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Chemical composition of magnetic spherules collected from deep sea sediment

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Chemical composition of 15 magnetic spherules collected from deep sea sediment was determined by instrumental neutron activation analysis (INAA) under two different irradiation conditions using the Kyoto University Reactor (KUR). Based on their chemical composition, nine spherules were judged to be of extraterrestrial origin. The differences in the chemical composition of the nine spherules are discussed in terms of condensation temperatures for the elements. Comparing the detection limits derived from INAA under two different irradiation conditions, the sensitivity for INAA using KUR is discussed.

Introduction

Magnetic spherules were discovered from deep sea sediments in the Pacific Ocean by the Challenger Expedition for the first time, and some of them were reported to be extraterrestrial in origin.[1] Since then, the origin of those samples has been investigated in terms of their chemical composition, which was often measured by instrumental neutron activation analysis (INAA). INAA is useful because of its high sensitivity for Ir which is critical in judging the origin of spherules.[2–5] In our previous study, chemical composition of magnetic spherules recovered from the Pacific Ocean sea sediment was measured by INAA using the Kyoto University Reactor (KUR), and the criteria for identifying extraterrestrial spherules was discussed.[5] In this study, 15 magnetic spherules which were newly collected from the same location as that in our previous study was subjected not only to the conventional INAA using KUR[5] but also to INAA with higher neutron fluence rate and a longer irradiation time in order to reach higher sensitivity in the determination. Based on the results of two different irradiation conditions, we discuss the sensitivity in the elemental analysis using KUR through comparing detection limits for several elements of interest derived from the INAA applied for this study. Furthermore, as regards the cosmochemical issue, the differences in the chemical composition of spherules analyzed in this study are investigated from the view point of condensation temperature for the elements. It seems to be important to consider the condensation process of the elements constituting the spherules for discussion about the parent material and the formation mechanism of magnetic spherules, which has not been explained fully in terms of chemical composition obtained by INAA.

Experimental

Fifteen magnetic spherules were collected from the Pacific Ocean sea sediment. The method of sampling for the spherules has been reported elsewhere.[5] The chemical composition of the spherules was analyzed by INAA under two different irradiation conditions using KUR: (1) 50-minute irradiation using the pneumatic transport system with thermal neutron fluence rate (n_{th}) of $2.75\cdot10^{13}$ cm$^{-2}\cdot$s^{-1} and fast neutron fluence rate (n_f) of $6.0\cdot10^{12}$ cm$^{-2}\cdot$s^{-1} and (2) 50–70-hour irradiation at the inner reactor site with n_{th} of $4.65\cdot10^{13}$ cm$^{-2}\cdot$s^{-1}and n_f of $1.4\cdot10^{13}$ cm$^{-2}\cdot$s^{-1}. The values of the neutron fluence rate were estimated by TAKEUCHI.[6] Details of sample preparation in irradiation (1) have been reported elsewhere.[5] For irradiation (2), each spherule sample was washed with ethanol, and then sealed in an aluminum foil bag. The spherule samples and a reference standard were packed in an irradiation capsule made of aluminum. As the reference standard for irradiation (2), we used impurities in high-purity aluminum sheet (Al: 99.999%) and in a nickel sheet whose contents were determined in a separate experiment using INAA. After neutron irradiation, γ-rays emitted from the samples were measured by a low background Ge detector.

All spherules were firstly subjected to irradiation (1). The samples were allowed to decay for 1–2 hours and then individually counted for 300–1800 seconds for analysis of Mn. Next, the samples were allowed to decay for one week and then individually counted for 80,000–170,000 seconds for Sc, Cr, Fe, Co, Ni, and Ir. After an interval of 2–6 months, the spherules in which Ir contents had been lower than the detection limit in irradiation (1) were subjected to irradiation (2).

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After irradiation (2), those spherules were allowed to decay for one week and counted for 80,000–170,000 seconds for measurement of Sc, Co, Ni, and Ir whose contents had been lower than the detection limits in irradiation (1). By INAA, therefore, under the two different irradiation conditions using KUR, we measured Fe, Co, Ni, Ir, Sc, Mn, Cr contents of the spherules. Manganese contents of all the spherules were corrected by subtracting the contribution of ^{56}Mn produced by the first neutron induced reaction of ^{56}Fe(n,p)^{56}Mn, which was determined by irradiating a high grade pure iron sample containing 30 $\mu g \cdot kg^{-1}$ Mn as an impurity under the same irradiation conditions.

Results and discussion

Comparison of the detection limits derived from INAA under two different irradiation conditions

The detection limits obtained for Fe, Co, Ni, Ir, Sc, Mn, and Cr by INAA under two different irradiation conditions using KUR are shown in Table 1. A detection limit in this study is defined as a value corresponding to three sigma of the background counts at the peak area of the gamma-ray emitted by a nuclide of interest.

Since Ni was determined by counting ^{58}Co produced by an (n,p) reaction on ^{58}Ni, the detection limit of Ni is affected by the different fast neutron fluence between the two irradiation conditions. Considering the difference in thermal or fast neutron fluence between the two irradiation conditions, the detection limits for irradiation (2) are expected to be lower than those for irradiation (1) by more than two orders of magnitude. From Table 1, however, it can be generally noticed that those for (2) are systematically lower than those for (1) by a range between one and two orders of magnitude. It should be noted that the detection limit in INAA depends not only on the neutron fluence but also other experimental conditions such as sample size, detector efficiency and so on. Among them the effects from co-existing elements, particularly Fe in the case of the magnetic spherules in this study, are highly crucial. It is suggested that the effects of co-existing elements lowered the difference in the detection limits between the two irradiation conditions.

Neutron irradiation at the inner reactor site of KUR is usually used for radioisotope production and has never been used for INAA. Therefore, it was the first time that the values from irradiation (2), shown in Table 1, were obtained by applying the neutron irradiation at the inner reactor site to INAA. It is, therefore, important to present here some detection limit values for the analysis of similar samples to spherules when using irradiation (2) in the future.

Chemical composition of magnetic spherules

Eight magnetic spherules (SS121–SS128) were subjected only to irradiation (1), and seven (SS129–SS135) to both (1) and (2). Measured contents of seven elements (Ir, Co, Ni, Fe, Mn, Cr, and Sc) in 15 magnetic spherules are summarized in Table 2. In SS129–SS135, upper limit values given in (1) were replaced by the results from (2). Uncertainties refer only to counting statistics (1σ) from gamma-ray spectrometry of (1) and (2), respectively.

Since the abundance of siderophile elements represented by Ir in the earth crust and mantle is much lower than that in chondrites and iron meteorites,[2] the content of Ir becomes a good indicator for extraterrestrial matter. Therefore, nine spherules among 15 in this study (SS121–SS129), in which Ir contents were determined to be more than 0.37 $mg \cdot kg^{-1}$, are judged to be of extraterrestrial origin. Although the remaining six spherules in which Ir contents were lower than the detection limit (SS130–SS135) are also assumed to be of extraterrestrial origin on the basis of the criterion about Fe and Co contents,[5] only the spherules which are safely judged to be of extraterrestrial origin due to their Ir contents are discussed in this study.

The nine extraterrestrial spherules can be classified into two groups; spherules in which Sc contents were lower than the detection limits (SS121–SS126) and Sc-detected spherules (SS127–SS129). The elemental abundances normalized to those of CI chondrite in the nine extraterrestrial spherules are shown in Fig. 1.[13]

Table 1. Detection limits of Fe, Co, Ni, Ir, Sc, Mn, and Cr in this study

Element:	Fe, μg	Co, pg	Ni, ng	Ir, pg	Sc, pg	Cr, ng	Mn, pg
Detection limit (1):	0.11–0.55	110–530	22–97	2.2–11	12–66	1.6–6.0	14–390
Detection limit (2):	N.M.	4.4–34	0.86–3.9	0.099–0.51	0.59–4.3	N.M.	N.M.

N.M.: Not measured.

Table 2. Measured contents of individual magnetic spherules

Sample	Weight, μg	Ir, $mg \cdot kg^{-1}$	Co, $mg \cdot kg^{-1}$	Ni, %	Fe, %	Mn, $mg \cdot kg^{-1}$	Cr, $mg \cdot kg^{-1}$	Sc, $mg \cdot kg^{-1}$
SS121	8.4	12 ± 1	3400 ± 100	9.7 ± 0.6	68 ± 4	67 ± 3	910 ± 270	<3.0
SS122	3.9	7.8 ± 0.7	1800 ± 100	1.4 ± 0.3	65 ± 4	55 ± 4	(1200 ± 600)	<3.6
SS123	33.0	8.22 ± 0.26	3490 ± 60	3.80 ± 0.18	71.9 ± 2.3	5 ± 1	673 ± 86	<1.03
SS124	34.8	6.85 ± 0.29	3900 ± 90	3.52 ± 0.24	74.8 ± 2.6	8 ± 1	307 ± 99	<1.89
SS125	10.9	3.98 ± 0.32	4750 ± 190	6.30 ± 0.54	66.7 ± 3.8	207 ± 8	539 ± 147	<3.42
SS126	11.6	17.1 ± 0.5	2240 ± 110	4.41 ± 0.44	64.0 ± 3.5	12 ± 2	1240 ± 190	<2.74
SS127	12.7	(0.37 ± 0.13)	625 ± 19	1.05 ± 0.11	20.1 ± 1.3	1090 ± 50	1480 ± 180	5.63 ± 0.65
SS128	25.8	0.92 ± 0.11	698 ± 22	1.68 ± 0.11	31.5 ± 1.2	1570 ± 40	4190 ± 220	4.19 ± 0.51
SS129	2.3	0.44 ± 0.04*	220 ± 60	0.51 ± 0.03*	21 ± 3	570 ± 20	1900 ± 300	14 ± 3
SS130	13.2	<0.023*	134 ± 15	<0.030*	54.0 ± 2.0	3230 ± 70	(140 ± 60)	55.7 ± 2.6
SS131	13.1	<0.039*	3030 ± 70	2.32 ± 0.17	70.5 ± 2.1	115 ± 4	783 ± 93	1.03 ± 0.20*
SS132	11.6	<0.013*	697 ± 27	0.220 ± 0.008*	27.2 ± 1.6	1460 ± 50	3590 ± 310	5.74 ± 0.92
SS133	28.6	<0.013*	160 ± 18	<0.009*	56.5 ± 2.0	2490 ± 70	469 ± 62	36.6 ± 1.6
SS134	21.9	<0.011*	206 ± 12	0.024 ± 0.006*	61.2 ± 1.6	2070 ± 60	500 ± 63	26.9 ± 0.9
SS135	32.2	<0.007*	70.2 ± 8.6	0.063 ± 0.004*	11.5 ± 0.8	2620 ± 60	3150 ± 190	14.5 ± 1.1
Chondrite:[a]		0.36–0.76	490–840	1.02–1.75	18.2–29.0	1450–2620	2650–3880	5.7–11.4
Iron meteorite:		0.01–60[b]	3800–9200[c]	5.3–25[b]	79.6–93.6[d]	<0.1[e]	<1–2360[c]	0.002–2.52**[f]

( ) Values near the detection limits.
* Results from the irradiation (2).
** $\mu g \cdot kg^{-1}$.
[a] Data from WASSON and KALLEMEYN (1988).[7]
[b] Data from WASSON (1985).[8]
[c] Data from LOVERING et al. (1957).[10]
[d] Data from BUDDHUE (1946).[9]
[e] Data from HONDA et al. (1991).[11]
[f] Data from HONDA et al. (1988).[12]

The CI chondrites belong to the most primitive meteorites and their elemental abundances represent the original parent material for the solar system. From Fig. 1, it is found that the elemental abundances in SS121–SS126 are different from those in CI chondrite. Iridium, Co, and Ni which belong to the siderophile elements, and Fe contents in SS121–SS126 are higher than those in CI chondrite, whereas Mn and Cr, which belong to the lithophile elements, are lower. The condensation temperatures for Ir, Co, Ni, Fe, Mn, Cr, and Sc are 1603 K, 1356 K, 1354 K, 1337 K, 1190 K, 1301 K, and 1652 K, respectively.[14–16] Manganese has the lowest condensation temperature among the seven elements. Manganese abundances in SS121–SS126 normalized to the CI chondrite values are the lowest among the elements discussed. The higher the condensation temperature of the element is, the higher CI-normalized abundances for five elements except for Sc tend to be in SS121–SS126. On the other hand, CI-normalized abundances for seven elements have approximately identical values in SS127–SS129. From the difference in CI-normalized abundances between SS121–SS126 and SS127–SS129, it is suggested that the parent material of the one type of spherule is different from that of the other type of spherule and that these two types of spherules are formed through different mechanisms. At the present stage, it is suggested that SS127–SS129 containing over a few $mg \cdot kg^{-1}$ of Mn and Sc would not be produced from iron meteorites with low contents of Mn and Sc as shown in Table 2. Therefore, the parent material of SS127–SS129 is suggested to be chondrites. To elucidate the parent material of SS121–SS126 and the formation mechanism of extraterrestrial spherules in detail, further studies along this line are in progress.

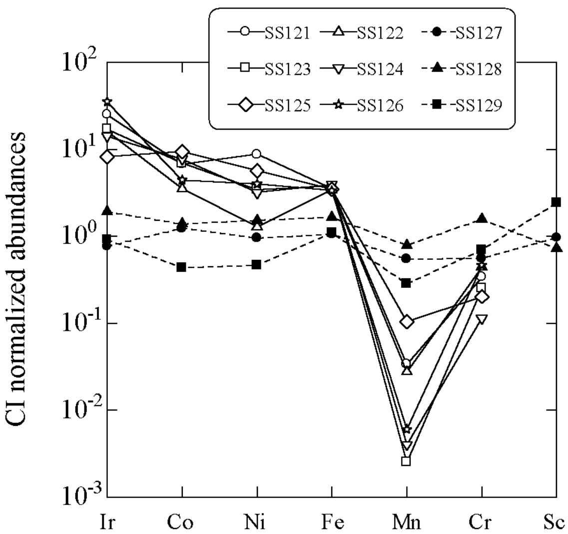

Fig. 1. CI normalized abundances of Ir, Co, Ni, Fe, Mn, Cr, and Sc in extraterrestrial spherules

Conclusions

Chemical composition of 15 magnetic spherules was determined by INAA using KUR. From the detection limits derived from the INAA under two different irradiation conditions, the sensitivity for elemental analysis using KUR was discussed. Based on the Ir contents in spherules, nine spherules were judged to be extraterrestrial in origin. It is shown that extraterrestrial spherules can be divided into two groups: one containing spherules in which CI-normalized abundances differ among the element analyzed, Ir, Co, Ni, Fe, Mn, and Cr, and the other containing spherules in which CI-normalized abundances have approximately identical values. In the former group of spherules, CI-normalized abundances may have been controlled by condensation process for the elements.

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