sc	0.4	0.03	6 - 11 mg kg^{-1}	0.30 - 0.55
Cr	40	4	2650 - 4160 mg kg^{-1}	133 - 208
Fe	2800	270	18 - 38 %	9100 - 19000
Co	3	0.4	480 - 1100 mg kg^{-1}	24 - 55
Ni	340	110 [e,f]	1.1 - 2.6 %	550 - 1285
Zn	150	12	18 - 315 mg kg^{-1}	0.9 - 15.8
La	0.5	0.1	235 - 585 μg kg^{-1}	0.012 - 0.029
Sm	0.1	0.02	140 - 294 μg kg^{-1}	0.007 - 0.015
Ir	0.3 [d]	0.02 [e,f]	380 - 1070 μg kg^{-1}	0.019 - 0.054
Au	0.02	0.01	120 - 330 μg kg^{-1}	0.006 - 0.017

[a] Calculated for the piece of Kilabo, unless otherwise noted. [b] Calculated for Itokawa particle (0.017-0.048 μg), unless otherwise noted. [c] Data from [15]. [d] Calculated for spherule (6.5 μg). [e] Calculated for Itokawa particle (1.66 μg). [f] Obtained by run-3 (19 h irradiation under 5MW operation).

To evaluate the applicability of the INAA procedure described in this study, the deduced detection limits are compared with the estimated elemental contents in 0.05 μg of chondritic meteorites [15] in Table 3. It is obvious that Na, Cr, Fe, Co and Ni can be easily determined for 0.05 μg of chondrite by INAA with 45 h irradiation under 1MW operation (this work), while INAA with more than 28 h irradiation under 5MW operation is required to determine Sc, Zn, Ir and Au. Even with the highest neutron doze (53 h irradiation under 5 MW operation) available at KUR, La and Sm may not be determined for such a small sample.

Degree of increase in isotopic abundance induced by neutron irradiation

As INAA is a nondestructive method of elemental analysis, the same sample once subjected to INAA can be reused for different analytical purposes. For such a case, effects caused by neutron irradiation are of concern. Major concerns are the induced radioactivity and the increase in isotopic abundance including the production of long-lived radioactive nuclides. Scientifically, the latter case is important by far and, therefore, is considered here. In order to make the evaluation of degree of the increase in isotopic abundance meaningful, used are the data from the experiment at run-3 [7], where 1.66 μg of a tiny grain from the asteroid Itokawa was irradiated by neutrons under the condition listed in Table 1. Assuming the elemental composition of bulk LL chondrite [15] for this grain, the number of produced nuclides with neutron irradiation was calculated based on the Monte-Calro simulation code (MVP 2.0) [16] and the reaction cross section data (JENDL-4.0) [17]. Both stable and unstable (radioactive) nuclides could be produced and the result is summarized in Table 4. In calculation, the position of control rod, temperature of the reactor core, and the combustion rate of nuclear fuel were all taken into consideration, because the neutron irradiation of run-3 was performed near the reactor core and, therefore, these factors affect the neutron energy spectrum. The produced nuclides in Table 4 are grouped into stable nuclides (^{21}Ne, ^{22}Ne and ^{38}Ar) and long-lived radioactive nuclides (^{36}Cl, ^{26}Al and ^{10}Be). These nuclides are typical cosmogenic nuclides and radionuclides produced by nuclear reactions triggered by cosmic rays and commonly detected in extraterrestrial materials like meteorites.

Table 4 Production of some cosmogenic nuclides from 1.66 μg of LL chondrite by neutron-induced reaction in INAA[a]

Target nuclides	Reaction	Produced nuclides	Number of Produced nuclides	Number of nuclides (original)
Stable nuclides (noble gas)-production				
^{24}Mg	(n,α)	^{21}Ne	1.58×10^8	1.15×10^7
^{25}Mg	(n,α)	^{22}Ne	5.21×10^7	3.49×10^8
^{37}Cl	(n,γ), β^-	^{38}Ar	7.97×10^6	1.78×10^7
Radioactive nuclides-production				
^{35}Cl	(n,γ)	^{36}Cl	2.53×10^9	9.06×10^2
^{39}K	(n,α)	^{36}Cl	3.24×10^7	9.06×10^2
^{27}Al	(n,2n)	^{26}Al	1.30×10^5	3.73×10^3
^{13}C	(n,α)	^{10}Be	3.03×10^4	2.07×10^3

[a]Under the condition of run-3 in **Table 2**.

In Table 4, the calculated values are compared with numbers of corresponding nuclides observed in extraterrestrial samples. For stable nuclides (of noble gases), measured values for a different Itokawa grain are given for comparison [18]. It is well acknowledged that noble gases are extremely sensitive in mass spectrometry. As seen in Table 4, calculated values and measured values in the Itokawa grain are mostly comparable for all three nuclides. For long-lived radionuclides, concentrations in the Gold Basin L4 chondrite (a shower sample, UA-1188) [19] are given for comparison in Table 4. These data were obtained by accelerator mass spectrometry. The measured values are smaller or much smaller than the calculated values, with the difference varying by an order to six orders of magnitude. Evidently the reuse of neutron-irradiated samples should not be allowed for noble gas mass spectrometry and accelerator mass spectrometry for the study on noble gas nuclides and long-lived radioactive nuclides, respectively.

Conclusions

In considering the cosmochemical importance of small grain samples, we developed the INAA procedure for analyzing micro gram scale of solid samples. For quantification in this INAA procedure a relative method using the Allende meteorite and the JB-1 basalt was used. From a detailed comparison in the gamma-ray intensity for individual nuclides

between Allende and JB-1, it was confirmed that a few mg of Allende and JB-1 can be used as reference monitors for a relative method and that Cr data in JB-1 should be the proposed value of 475 mg kg^{-1}.

Using this INAA procedure, elemental abundances for the Kilabo grain as meteoritic sample and a magnetic spherule were obtained. This spherule sample was judged to be extraterrestrial in origin from its Ir concentration and seemed to be similar to the other spherules analyzed previously which have high CI-normalized abundances of siderophile elements and low abundances of lithophile elements. The Kilabo grain appeared to be similar to the silicate grain recovered from the asteroid Itokawa by the Hayabusa spacecraft based on its Co and Ni contents.

To evaluate the applicability of this INAA procedure, detection limit values were deduced. In 0.05 μg of chondrite sample, Na, Cr, Fe, Co and Ni can be easily determined by this INAA procedure with 45 h irradiation under 1MW operation, while INAA with more than 28 h irradiation under 5MW operation is required to determine Sc, Zn, Ir and Au. From evaluating degree of the increase in isotopic abundance induced by neutron irradiation, evidently the reuse of neutron-irradiated samples should not be allowed for noble gas mass spectrometry and accelerator mass spectrometry for the study on noble gas nuclides (^{21}Ne, ^{22}Ne and ^{38}Ar) and long-lived radioactive nuclides (^{36}Cl, ^{26}Al and ^{10}Be), respectively.

Acknowledgements

We thank Dr. T. Sano (Kyoto University Research Reactor Institute, KURRI) for calculation of the number of stable and radioactive nuclides produced by neutron irradiation. We are grateful to Prof. T. Ohtsuki (KURRI) for his help in the method for neutron irradiation of small samples. The authors express their gratitude to the members of the research reactor group in KURRI for the preparation and operation in the neutron irradiation. This study was supported by Kyoto University Global COE Program “International Center for Integrated Research and Advanced Education in Material

Science" (to SS). This study was supported by a grant-in-aid from the Ministry of Education, Science and Culture (KAKENHI 25790081) in Japan for SS.

References

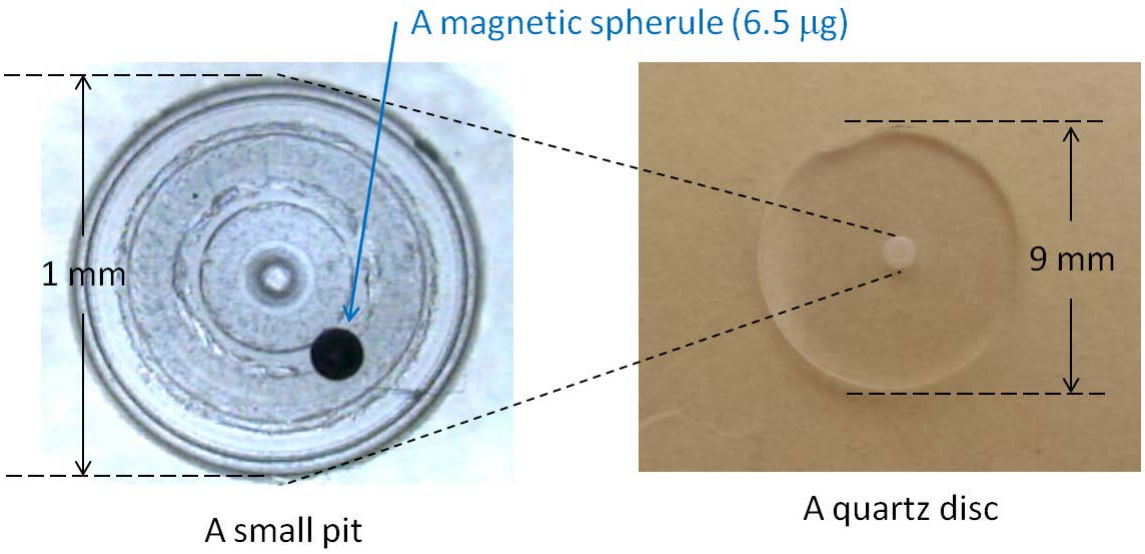
1. Ganapathy R, Brownlee DE, Hodge PW (1978) Silicate spherules from deep-sea sediments: confirmation of extraterrestrial origin. Science 201:1119-1121
2. Sekimoto S, Kobayashi T, Takamiya K, Ebihara M, Shibata S (2007) Instrumental neutron activation analysis of spherule samples recovered from the Pacific ocean sea sediment and Antarctic ice sheet. J Radioanal Nucl Chem. 272:447-450
3. Kong P, Ebihara M, Nakahara H (1996) Determination of 18 siderophile elements including all platinum group elements in chondritic metals and iron meteorites by instrumental neutron activation. Anal Chem. 68:4130-4134
4. Ebihara M, Shirai N, Sekimoto S, Nakamura T, Tsuchiyama A, Matsuno J, Matsumoto T, Abe M, Fujimura A, Ishibashi Y, Karouji Y, Mukai T, Okada T, Uesugi M, Yada T (2015) Chemical and mineralogical compositions of two grains recovered from asteroid Itokawa. Meteorit Planet Sci. 50:243-254
5. Jarosewich E, Clarke RS Jr., Barrows JN (1987) The Allende Meteorite reference sample. Smithson Contrib Earth Sci. 27:1- 12
6. Imai N, Terashima S, Itoh S, Ando A (1995) 1994 Compilation values for GSJ reference samples, igneous rock series. Geochem J. 29: 91-95
7. Ebihara M, Sekimoto S, Shirai N, Hamajima Y, Yamamoto M, Kumagai K, Oura Y, Ireland TR, Kitajima F, Nagao K, Nakamura T, Naraoka H, Noguchi T, Okazaki R, Tsuchiyama A, Uesugi M, Yurimoto H, Zolensky ME, Abe M, Fujimura A, Mukai T, Yada T (2011) Neutron activation analysis of a particle returned from asteroid Itokawa. Science 333:1119–1121.
8. Kong P, Ebihara M (1997) Reproducibility of elemental concentrations for JB-1, a GSJ rock reference sample, with special reference to Mo, W and Ta. Geochem J. 31: 339-344.
9. Murray J, Renard AF (1891) Report on Deep-Sea Deposits based on the specimens collected during the voyage of H.M.S. Challenger in the years 1872 to 1876, Neill

and Company, Edinburgh

10. Anders E, Grevesse N (1989) Abundances of the elements: Meteoritic and solar. Geochim Cosmochim Acta. 53:197–214
11. Sekimoto S, Kobayashi T, Takamiya K, Ebihara M, Shibata S (2008) Chemical composition of magnetic spherules collected from deep sea sediment. J Radioanal Nucl Chem. 278: 319-322
12. Wasson JT (1985) Meteorites-Their Record of Early Solar-System History, W. H Freeman and Company, New York
13. Kallemeyn GW, Rubin AE, Wang D, Wasson JT (1989) Ordinary chondrites: Bulk compositions, classification, lithophile-element fractionations and composition-petrographic type relationships. Geochim Cosmochim Acta. 53: 2747-2767
14. Kong P, Ebihara M (1997) The origin and nebular history of the metal phase of ordinary chondrites. Geochim Cosmochim Acta. 61:2317–2329
15. Wasson JT, Kallemeyn GW (1988) Compositions of chondrites. Phil Trans R Soc A. 325:535–544
16. Nagaya Y, Okumura K, Mori T, Nakagawa M (2005) MVP/GMVP II: General purpose Monte Carlo codes for neutron and photon transport calculations based on continuous energy and multigroup methods. JAERI Rep. 1348:1-388
17. Shibata K, Iwamoto O, Nakagawa T, Iwamoto N, Ichihara A, Kunieda S, Chiba S, Furutaka K, Otuka N, Ohsawa T, Murata T, Matsunobu H, Zukeran A, Kamada S, Katakura J (2011) JENDL-4.0: A new library for nuclear science and engineering. J Nucl Sci Technol. 48:1-30
18. Nagao K, Okazaki R, Nakamura T, Miura YN, Osawa T, Bajo K, Matsuda S, Ebihara M, Ireland TR, Kitajima F, Naraoka H, Noguchi T, Tsuchiyama A, Yurimoto H, Zolensky ME, Uesugi M, Shirai K, Abe M, Yada T, Ishibashi Y, Fujimura A, Mukai T, Ueno M, Okada T, Yoshikawa M, Kawaguchi J (2011) Irradiation history of Itokawa regolith material deduced from noble gases in the Hayabusa samples. Science 333:1128–1131
19. Welten KC, Caffee MW, Leya I, Masarik J, Nishiizumi K, Wieler R (2003) Noble gases and cosmogenic radionuclides in the Gold Basin L4 chondrite shower: Thermal history, exposure history, and pre-atmospheric size. Meteorit Planet Sci. 38:157-173

Supplementary information

The manner in which the spherule sample is placed into the pit in the quartz disc is shown in Figure 1.



Nuclear data related to this study are summarized in the following Table 1.

Table 1 Data of measured nuclides [S1]

Element	Nuclear reaction	Thermal neutron cross section (barn)	Produced nuclide	Half life	γ-ray energy used for determination (keV)
$_{11}$Na	^{23}Na (n,γ)	0.53	^{24}Na	14.96 h	1369
$_{21}$Sc	^{45}Sc (n,γ)	27	^{46}Sc	83.8 d	889
$_{24}$Cr	^{50}Cr (n,γ)	15	^{51}Cr	27.7 d	320
$_{26}$Fe	^{58}Fe (n,γ)	1.3	^{59}Fe	44.5 d	1099
$_{27}$Co	^{59}Co (n,γ)	37.2	^{60}Co	5.27 y	1332
$_{28}$Ni	^{58}Ni (n,p)	0.5[a]	^{58}Co	70.9 d	811
$_{30}$Zn	^{64}Zn (n, γ)	0.74	^{65}Zn	244.3 d	1115
$_{57}$La	^{139}La (n,γ)	9.2	^{140}La	40.272 h	1595
$_{62}$Sm	^{152}Sm (n,γ)	206	^{153}Sm	46.27 h	103
$_{77}$Ir	^{191}Ir (n,γ)	920	^{192}Ir	73.8 d	317

$_{79}$Au	^{197}Au (n,γ)	98.7	^{198}Au	2.69d	411

[a]Fast neutron cross section [S2].

S1. Magill J, Pfennig G, Galy J (2006) Karlsruhe Chart of the Nuclides, 7th Edition. European Commission, Joint Research Centre, Luxembourg

S2. Shibata K, Iwamoto O, Nakagawa T, Iwamoto N, Ichihara A, Kunieda S, Chiba S, Furutaka K, Otuka N, Ohsawa T, Murata T, Matsunobu H, Zukeran A, Kamada S, Katakura J (2011) JENDL-4.0: A new library for nuclear science and engineering. J Nucl Sci Technol. 48:1-30