

Non-destructive analysis of unknown samples named 1G and 2G by using nuclear analytical methods

By

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Abstract: For the initial analysis of the sample returned from space, it must be highly essential that the sample is not physically destroyed. Using three nuclear analytical methods, namely instrumental neutron activation analysis (INAA), instrumental photon activation analysis (IPAA) and neutron - induced prompt gamma-ray analysis (PGA), we could non-destructively determine a total of 37 elements including most major and minor elements. Based on elemental abundances obtained, we have tentatively assigned two unknown samples, 1G and 2G as metal-missing L chondrite and CV chondrite, respectively. Thus, this study clearly demonstrates that the analytical scheme once proposed for the first phase of the competition can best work for the initial chemical analysis of the sample returned by the MUSES-C space mission.

1. INTRODUCTION

The systematic recovery of meteorite samples from Antarctica has greatly increased the number of extra - terrestrial materials accessible to us. Besides such samples as those passively obtained by chance, we also possessed another category of extra - terrestrial samples, that is, the returned sample from space by space mission. These samples have been so far limited to those from the moon recovered by the Luna mission of the former Soviet Union and the Apollo mission of the United States. In coming ten years, such a chance of getting positively extraterrestrial samples by space missions will be increasing.

The MUSES-C space mission program of ISAS, Japan is of great significance because it aims to return the asteroidal material to the earth as the first trial to recover the extra - terrestrial samples from planets other than the moon. When the sample is successfully returned to the earth, it will be subjected to the initial inspection from several scientific viewpoints. The importance of the initial analysis of the material returned from space must be understood if recalling the experience with the first lunar samples recovered by the Apollo 11. One of the most essential requirements for the initial analysis is to derive as much information as possible from

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as small amount as possible. Much more severe requirement will be placed for the MUSES-C than that for the Apollo missions, because the total amount to be recovered by the MUSES-C mission is far small compared with that by a series of the Apollo missions.

When elemental composition is focused, an analytical method having high sensitivity for many elements is highly desired. In addition to this requirement, non-destructivity can also be regarded as a similarly essential merit for the method applied for the initial analysis. Nuclear analytical methods represented by neutron activation analysis (NAA) can satisfy these two requirements. Considering such a suitability, we decided to propose an analytical scheme applicable to the sample returned by the MUSES-C space mission program. After passing the first phase of the competition for joining the initial analysis team, we were supplied two unknown samples, named 1G and 2G, for the second phase of competition.

Nuclear analytical methods applied in this work consist of instrumental NAA (INAA), prompt gamma-ray analysis (PGA) and instrumental photon activation analysis (IPAA). Reactor neutrons are used in both INAA and PGA. In INAA, gamma-ray (decay gamma-ray) emitted from a daughter nuclide decayed from a parent (neutron-captured) nuclide is measured, whereas gamma-ray (prompt gamma-ray) emitted from the neutron-captured nuclide is used in PGA. We have already demonstrated that PGA is one of the most advantageous analytical methods for determining chemical composition of the returned samples from space (Ebihara & Oura 2001). Great merits of PGA are its non-destructivity and high analytical sensitivity for most major elements including hydrogen and sulfur (Latif et al. 1999). As neutron is used to activate elements (nuclides), bulk elemental composition can be determined for relatively thick samples. This is contrast to X-ray fluorescence (XRF) analysis and electron-probe microanalysis (EMPA), which yield elemental composition for the surface or the thin layer of samples. Neutron flux used in PGA is several orders of magnitude lower than that in conventional NAA, making samples once used in PGA be reusable for other inspections without worrying any effect on elemental and isotopic compositions.

In our proposed scheme for the first phase of competition, the samples once used in PGA is split into two portions, which are then analyzed by INAA and IPAA, respectively. If the sample size is limited, the same sample could be successively analyzed by PGA, INAA and IPAA in this order. An order of the last two methods can be switched, depending upon the restriction of facilities, but some uncorrectable interferences occur. In INAA, (n, γ) reaction is normally used, whereas (γ, n) reaction is used in IPAA. Thus, INAA and IPAA can be used somewhat complementarily and are equally suitable for determining elemental abundances of cosmochemical samples (Ebihara et al. 2000). In this study, two unknown test samples (1G and 2G) were analyzed by PGA, INAA and IPAA, separately, and their analytical data are presented. Based on these data, we have tried to characterize these unknown samples in the light of bulk chemical composition.

2. EXPERIMENTAL PROCEDURES

We analyzed two test samples allocated to us (1G and 2G) by PGA, INAA, and IPAA. Analyses were carried in this sequence. The whole powder samples supplied were firstly subjected to PGA. After sufficient cooling, the samples used for PGA were divided into two aliquots, which were subsequently analyzed by INAA or IPAA, respectively. As each sample supplied to us weighs about 100 mg. INAA and IPAA was performed by using its aliquots. The details of individual analytical procedures are summarized in Table 1 and are described briefly in the following.

Table 1: Analytical procedures of three nuclear analytical methods

	Facility	Irrad. time	Determined elements	Reference samples
PGA	JRR-3, JAERI	2 h	H, B, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni	NH ₄ Cl for H and Cl Na ₂ SO ₄ for S Allende ¹ for Cr, Co, Ni JB-1 for others
INAA	JRR-3, JAERI	10 s	Mg, Al, Ca, V, Mn	JB-1
	JRR-3, JAERI	1 min	Ga, Na, K	JB-1
	JRR-4, JAERI	20 min	K, Ca, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, La, Sm, Eu, Lu, Os, Ir, Au, Hg	Allende ²
IPAA ³	LINAC, Tohoku Univ.	30 min	Si, Ca, Fe, Sr	JB-1
	LINAC, Tohoku Univ.	6 h	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, Rb, Y, Zr, Nb, Ce	NaCl for Na MgO for Mg Allende ¹ for Cr JB-1 for others

¹Prepared by the Smithsonian Institute. Elemental contents adapted were from Jarosewich et al. (1987).

²Prepared by us. Elemental contents were taken from Kallemeyn et al. (1989).

³Irradiated by bremsstrahlung with 30 MeV of end-point energy.

2.1 PGA

Each sample (~100 mg) was put into a thin fluorinated ethylene propylene resin film bag and was irradiated at the prompt gamma-ray analyzing system for about 2 hours by cold neutron beam guided out from the JRR-3M research reactor at the Japan Atomic Energy Research Institute (JAERI). Prompt gamma-rays were detected by a Ge detector coupled with a 16k channel pulse-height analyzer. The Ge detector is surrounded by BGO detectors to suppress Compton gamma-rays induced by high-energy prompt gamma-rays. JB-1 issued by the Geological Survey of Japan and the Smithsonian Allende meteorite powder were used as references for the determination of elemental contents. A reagent of NH₄Cl was used for determining H and Cl, and Na₂SO₄ for S. Detailed analytical procedures for geological and cosmochemical samples are described by Latif et al. (1999).

2.2 INAA

Aliquots (~50 mg) of the samples used for PGA were sealed doubly in clean polyethylene bags and were irradiated by neutrons. Three successive irradiations were performed at the JAERI research reactors. Irradiations for 10 s and for 1 min were carried out at JRR-3 and an irradiation for 20 min was at JRR-4. After irradiations of 10 s and 1 min, the samples were measured for gamma-rays only once. After an irradiation of 20 min, gamma-ray measurements were repeated for several times with different cooling intervals, in order to follow radioactive decays of neutron-captured radionuclides. Both JB-1 and an in-house Allende meteorite powder sample (named TMU-1) were used as references for the determination of elemental contents.

2.3 IPAA

Another set of aliquots (~ 50 mg) of the samples used for PGA were wrapped with Al foil and were irradiated by bremsstrahlung (end point energy: 30 MeV) generated by an electron linear accelerator at the Laboratory of Nuclear Science (LNS), Tohoku University. Samples were irradiated successively for 30 min and 6 h. After each irradiation, samples were measured

for gamma-rays several times with different cooling intervals by high purity Ge detectors. Both JB-1 and the Smithsonian Allende powder samples were used as references for the determination of elemental contents in unknown samples. Analytical grade chemicals also were used for some elements as reference samples. An application of IPAA to chondritic meteorite samples is described by Ebihara et al. (2000) in detail.

3. ANALYTICAL RESULTS

Analytical results are summarized in Table 2. Several elements were determined in duplicate or even in triplicate. In Table 2, individual values as well as mean values are listed. In calculating mean values, apparent outliers printed in italics were excluded. Values of H (hydrogen) for Allende and two unknown samples are just for information, considering a background abundance of H in the surroundings. Please note, however, that H is non-destructively measurable by PGA. Under a strict control, it will be possible to obtain H contents in several hundreds ppm in 100 mg samples.

4. DISCUSSION

By using three activation analyses, a total of 37 elements were determined, with Br and Os values for 1G and Nb content for 2G left blank. Elements determined include most major and minor elements. Among elements having sub - % or higher abundance in geological and cosmochemical samples, only element not included in Table 2 is P (phosphorus). As H can be reliably determined by PGA as noted above, major element compositions of primitive meteorites like CI and CM can be non-destructively determined by a combination of three analytical methods used in this work. Among these methods, PGA is especially effective. It provides elemental abundances for most major elements including Si (and H for meteorites such as CI and CM). The effectiveness of PGA for the initial analysis of the sample returned from space is discussed in detail by Ebihara and Oura (2001).

From chemical compositions obtained in this work, we infer the nature of 1G and 2G. Undoubtedly, these samples can be judged to be non-crustal materials from high siderophile abundances and low REE abundances. Elemental abundances of these elements are in the range for chondritic meteorites. Kallemeyn et al. (1991) proposed a diagram for judging chemical classes of carbonaceous chondrites. We proposed a similar diagram for the same purpose (Oura et al. 2002). Our diagram is drawn based on only PGA data. As discussed by Ebihara and Oura (2001), PGA has such a great merit that residual radioactivity in samples subjected to PGA decreases down to the background level after an appropriate cooling (typically several weeks). In fact, this advantage made it possible in this study that the same specimen used for PGA was reused for INAA and IPAA. Our diagram of Al/Mn vs. S/Mn is shown in Fig. 1, in which individual chemical groups cluster with sufficient distance to each other, supporting that this diagram is as useful as the diagram of Kallemeyn et al. (1991), in which Al/Mn and Zn/Mn ratios are plotted.

In Fig. 1, data for 1G and 2G are plotted. From this figure, 2G is assumed to be analogous to chondrites in chemical composition. Actually, its elemental composition is very similar to that of the Allende CV chondrite. If 2G is plotted on a diagram of Al/Mn vs. Zn/Mn, it also falls in a cluster corresponding to a CV group (Fig. 2). Thus, we are confident that 2G belongs to CV chondrites in chemical composition. In contrast to 2G, 1G is a stray in Fig. 1. The sample 1G is characterized by lower contents of Al, Ca and REE and high contents of Na, Si

Table 2: Analytical results for unknown samples, 1G and 2G

		Method ¹	1G	2G	Reference sample ²
H	%	PGA	0.0152 ± 0.00259	0.0244 ± 0.00268	NH ₄ Cl
B	ppm	PGA	1.89 ± 0.80	1.66 ± 0.47	JB-1
Na	%	IPAA(l)	0.927 ± 0.009	0.331 ± 0.010	NaCl
		INAA(m)	0.827 ± 0.008	0.361 ± 0.003	JB-1
		PGA	0.762 ± 0.042	0.301 ± 0.042	JB-1
		mean	0.839 ± 0.083	0.331 ± 0.030	
Mg	%	IPAA(l)	17.8 ± 0.8	14.1 ± 0.7	MgO
		INAA(s)	16.4 ± 1.0	14.8 ± 0.9	JB-1
		PGA	20.8 ± 4.5 ³	17.4 ± 3.9	JB-1
		mean	17.1 ± 1.0	14.5 ± 0.5	
Al	%	INAA(s)	1.29 ± 0.01	1.73 ± 0.02	JB-1
		PGA	1.34 ± 0.09	1.57 ± 0.11	JB-1
		mean	1.315 ± 0.04	1.65 ± 0.11	
Si	%	IPAA(s)	20.3 ± 1.1	18.8 ± 0.8	JB-1
		PGA	20.9 ± 0.6	15.9 ± 0.6	JB-1
		mean	20.6 ± 0.4	17.4 ± 2.1	
S	%	PGA	2.28 ± 0.06	2.34 ± 0.07	Na ₂ SO ₄
Cl	ppm	PGA	75 ± 11	338 ± 18	NH ₄ Cl
K	%	INAA(m)	0.101 ± 0.017	0.019 ± 0.011	JB-1
		INAA(l)	0.0756 ± 0.0133	0.026 ± 0.0062	Allende (TMU-1)
		PGA	0.101 ± 0.013		JB-1
		mean	0.101 ± 0.0003		
Ca	%	IPAA(l)	1.46 ± 0.03	1.92 ± 0.04	JB-1
		INAA(s)	1.1 ± 0.1	2.05 ± 0.13	JB-1
		INAA(l)	1.40 ± 0.06	2.01 ± 0.06	Allende (TMU-1)
		PGA	1.41 ± 0.09	1.84 ± 0.09	JB-1
		mean	1.42 ± 0.03	1.96 ± 0.09	
Sc	ppm	INAA(l)	9.91 ± 0.04	12.3 ± 0.1	Allende (TMU-1)
Ti	%	IPAA(l)	0.0760 ± 0.0036	0.0684 ± 0.0041	JB-1
		PGA	0.0683 ± 0.0044	0.0870 ± 0.0050	JB-1
		mean	0.0722 ± 0.0054	0.0777 ± 0.0132	
V	ppm	INAA(s)	70.1 ± 1.9	90.6 ± 2.1	JB-1
Cr	%	IPAA(l)	0.395 ± 0.008	0.366 ± 0.007	Allende(SI)
		INAA(l)	0.392 ± 0.002	0.354 ± 0.001	Allende (TMU-1)
		PGA	0.433 ± 0.025	0.372 ± 0.023	Allende(SI)
		mean	0.407 ± 0.023	0.364 ± 0.009	
Mn	%	IPAA(l)	0.351 ± 0.10	0.163 ± 0.006	JB-1
		INAA(s)	0.286 ± 0.008	0.141 ± 0.004	JB-1
		PGA	0.291 ± 0.017	0.128 ± 0.010	JB-1
		mean	0.289 ± 0.004	0.135 ± 0.009	

Table 2: continued.

		Method	1G	2G	Reference sample
Fe	%	IPAA(s)	<i>19.4 ± 1.5</i>	<i>25.6 ± 1.1</i>	JB-1
		PGA	16.5 ± 0.6	22.6 ± 0.9	JB-1
		INAA(l)	17.4 ± 0.1	23.1 ± 0.1	Allende (TMU-1)
		mean	17.8 ± 1.5	22.5 ± 0.7	
Co	ppm	IPAA(l)	<i>217 ± 4</i>	<i>686 ± 14</i>	JB-1
		INAA(l)	170 ± 1	640 ± 1	Allende (TMU-1)
		PGA	198 ± 38	649 ± 115	Allende(SI)
		mean	184 ± 20	645 ± 6	
Ni	%	IPAA(l)	<i>0.778 ± 0.015</i>	1.44 ± 0.03	Allende(SI)
		INAA(l)	0.458 ± 0.002	<i>1.08 ± 0.01</i>	Allende (TMU-1)
		PGA	0.439 ± 0.026	1.35 ± 0.07	Allende(SI)
		mean	0.449 ± 0.013	1.40 ± 0.06	
Zn	ppm	IPAA(l)	62.4 ± 2.0	119 ± 16	JB-1
		INAA(l)	70.1 ± 2.3	116 ± 2	Allende (TMU-1)
		mean	66.3 ± 5.4	118 ± 2	
Ga	ppm	INAA(m)	8.0 ± 3.6	7.1 ± 2.5	Allende (TMU-1)
As	ppm	INAA(l)	0.333 ± 0.054	1.23 ± 0.06	Allende (TMU-1)
Se	ppm	INAA(l)	9.6 ± 0.6	5.4 ± 0.5	Allende (TMU-1)
Br	ppm	INAA(l)		1.9 ± 0.2	Allende (TMU-1)
Rb	ppm	IPAA(l)	4.76 ± 0.18	0.980 ± 0.098	JB-1
Sr	ppm	IPAA(s)	17.5 ± 5.9	16.7 ± 2.0	JB-1
Y	ppm	IPAA(l)	2.33 ± 0.11	3.05 ± 0.11	JB-1
Zr	ppm	IPAA(l)	7.08 ± 0.22	10.0 ± 0.3	JB-1
Nb	ppm	IPAA(l)	2.46 ± 0.56		JB-1
La	ppm	INAA(l)	0.320 ± 0.013	0.547 ± 0.016	Allende (TMU-1)
Ce	ppm	IPAA(l)	0.741 ± 0.046	1.41 ± 0.07	JB-1
Sm	ppm	INAA(l)	0.187 ± 0.003	0.318 ± 0.004	Allende (TMU-1)
Eu	ppm	INAA(l)	0.107 ± 0.009	0.115 ± 0.009	Allende (TMU-1)
Lu	ppm	INAA(l)	0.050 ± 0.005	0.045 ± 0.004	Allende (TMU-1)
Os	ppm	INAA(l)		0.65 ± 0.06	Allende (TMU-1)
Ir	ppm	INAA(l)	0.341 ± 0.004	0.830 ± 0.004	Allende (TMU-1)
Au	ppm	INAA(l)	0.0729 ± 0.0009	0.144 ± 0.001	Allende (TMU-1)
Hg	ppm	INAA(l)	0.040 ± 0.008	0.034 ± 0.005	Allende (TMU-1)

¹INAA(s): irradiation for 10 s, INAA(m): irradiation for 1 min, INAA(l): irradiation for 20 min. IPAA(s): irradiation for 30 min, IPAA(l): irradiation for 6 h.

²Allende(TMU-1): prepared by us, Allende(SI): prepared by the Smithsonian Institution.

³Italic values are not used for calculating mean values.

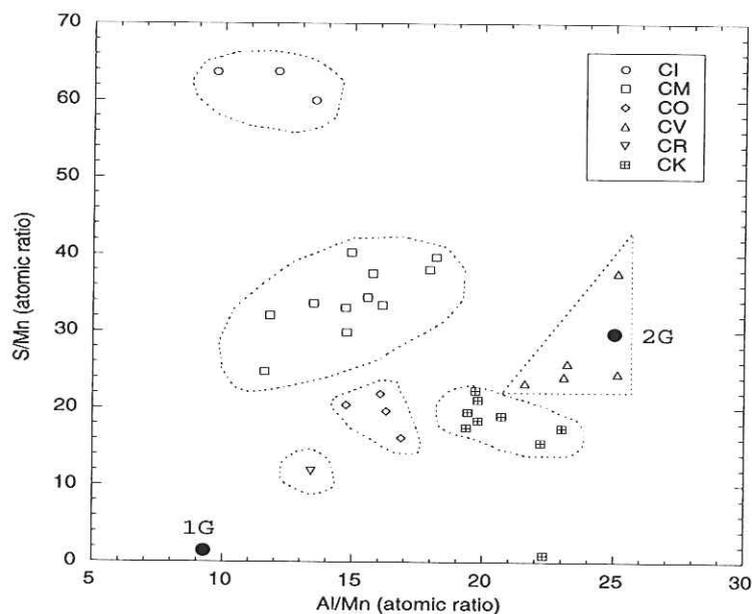


Fig. 1: S/Mn vs. Al/Mn diagram for carbonaceous chondrites.

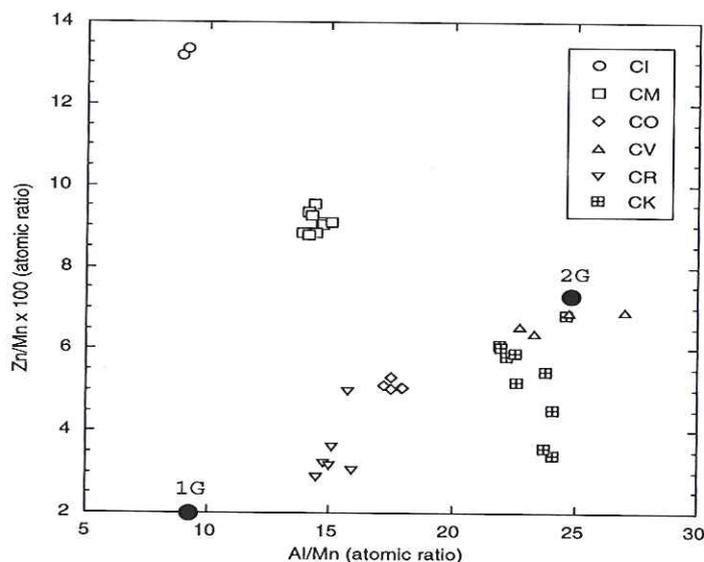


Fig. 2: Zn/Mn vs. Al/Mn diagram for carbonaceous chondrites.

and Mn compared with those of 2G. From these observations, it is inferred that 1G is ordinary chondrite-like material in chemical composition.

Chemical groups of ordinary chondrites are commonly judged based on petrological observations such as fayalite content in olivine and Co content in kamacite. Siderophile abundance was once proposed for a possible criterion for such classifications. After extensive analyses of

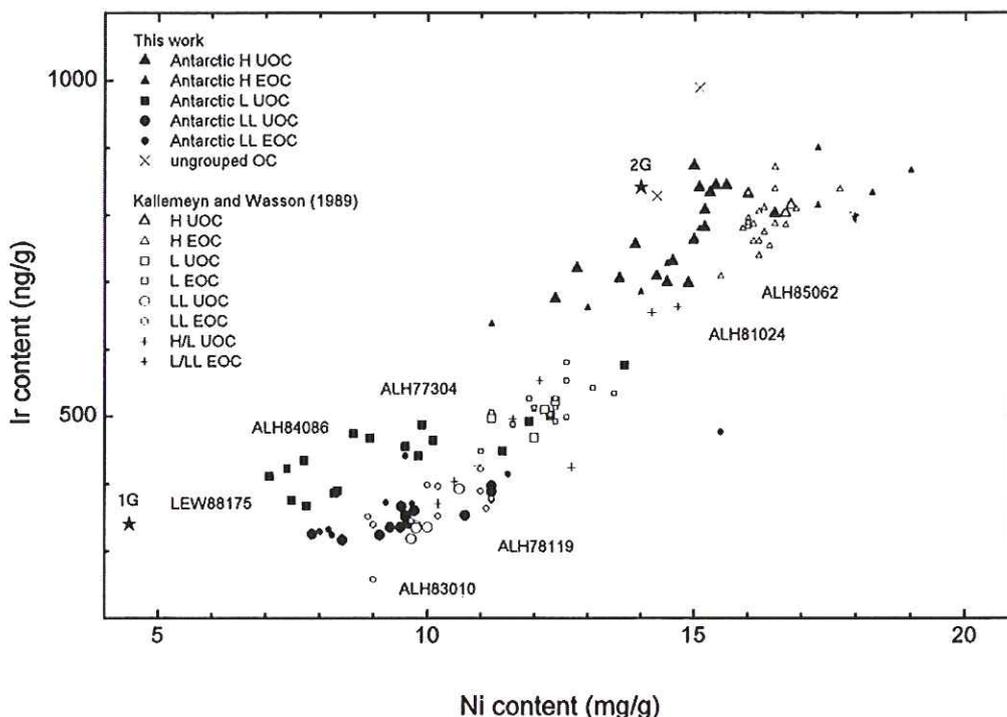


Fig. 3: Ir vs. Ni diagram for ordinary chondrites(Ozaki 1998), on which 1G and 2G are plotted.1G is plotted on a line extended from a trend of represented by L group chondrite.

Antarctic ordinary chondrites, Ozaki (1998) concluded that there is a limitation in applying siderophile contents to the classification of ordinary chondrites, especially for weathered meteorites like Antarctic meteorites, because metals are lost by terrestrial weathering to certain extent depending upon its degree. He examined his large INAA data and proposed a diagram of Ni vs. Ir for the classification of chemical groups of ordinary chondrites (Fig. 3). On this diagram, three chemical groups of ordinary chondrites are plotted discretely from each other, having correlation trends with different inclinations. If the sample 1G is plotted on this diagram, it does not seem to cluster with any group of ordinary chondrites as shown in Fig. 3. Nevertheless, its position is on a line extended from a trend represented by L group chondrites. As discussed by Ozaki (1998), Ir and Ni contents decrease with increasing the degree of weathering, being caused by loss of metals, but the correlation between Ni and Ir is kept unchanged. Based on these observations and discussions, we propose that 1G is ordinary chondrite in chemical composition and is classified as L. As the boundary between L and LL is obscure in some cases, a possibility of LL cannot be ruled out. Considering the location of 1G in Fig. 3 and its low abundance of siderophile elements, we suspect that metals were separated when 1G were prepared. Severely weathered ordinary chondrites may indicate similar characteristics, but a possibility that 1G is a heavily weathered (Antarctic) L chondrite must be deduced because the sample used in this work does not look rusty and no Antarctic meteorites show such extreme features in siderophile abundances.

Finally, it may be worth noting that the above discussion could be developed even for a sample of smaller amount. The analytical sensitivity for key elements used in discussion is relatively high in the activation analyses applied in this work. It may also be emphasized that the samples used in this study remain without any loss or physical destruction. In INAA and IPAA, radioactivity is induced by nuclear reactions, and some level of such radioactivity still remain after cooling for several months. This means that samples once used for INAA and IPAA need to be stored in the controlled area and the further use of the same samples is restricted. In other words, however, these samples can be reused for other purposes such as mineralogical and petrological studies within the restriction. Some destructive elemental analyses such as radiochemical NAA (RNAA) and inductively-coupled plasma mass spectrometry (ICP-MS) as well as isotopic measurements can also be performed for them. Thus, we conclude that the analytical scheme we proposed can work very effectively for characterizing a sample of small amount in elemental abundance and, hence, it can be best applied to the initial analysis of the sample returned from space by space missions like the MUSES-C.

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