



Original article

High sensitivity determination of iridium contents in ultra-basic rocks by INAA with coincidence gamma-ray detection

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ABSTRACT

Very low contents (in the range of 10^{-9} g/g) of Ir in mantle-derived rock samples (komatiites) were non-destructively determined by INAA coupled with coincidence gamma-ray spectrometry using 16 Ge detectors. Aliquots of the same samples were analyzed by NiS fire-assay ICP-MS for Ir and other platinum group elements. Because the INAA procedure used in this study is non-destructive and is almost free from spectral interference in gamma-ray spectrometry, the INAA values of Ir contents obtained in this study can be highly reliable. Iridium values obtained by ICP-MS were consistent with the INAA values, implying that the ICP-MS values of Ir obtained in this study are equally reliable. Under the present experimental conditions, detection limits were estimated to be 1 pg/g, which corresponds to 0.1 pg for a sample mass of 0.1 g. These levels can be even lowered by an order of magnitude, if necessary, which cannot be achieved by ICP-MS carried out in this study.

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1. Introduction

Iridium belongs to platinum group elements (PGEs). PGEs are one of the most informative element groups in geo- and planetary sciences [e.g., 1,2]. Because of their strong siderophile nature, PGEs are highly compatible with metallic phase. In the Earth, therefore, PGEs were mostly concentrated in the core during the differentiation of the Earth at early stage of the solar system formation. Such a process, in turn, yielded severe depletion of PGEs in mantle and, especially, in crust. For determining very low contents of PGEs in the Earth silicate samples, analytical methods having high sensitivity for the PGE quantification are needed.

In the past, radiochemical neutron activation analysis (RNAA) was actively applied to accessible Earth silicate samples [e.g., 3]. In RNAA of PGEs in silicate samples, high neutron doses are required in order to achieve high analytical sensitivities of most PGEs. After the neutron irradiation, the activated samples are to be cooled for

certain period for safe handling of radioactive materials. Nowadays, inductively coupled plasma mass spectrometry (ICP-MS) has taken the place of RNAA [e.g., 4]. In determining very low amounts of PGEs in silicate samples by ICP-MS, the target elements (here, PGEs) are to be concentrated through chemical separation procedures after decomposing silicate materials either by acid digestion or by alkaline fusion [e.g., 5]. An isotope dilution (ID) technique is often applied for obtaining accurate analytical results of multi-isotope elements. Even with ID, final data cannot be accurate when contamination of analytes and/or incomplete decomposition of solid samples occur [5]. RNAA with strong alkaline flux like Na_2O_2 can mostly avoid these analytical difficulties [6]. In this sense, RNAA can serve as a definitive method even now and probably forever, although RNAA values tend to be accompanied with relatively large uncertainties compared with ICP-MS values [7].

For circumventing these analytical problems, non-destructive methods like instrumental NAA (INAA) can be the best choice if applicable. Among PGEs, Ir has a high sensitivity in NAA as implied by a relatively large neutron capture cross section for the (n,γ) reaction on ^{191}Ir (Table 1) and can be reliably determined by INAA for its contents in primitive meteorite samples [e.g., 10,11], where Ir contents are around 500–800 ng/g, not being depleted along with

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Table 1
Nuclear properties related to the (n,γ) reaction on $^{191}\text{Ir}^a$.

^{191}Ir		
	isotopic abundance (%)	37.3
	thermal neutron cross section (barn)	260 + 660 ^b
	resonance integral (barn)	1100 + 4000 ^b
$^{192m1}\text{Ir}$		
	half-life	1.45 m
	decay mode (%) [‡]	IT (99.98), β ⁻ (0.02)
^{192}Ir		
	half-life	73.83 d
	decay mode (%) ^c	β ⁻ (95.24), EC (4.76)
	gamma-ray energy (keV) followed by branching ratio (%) in parentheses	296.0 (28.71)
		308.5 (29.70)
		316.5 (82.86)
		468.1 (47.84)
		604.4 (8.22)
		612.5 (5.34)

^a [8,9].

^b Leading to isomeric + ground state.

^c IT: isomer transition, β⁻: beta minus, EC: electron capture.

other PGEs compared with their solar system abundances [12]. For the terrestrial silicate samples, however, Ir contents can hardly be determined by conventional INAA method because of severe depletion of Ir in these samples [13]. In this study, we have determined Ir contents in komatiite, a volcanic rock derived from ultrabasic mantle, by INAA using a sophisticated Ge-semiconductor detector system consisting of multiple Ge detectors for counting coincident gamma-rays emitted by ^{192}Ir . (Hereafter, this method of INAA is called INAA-CG.) In addition, an aliquot of each komatiite sample was analyzed for Ir and other PGEs by using a quadrupole ICP-MS instrument, and ICP-MS-derived Ir values obtained in this study and by other workers were compared with our INAA-CG data. Based on the obtained results, the characteristics and reliability of the INAA-CG applied in this study were described.

2. Experimental

2.1. Instrumental neutron activation analysis with coincident gamma-rays (INAA-CG)

Sample preparation A total of five samples were analyzed. Those samples are all komatiites, which are Mg-rich and Si-poor volcanic rocks, probably delivered from ultramafic mantle beneath the Earth crust. In Table 2, names and related descriptions of these samples are summarized. Each sample in powder was donated by Prof. M. Humayun of Florida State University. About 100 mg of each sample was sealed in an ultra-high purity synthetic quartz tube (Shin-Etsu Chemical Co., Ltd.; 3 mm inner diameter x 4 cm long), which was washed with nitric acid, rinsed with ultra-pure water (so-called Milli-Q water) and dried before the use. For the quantification of Ir, a reagent standard sample was prepared by doping a known amount of the certified Ir solution (SPEX CertiPrep, U.S.) on the ultra-pure MgO (specpure-grade) in a quartz tube. The Allende meteorite powder sample prepared by the Smithsonian

Institution, Washington, D.C [14]. was used as a monitor sample. These reference samples were prepared in the same fashion as that for komatiite samples. Quartz tubes containing komatiite samples and two kinds of reference materials along with an empty tube were individually wrapped with high purity Al foil, bundled together with Al foil and inserted into a irradiation capsule for neutron irradiation.

Neutron irradiation The neutron irradiation was carried in the JRR-3 reactor of Japan Atomic Energy Agency (JAEA) with a neutron flux of $9.6 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ for 48 h. After cooling for one month, quartz tubes were rinsed with nitric acid and water. Although some fission fragments from ^{235}U in Al foil may have remained in the outer layer of the quartz tubes, no further washing was conducted in considering that significant interference could hardly occur in the gamma-ray counting system used in this study as described below.

Gamma-ray counting Gamma-ray counting was conducted with a detector system named GEMINI-II [15] (Fig. 1), which consists of 16 Ge semiconductor detectors with coincidence gamma-ray detection circuit, located at the Tandem accelerator building of JAEA. Fig. 1a shows an external appearance of GEMINI-II. Each irradiated sample in a tube was placed at the center of the detector assembly (Fig. 1b) and counted for a few hours to half a day. An absolute counting efficiency at 1332 keV of ^{60}Co was about 2%.

2.2. Inductively coupled plasma mass spectrometry (ICP-MS)

Sample preparation To enhance the signal-to-noise ratio in ICP-MS measurements, Ir and other PGEs were extracted from komatiite samples. The extraction procedure is essentially the same as previously described [13] and briefly outlined here. Each komatiite powder sample weighing about 5 g was spiked with enriched isotopes of ^{191}Ir (and other PGE spikes), and fused with Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ along with Ni powder and sulfur in a ceramic

Table 2
Descriptions of komatiite samples analyzed in this study.

Sample name	Texture	Location
KAL-1	Random olivine spinifex	Alexo, Abitibi greenstone belt, Canada
ALX-21	Olivine cumulate	Alexo, Abitibi greenstone belt, Canada
9490	Olivine cumulate	Kostomuksha, Kostomuksha greenstone belt, Russia
9493	Upper chilled margin	Kostomuksha, Kostomuksha greenstone belt, Russia
94,111	Upper chilled margin	Kostomuksha, Kostomuksha greenstone belt, Russia

(a)

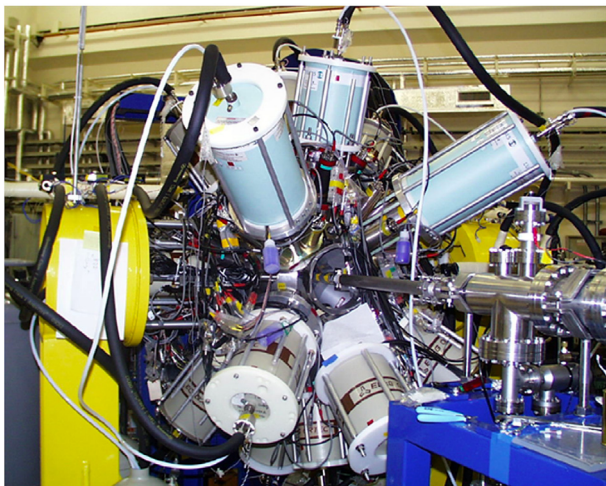


Fig. 1a. External appearance of GEMINI-II, an array of 16 Ge detectors.

crucible for 2 h at 1000 °C. After cooling, NiS buttons, in which PGEs were concentrated as sulfides, were mechanically separated, and dissolved in 6 M HCl. The solution was filtered with 0.2 μm polytetrafluoroethylene membrane filter (Advantec, Tokyo, Japan), with Ni being in the filtrate. Insoluble PGE sulfides were collected on a filter and dissolved in 12 M HCl with 30% H₂O₂.

ICP-MS measurements After known amounts of In and Tl were added as internal standards, PGEs-enriched solutions were properly diluted with Milli-Q water and introduced to a quadrupole ICP-MS instrument (Plasma Quad 3, Fissons Instruments, UK.). Iridium contents were determined by an ID method.

3. Results and discussion

3.1. Quality control on our ICP-MS data

Among the five komatiite samples analyzed in this work, KAL-1 [16] is distributed as a komatiite reference material, for which Ir and other PGE contents have been reported in several studies [13–15] and are summarized in Table 3. Our Ir values are reported as a mean ± internal repeatability (1s for n = 10). It is to be noted that uncertainties for literature values are quoted from corresponding references and may not be defined on the same criterion. Among the three literature value sets, those by Puchtel and Humayun [17] were obtained by using a sector-type ICP-MS with ID method, where komatiite samples were fused with alkaline flux and PGEs were extracted by NiS fire-assay method, while those by Rehkämper et al. [18] were obtained by using a multi-collector sector-type ICP-MS with ID method, where samples were

Table 3

Ir contents (ng/g) in komatiite reference sample KAL-1 determined by ICP-MS.

	Ir
This work ^a	1.64 ± 0.07
Literature values	
[17]	1.71 ± 0.06
[18]	1.71 ± 0.03
[19]	1.89 ± 0.18

^a Mean ± standard deviation due to internal repeatability (n = 10).

decomposed in Carius tubes with aqua regia followed by desilicification in PFA (perfluoroalkoxy alkane) beakers using hydrochloric acid and hydrofluoric acid. The data set reported by Meisel and Moser [19] were obtained by using a quadrupole-type ICP-MS with ID method, where samples were decomposed with reverse aqua regia in a high-pressure asher and Ir was chemically separated by ion chromatography. As shown in Table 3, our value is in good agreement with the literature values, with the Meisel and Moser [19] value being a bit higher. Despite of the difference in preparing the sample solutions including sample decomposition/digestion methods and the type of ICP-MS instruments, all Ir values are consistent within the reported uncertainty margins. This suggests that our Ir values obtained by ICP-MS are reliable and that their comparison with INAA data is meaningful.

3.2. Ir contents determined by INAA-CG and their comparison with ICP-MS data

In NAA of Ir in rock samples, the (n,γ) reaction on ¹⁹¹Ir is commonly used. On neutron irradiation, ¹⁹¹Ir is converted to ^{192m}Ir or ¹⁹²Ir, which is transitioned to ¹⁹²Ir with a half-life of 1.45 m. ¹⁹²Ir then decays to ¹⁹²Pt with a half-life of 73.8 d. In this decay, a ¹⁹²Pt nuclide emits a number of gamma-rays during its transition from higher energy states to lower (or grand) states. In Table 3, nuclear properties related to the (n,γ) reaction on ¹⁹¹Ir are summarized. Fig. 2 illustrates a conventional gamma-ray spectrum of the neutron-activated Allende meteorite sample, where about 35 mg of the sample was irradiated with neutrons for 20 min, cooled for 9 d, and subjected to gamma-ray counting for 6 h. In Fig. 2, four major gamma-ray peaks (with emission probabilities larger than 10%) emitted on the ¹⁹²Ir decay can be recognized. Iridium concentration in this meteorite sample was determined to be 789 (±24) ng/g (ppb) by INAA-CG in this work, which is very close to a literature value of 788 (±17) [10] ng/g. This content corresponds to about 26 ng of Ir absolute mass. Because ¹⁹¹I has relatively large cross section (about 920 b as a summed values of two mode productions of ¹⁹²Ir; Table 1) for the thermal neutron capture reaction, Ir contents can be nondestructively determined for such samples under the experimental condition described above. It may be noted that ¹⁹¹I has a higher sensitivity in INAA than that implied by a thermal neutron capture cross section, because ¹⁹¹Ir has a resonance

(b)

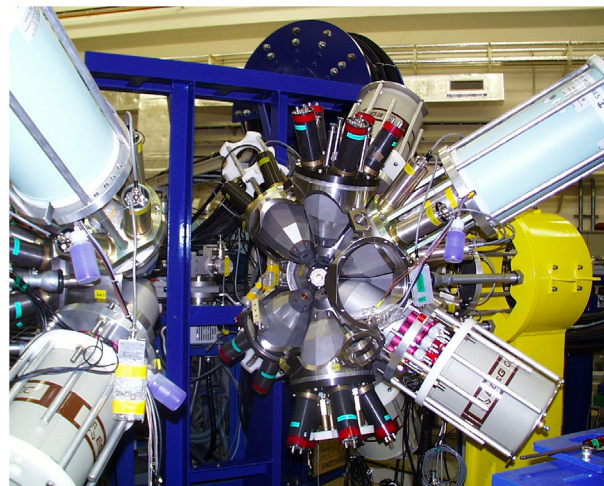


Fig. 1b. Internal appearance of GEMINI-II. An irradiated sample sealed in a quartz tube is placed in the center of detector heads.

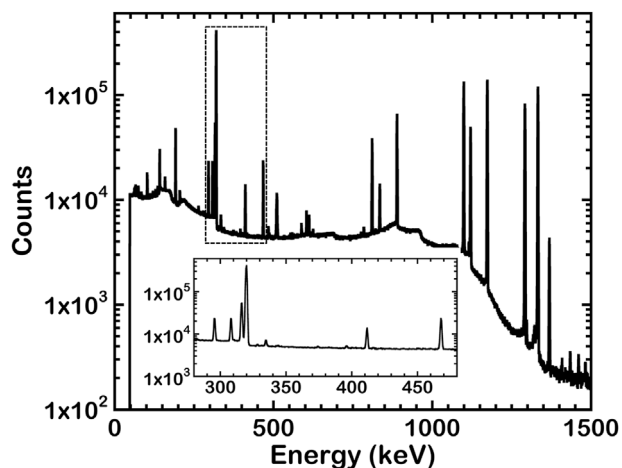


Fig. 2. Gamma-ray spectrum of the Allende meteorite (sample mass: 35 mg; irradiation time: 20 min; cooling time: 8.6 d; counting time: 6 h). An energy range from 280 keV to 480 keV is enlarged and inserted. In this enlargement, four major gamma-ray peaks appear due to the decay of ¹⁹²Ir, along with a large peak due to ⁵¹Cr at 320 keV.

integral of 5100 b (as a summed value; Table 1) for the capture of epithermal neutrons. In the spectrum of Fig. 2, background counts at 300 keV are about 7×10^3 per channel and the peak corresponding to 316.5 keV due to ¹⁹²Ir decay is 6×10^4 counts. Based on these values, a rough calculation shows that $\mu\text{g/g}$ levels of Ir in most terrestrial silicate samples cannot be quantitatively determined by the above-mentioned INAA procedure applied to the Allende meteorite sample.

Fig. 3 illustrates a two-dimensional plot for the coincidence detection of two gamma-rays measured by using GEMINI-II. This plot was obtained from the neutron-irradiated Allende meteorite sample weighing 91.3 mg, which was irradiated for 24 h, cooled for 71 h and counted for 24 h. Among the four major gamma-rays emitted on the decay of ¹⁹²Ir, paired gamma-rays of 468.1 keV and 316.5 keV (emission probabilities of 47.8% and 82.9%, respectively) (Table 1) are emitted in cascade in the ps scale and coincident counts of these two gamma-rays yield a red spot at the intersection of two arrows corresponding to the two gamma-rays in Fig. 3. From similar plots for komatiite samples, their Ir contents were quantified as follows. The gated gamma-ray spectrum is

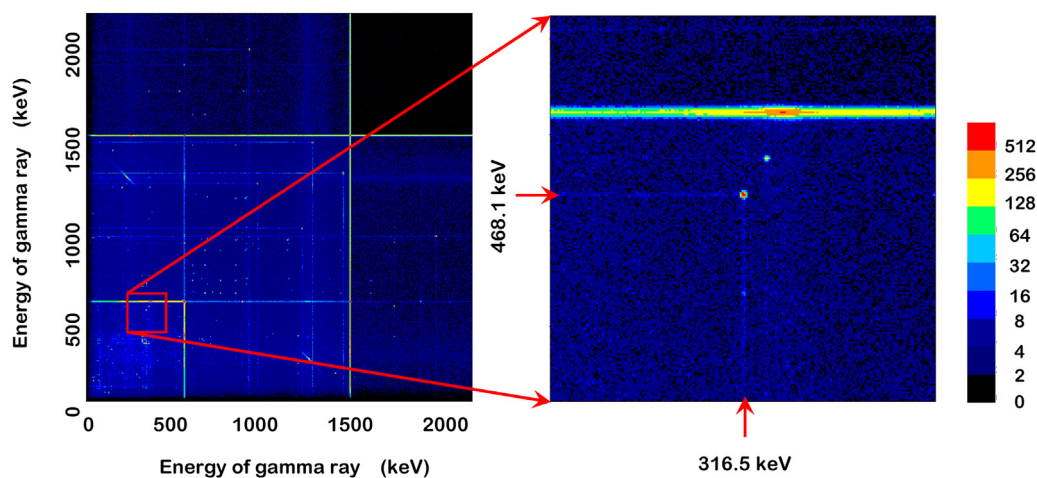


Fig. 3. Two dimensional plot of coincidence counts. A small area (in the left picture) covering two major gamma-rays emitted in cascade due to the decay of ¹⁹²Ir to ¹⁹²Pt is enlarged on the right. A red spot at an intersection of 316.5 keV and 468.1 keV corresponds to their coincidence counts. A yellowish bright, horizontal line corresponds to the annihilation radiation at 511 keV. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Ir contents (ng/g) in komatiite samples analyzed by different analytical methods.

Sample Name	This work		Reference values	
	INAA-CG ^a	ICP-MS ^b	NiS fire-assay ^c	Carius tube ^d
KAL-1	1.86 ± 0.09	1.64 ± 0.07	1.71	1.65
ALX-21	2.19 ± 0.10	1.97 ± 0.07		2.11, 2.13
9490	2.85 ± 0.17	3.30 ± 0.13	6.15	4.15, 4.26
9493	1.81 ± 0.11	1.78 ± 0.06	1.35, 1.43	1.77, 1.85, 1.98
94,111	1.80 ± 0.11	1.57 ± 0.06	1.38, 1.46	1.67, 1.76

^a Value ± statistical counting error.
^b Mean ± standard deviation due to internal repeatability (n = 10).
^c [17].
^d [21,22].

obtained by gating on one proper gamma-ray (either 316.5 keV or 468.1 keV) and analyzed in the same manner as that for a conventional INAA. Iridium contents were determined by a direct comparator method [20] using the Ir reagent sample as reference standard samples.

INAA-CG values of Ir contents thus calculated are compared with our ICP-MS data for five komatiite samples including KAL in Table 4. Iridium contents are all in the range of ng/g, being lower than the determination limit for conventional INAA. Among the data of this work, INAA-CG values are all consistent with ICP-MS values, being within 2 times statistical counting error for four samples (KAL-1, ALX-21, #9490 and #04111) and 1 times statistical counting error for one sample (#9493). Please note that uncertainties accompanied by INAA data and ICP-MS data cannot be compared on the same basis. As mentioned earlier, uncertainties for ICP-MS data are due to internal repeatability for 10 repeated measurements using the same sample solution and largely dependent on the instrumental stability. With well-tuned instruments, they tend to be within a few percent for 1 standard deviation, which was the case of this study as shown in Table 4. In the present study, samples of about 100 mg were used in INAA, while about 5 g was used in ICP-MS. Considering that consistent values were obtained by both methods, the powdered samples used in this study were carefully prepared in terms of homogeneity for the sample size of 100 mg. Except for one sample (#9490), INAA-CG values seem to be a little but systematically larger than ICP-MS values, as implied by an average ratio of 1.10 with a standard deviation of 0.06 (n = 4).

In Table 4, literature values determined by ICP-MS also are referred [17, 21,22]. These values were obtained by analyzing

Table 5
Detection limits of Ir obtained by INAA-CG and ICP-MS^a.

	INAA-CG	ICP-MS
Sample Size (g)	0.1	5
Destructive/non-destructive	Non-destructive	destructive
Detection limit (pg/g)	1	10
Detection limit (pg)	0.1	50

^a See the text for definition of the detection limit.

aliquots of the powder samples we used in this study. INAA and ICP-MS data obtained in this study are well consistent with those literature values except for one sample (#9490), whose literature values differ by a factor up to approximately two. In Table 4, the literature values of ICP-MS were separately listed for two different decomposition procedures, namely NiS fire-assay and Carius tube methods. Methodologically, a Carius tube method is acknowledged to be more effective in decomposing geological, solid samples compared with a NiS fire-assay method [21]. A fact that the Carius tube data are systematically higher than the NiS fire-assay data for #9493 and #94111 among literature values supports the above statement. In ICP-MS of this study, a NiS fire-assay procedure was applied in decomposing komatiite samples. Nevertheless, our ICP-MS data are more consistent with the ICP-MS data obtained by using the Carius tube method rather than those by the NiS fire-assay method in other studies. Experimental conditions of the NiS fire-assay (such as temperature and duration of assay and a sample/flux ratio) may control the decomposition efficiency. It is likely that severer conditions must have been realized in our NiS fire-assay procedure compared with those in other studies. It may be pointed out that our INAA-CG values, which are systematically higher than ICP-MS values of this work as mentioned above, are in excellent agreement with the literature data of ICP-MS with Carius tube for ALX-21, #9493 and #94111, suggesting that the Carius tube procedure performed by other authors completely decomposed these samples and that Ir in these samples was quantitatively recovered in the final solution introduced to an ICP-MS instrument. In comparing all the data in Table 4, it can be claimed that INAA-CG can serve as a benchmark method in assessment of the accuracy of Ir data. As for the #9490 sample, although a small difference was observed between our INAA and ICP-MS data, there seems to be a considerable variation among all values including literature ones, which could be caused by the heterogeneity of the powdered #9490 sample.

3.3. Methodological comparison between INAA-CG and ICP-MS

Comparing the two decomposition procedures for solution-based ICP-MS, there is a size limitation for the Carius tube method compared with that for the NiS fire-assay method; a larger sample mass (e.g., 5 g) can be processed in NiS-fire assay. In this sense, analytical uncertainty due to the sample heterogeneity can be suppressed and more representative values can be obtained when the NiS fire-assay method rather than the Carius tube method is applied for the preparation of sample solutions in ICP-MS. Such an analytical limitation as that for the ICP-MS coupled with Carius tube may also be imposed on INAA-CG. As for the accuracy of the data obtained, however, INAA-CG has a great advantage. Because INAA-CG is a nondestructive method and, hence, Ir data obtained by this method scarcely involve procedural contamination and are less affected by improper experimental treatment.

In Table 5, detection limits of Ir are compared for INAA-CG and ICP-MS procedures under the experimental conditions of this study. In the table, two detection limits (the mass fraction, pg/g and

the absolute mass, pg) are shown. As seen in Table 5, the mass fraction limit of Ir is ten times lower for INAA-CG than that for ICP-MS (1 pg/g vs. 10 pg/g, respectively), while INAA-CG yielded five hundred times lower the absolute mass detection limit (0.1 pg) than that by ICP-MS (50 pg). Increasing the sample mass could be done for both INAA and ICP-MS, but it doesn't seem to be practical for either method. In INAA-CG in this work, samples were irradiated for 48 h. Considering a half-life of ¹⁹²Ir (73.8 d), detection limits for INAA-CG could practically be lowered by at least several times and even by one order of magnitude by prolonging the irradiation time. In addition, INAA-CG is essentially free from spectral interference in gamma-ray spectrometry and, hence, the data reliability is not dependent on matrix compositions of the samples, which is completely different from conventional INAA. Thus, the INAA method coupled with coincidence gamma-ray detection described in this study can be not only the most sensitive but also the most reliable analytical method for the determination of ultra-trace amounts of Ir in rock samples.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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