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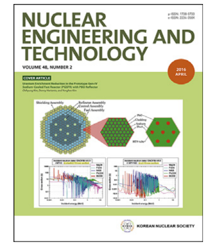

Invited Article

Origin of Spherule Samples Recovered from Antarctic Ice Sheet—Terrestrial or Extraterrestrial?

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ABSTRACT

Thirty-eight spherules from the Antarctic ice sheet were analyzed using neutron activation analysis under two different conditions to investigate their origin. In almost all of these spherules, the contents of iron, cobalt, and manganese were determined to be 31% to 88%, 17 mg/kg to 810 mg/kg, and 0.017% to 7%, respectively. A detectable iridium content of 0.84 mg/kg was found in only one spherule, which was judged to be extraterrestrial in origin. A comparison of elemental compositions of the Antarctic spherules analyzed in this study with those of deep-sea sediment spherules and those of terrestrial materials revealed that most of the Antarctic spherules except for the sample in which iridium was detected could not be identified as extraterrestrial in origin.

1. Introduction

The *Challenger* expedition detected spherule samples for the first time from deep-sea sediments in the Pacific Ocean, some of which were reported to be extraterrestrial in origin [1]. Since then, the origin of those samples has been investigated in terms of their chemical compositions [2–4]. Spherule samples were found in the Antarctic and Greenland ice sheets as well as in deep-sea sediments [5]. Although many terrestrial and artificial contaminants were also detected in the Antarctic ice sheet, particles with matrix element compositions similar to those of the Allende and Murchison carbonaceous chondrites were separated from terrestrial contaminants by using a scanning electron microscope with an energy dispersive X-ray spectrometer [6]. Those particles, which included spherical and irregular shapes, are defined as Antarctic micrometeorites [6]. The measurement of noble gas compositions revealed that these Antarctic micrometeorites are extraterrestrial in origin and originated from carbonaceous chondrites [7,8]. We measured the chemical compositions of spherule samples recovered from the Pacific Ocean sea sediments through instrumental neutron activation analysis (INAA) by using the

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Kyoto University Reactor (KUR), and we designated spherules with relatively high iridium contents of 0.37–38 mg/kg as extraterrestrial [9,10]. In this study, the chemical compositions of 38 spherules from the Antarctic ice sheet were determined using INAA. In terms of both siderophile and lithophile element contents, the differences between the 38 Antarctic spherules and spherules from sea sediment measured in our previous study [9–11] were revealed. Additionally, whether the origin of the Antarctic spherules is terrestrial or extraterrestrial is discussed on the basis of the criteria used by Kobayashi and Ebihara [4] and Sekimoto et al [9] to judge the origin of spherules.

2. Materials and methods

The 38 spherule samples measured in this study were detected through microscopy from precipitated particles in a water tank at Dome Fuji station in Antarctica. The precipitated particles were F97B series supplied by the National Institute of Polar Research. By using a separation method based on grain size, magnetism, and other parameters [6], the F97B series were separated from the residue identified as 971127-2 by the National Institute of Polar Research after filtering the contents of the water tank. The diameters and weights of the 38 spherule samples ranged from several tens to hundreds of microns and a few to a few tens of micrograms, respectively. The elemental compositions of the spherules were analyzed with INAA under two different conditions using the KUR: (i) 50-minute irradiation using the pneumatic transport system (Pn-2) with a thermal neutron flux (n_{th}) of 2.75×10^{13} cm^2/s [12] and (ii) 50- to 70-hour irradiation at the inner reactor site with an n_{th} of 4.65×10^{13} cm^2/s. For the type ii irradiation, 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

Table 1 – Measured contents of the 38 Antarctic spherules evaluated in this study.

Sample	Weight (μg)	Fe (%)	Co (mg/kg)	Ni (%)	Ir (mg/kg)	Sc (mg/kg)	Mn (%)	Sb (mg/kg)	Co/Fe × 10^{-3}
1 spherule: Co/Fe ratio > 2.0 × 10^{-3}									
F97BN032	5.1	31.3 ± 1.5	675 ± 24	1.60 ± 0.15	0.84 ± 0.22	13.8 ± 1.4	0.237 ± 0.008	–	2.2
15 spherules: 0.085 × 10^{-3} < Co/Fe ratio < 2.0 × 10^{-3}									
F97BN005	6.0	62.7 ± 2.0	104 ± 13	<0.22	<0.03	4.5 ± 0.9	0.221 ± 0.003	<1.51	0.17
F97BN009	4.2	61.9 ± 4.4	807 ± 80	<0.70	<0.02	(0.13 ± 0.06)	0.594 ± 0.007	0.45 ± 0.09	1.3
F97BN010	4.5	65.5 ± 3.6	113 ± 33	<0.53	<0.92	<3.6	0.092 ± 0.002	–	0.17
F97BN011	2.3	80.8 ± 4.6	1,480 ± 86	<0.78	<0.04	0.69 ± 0.11	0.742 ± 0.010	1.5 ± 0.8	1.8
F97BN012	5.5	63.5 ± 2.8	229 ± 31	<0.34	<0.03	<0.19	0.419 ± 0.005	4.50 ± 0.95	0.36
F97BN013	10.0	65.5 ± 3.2	541 ± 41	<0.36	<0.04	<0.23	0.430 ± 0.005	1.7 ± 0.8	0.83
F97BN014	17.1	62.3 ± 1.4	634 ± 12	(0.08 ± 0.04)	<0.01	(0.11 ± 0.04)	0.429 ± 0.004	1.13 ± 0.27	1.0
F97BN017	3.2	76.6 ± 3.5	119 ± 34	<0.48	<0.06	<0.40	0.387 ± 0.006	4.88 ± 1.17	0.16
F97BN024	2.5	56.1 ± 4.2	568 ± 74	<0.74	<0.03	2.1 ± 0.2	0.516 ± 0.007	0.30 ± 0.08	1.0
F97BN027	10.4	41.3 ± 2.0	108 ± 17	<0.24	<0.02	(0.11 ± 0.06)	0.108 ± 0.004	<0.47	0.26
F97BN029	6.0	74.7 ± 2.4	1,530 ± 52	<0.28	<0.04	<0.29	0.348 ± 0.004	<1.83	2.0
F97BN030	5.3	39.4 ± 3.1	<45	<0.55	<0.03	25.2 ± 3.9	7.166 ± 0.163	<2.24	<0.11
F97BN036	5.0	67.3 ± 3.8	155 ± 32	<0.46	<0.05	<0.32	0.017 ± 0.001	<1.94	0.23
F97BN107	18.4	71.9 ± 5.5	63.4 ± 14.0	<0.10	<0.03	<0.19	0.326 ± 0.009	2.72 ± 0.19	0.088
F97BN116	3.0	69.0 ± 4.3	119 ± 34	<0.71	<1.25	<4.5	0.265 ± 0.009	–	0.17
22 spherules: Co/Fe ratio < 0.085 × 10^{-3}									
F97BN008	11.2	86.2 ± 3.5	37.3 ± 12.1	<0.27	<0.39	(1.8 ± 1.0)	–	–	0.043
F97BN015	8.0	64.9 ± 2.7	38.1 ± 10.6	(0.17 ± 0.11)	<0.02	<0.11	0.598 ± 0.022	1.63 ± 0.45	0.059
F97BN022	6.5	88.0 ± 4.1	(44 ± 19)	<0.40	<0.03	1.12 ± 0.12	0.324 ± 0.010	<0.86	0.050
F97BN026	12.8	77.5 ± 2.9	<17	<0.22	<0.02	<0.12	1.034 ± 0.026	1.42 ± 0.30	<0.022
F97BN028	18.6	83.0 ± 2.9	45.0 ± 8.5	0.17	<0.01	0.19 ± 0.06	0.534 ± 0.012	0.25 ± 0.12	0.054
F97BN035	10.1	81.9 ± 3.4	68.8 ± 16.0	<0.28	<0.41	<1.9	–	–	0.084
F97BN031	18.2	68.4 ± 2.6	50.1 ± 9.4	<0.18	<0.23	(1.8 ± 0.7)	0.382 ± 0.016	–	0.073
F97BN033	12.6	63.2 ± 2.8	(23 ± 11)	<0.23	<0.01	<0.07	0.323 ± 0.009	0.56 ± 0.16	0.036
F97BN101	24.0	69.3 ± 5.1	35.8 ± 8.0	<0.03	<0.02	(0.15 ± 0.07)	0.226 ± 0.006	0.25 ± 0.05	0.052
F97BN102	34.3	65.9 ± 1.6	40.6 ± 3.1	(0.08 ± 0.03)	<0.01	0.22 ± 0.09	0.342 ± 0.010	6.03 ± 0.32	0.062
F97BN103	21.7	78.0 ± 5.6	18.9 ± 4.0	<0.10	<0.02	1.5 ± 0.4	0.146 ± 0.004	0.88 ± 0.12	0.024
F97BN104	32.6	72.2 ± 1.8	15.7 ± 2.5	<0.07	<0.09	<0.50	0.073 ± 0.003	–	0.022
F97BN106	26.9	69.6 ± 1.8	50.6 ± 5.1	<0.09	<0.02	(0.12 ± 0.07)	0.111 ± 0.003	3.99 ± 0.23	0.073
F97BN110	16.1	67.9 ± 2.3	55.3 ± 9.3	<0.18	<0.02	0.36 ± 0.06	0.311 ± 0.009	3.87 ± 0.22	0.081
F97BN111	52.0	66.5 ± 4.8	42.1 ± 4.0	<0.02	<0.02	<0.14	0.262 ± 0.008	1.76 ± 0.14	0.063
F97BN112	29.1	71.3 ± 1.8	12.9 ± 3.5	<0.09	<0.12	<0.62	0.299 ± 0.009	–	0.018
F97BN113	14.6	71.0 ± 5.1	39.5 ± 10.0	<0.08	<0.03	<0.20	0.336 ± 0.010	1.28 ± 0.17	0.056
F97BN114	11.7	64.5 ± 2.1	(17 ± 7)	<0.18	<0.28	2.09 ± 0.67	1.274 ± 0.037	–	0.026
F97BN115	8.9	70.4 ± 5.6	53.4 ± 18.0	<0.25	<0.03	<0.26	0.365 ± 0.011	<0.35	0.076
F97BN117	5.7	68.1 ± 5.3	37.9 ± 17.0	<0.12	<0.13	<1.5	0.065 ± 0.003	–	0.056
F97BN119	3.0	67.9 ± 6.7	<45	<0.37	<0.24	<2.9	0.240 ± 0.009	–	<0.066
F97BN120	4.3	63.9 ± 2.4	(40 ± 16)	<0.31	<0.04	<0.28	0.231 ± 0.008	<0.40	0.063

–, Not measured; ( ), values are near the detection limit.

aluminum. As the reference standard for the type ii irradiation, we used impurities in the high-purity aluminum sheet (Al: 99.999%) of which the contents were determined in a separate experiment using INAA. For the type i irradiation, each spherule was sealed in a clean plastic bag. The spherule samples, a reference meteorite sample, and chemical standards were packed in an irradiation capsule composed of plastic. As the reference meteorite sample, powder of the Allende meteorite prepared by the Smithsonian Institution (split 11, position 11) was used [13]. The chemical standards of iron, cobalt, nickel, iridium, and manganese were prepared as follows. Appropriate amounts of standard solutions of these elements were dropped on filter papers that were then dried under an infrared lamp. After irradiation, γ rays emitted from the samples were measured by using a low background Ge detector. Through INAA under the two different conditions using the KUR, we measured the elemental contents of iron, cobalt, nickel, iridium, scandium, manganese, gold, lanthanum, cerium, samarium, antimony, and arsenic in the spherules. In determining the manganese content, the contribution of the fast-neutron-induced reaction of $^{56}Fe(n, p)^{56}Mn$ was corrected by irradiating a high-grade pure iron sample containing 30 μg/kg manganese as an impurity under the same irradiation conditions as those used for the spherule samples. The manganese content in all of the spherules was calculated by subtracting the contribution of ^{56}Mn produced by the (n, p) reaction from the total ^{56}Mn measured.

3. Results and discussion

3.1. *Chemical compositions of the Antarctic spherules*

The measured contents of iron, cobalt, nickel, iridium, scandium, manganese, and antimony in the 38 Antarctic spherules are summarized in Table 1. The other elements include lanthanum, at 0.05–5.42 mg/kg in seven spherules; samarium, at 0.03–0.79 mg/kg in five spherules; arsenic, at 1.7–3.2 mg/kg in four spherules; cerium, at 7–30 mg/kg in three spherules; and gold, at 0.008–0.009 mg/kg in two spherules.

On the basis of the iron, cobalt, nickel, and iridium contents, the characteristics of the Antarctic spherules and their origin were examined. Because the abundance of siderophile elements represented by iridium in the Earth's crust and mantle is much lower than that in chondrites and iron meteorites [2], the content of iridium is a good indicator of extraterrestrial matter. Of the 38 spherules analyzed in this

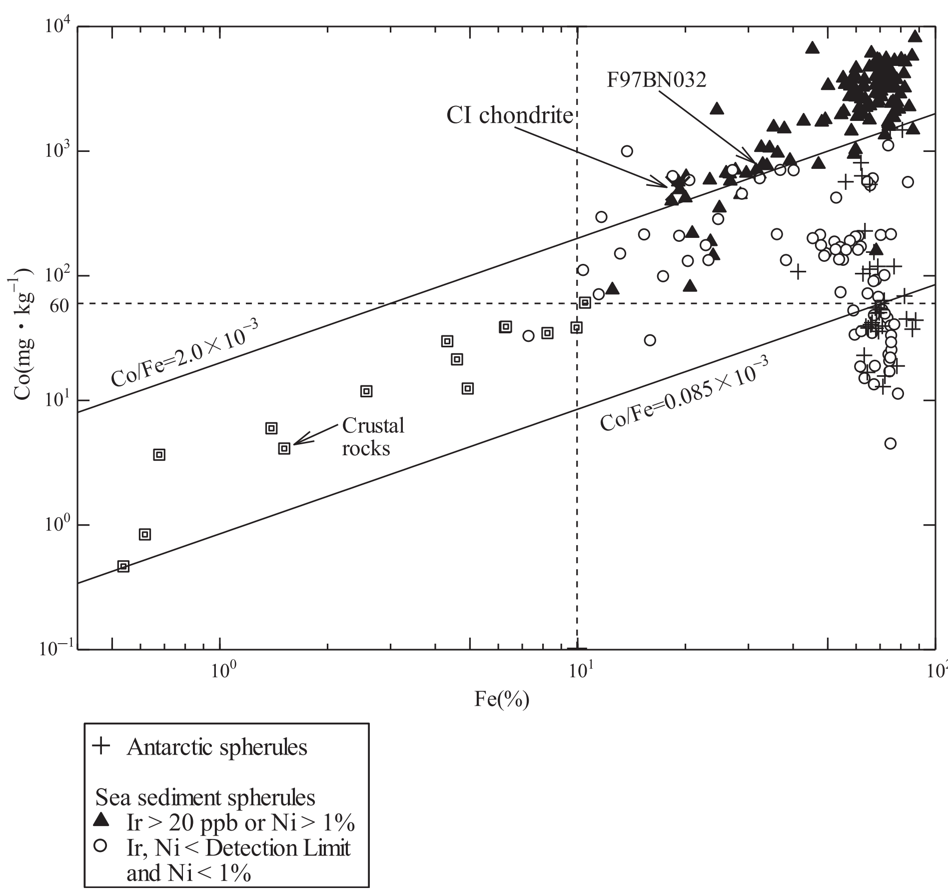

Fig. 1 – Correlation of iron and cobalt contents. Plus symbols indicate Antarctic spherules; the cross indicates CI chondrite [14]; and double squares indicate crustal rocks [15]. Triangles and circles denote sea sediment spherules [9–11]; closed triangles show spherules with greater than 20 μg/kg iridium or greater than 1% nickel; circles represent iridium and nickel contents lower than the detection limit or less than 1% nickel. Co/Fe ratios of 2.0×10^{-3} and 0.085×10^{-3} are represented by the upper and lower solid lines, respectively.

study, only one (F97BN032), in which the iridium content was measured to be 0.84 mg/kg, was judged to be extraterrestrial in origin. Our previous work on magnetic spherules collected from sea sediments proposed that the criterion for spherule samples to be extraterrestrial in origin is a nickel content greater than 1% [11]. However, no Antarctic spherules measured in this study satisfied this criterion except for F97BN032. Therefore, from the perspective of nickel and iridium contents, 37 of the 38 Antarctic spherules analyzed in this study could not be identified as extraterrestrial in origin.

3.2. *Iron and cobalt contents in the Antarctic spherules*

Because both iron and cobalt were able to be detected in almost all of the Antarctic spherules in this study and in the magnetic spherules from sea sediment, the correlation between iron and cobalt in the two types of spherules was investigated (Fig. 1). These elemental contents in crustal rock samples [15] and in CI chondrite [14] are also included in Fig. 1. The magnetic spherules from sea sediment tended to have greater than 10% iron and greater than 60 mg/kg of cobalt, and their contents were higher than those in the crustal rock samples. In particular, those in most of the magnetic spherules that were judged to be extraterrestrial in origin by detectable contents of iridium and nickel, as indicated by triangles in the figure, were higher than those in magnetic spherules in which the iridium and nickel contents were lower than the detection limits, as indicated by circles in the figure. Therefore, the iron and cobalt contents of the spherule samples may be suggested as criteria for discriminating extraterrestrial spherules. On the contrary, most of the Antarctic spherules have lower cobalt content than those of the magnetic spherules from sea sediment, which

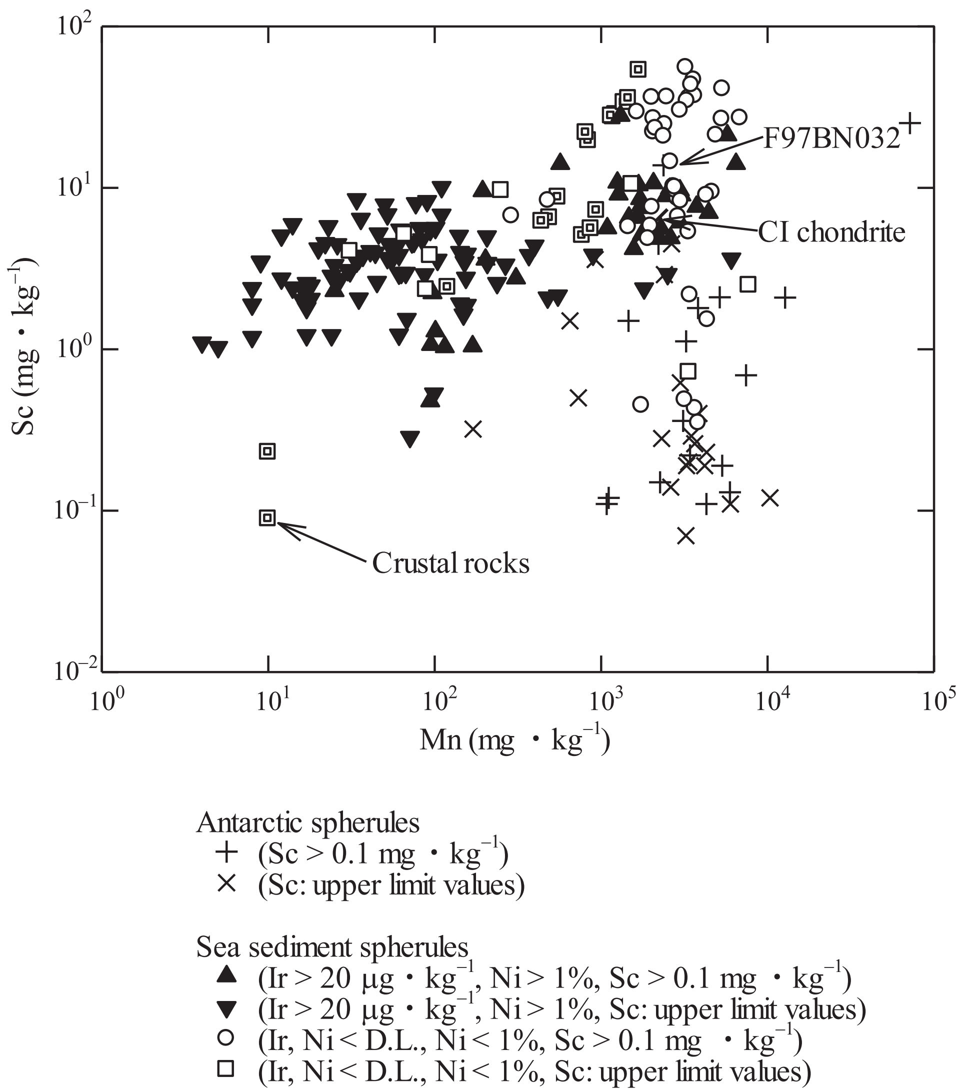

Fig. 2 – Correlation of manganese and scandium contents. Plus symbols and smaller cross symbols indicate Antarctic spherule values; the larger cross shows CI chondrite [14]; and double squares represent crustal rocks [15]. Triangles, circles, and squares denote sea sediment spherules [9–11]; closed triangles show spherules with greater than 20 μg/kg iridium; circles and squares represent iridium contents lower than the detection limits and less than 1% nickel. Smaller cross symbols, inverted triangles, and squares represent the upper limit values of scandium.

were judged to be extraterrestrial in origin based on iridium and nickel contents, as indicated by triangles in the figure [9–11].

The differences between the Antarctic spherules and the sea sediment samples were also investigated in terms of the Co/Fe ratio in addition to iron and cobalt contents (Fig. 1). It was reported that the magnetic spherules from sea sediment that were judged to be extraterrestrial in origin had Co/Fe ratios greater than 2.0×10^{-3} [4]. Fig. 1 shows that the Co/Fe ratios of most of the magnetic spherules from sea sediment that were judged to be extraterrestrial in origin in our previous work [9–11], that of F97BN032 in this study, and that of CI chondrite were greater than 2.0×10^{-3}, which is higher than those of crustal rocks. The Co/Fe ratios of crustal rocks range from 0.085×10^{-3} to 2.0×10^{-3} [15]. As shown in the figure, the Co/Fe ratios of crustal rocks were similar to those of 15 Antarctic spherules and most of the magnetic spherules from sea sediment in which the nickel and iridium contents were measured to be lower than the detection limits. Those of the remaining 22 Antarctic spherules were less than 0.085×10^{-3}.

Of the 37 Antarctic spherules in which the origin was not identified to be extraterrestrial according to the iridium and nickel contents, 15 spherules, which had Co/Fe ratios similar to those of crustal rocks, appeared to originate from natural and terrestrial materials such as crustal rocks. The remaining 22 appeared to originate from a source that is unnatural or not terrestrial.

3.3. *Manganese and scandium contents in magnetic spherules*

To discuss the characteristics of Antarctic spherules based the contents of manganese and scandium, which are classified as lithophile elements, the correlation between the manganese and scandium contents in two types of spherule samples was investigated (Fig. 2). These contents for crustal rocks [15] and CI chondrite [14] are also included in Fig. 2. In the figure, the scandium values in the following symbols are the upper limits: cross symbols indicating the Antarctic spherules, inverted closed triangles and open squares representing the sea sediment spherules. The magnetic spherules from sea sediment with less than 100 mg/kg Mn tended to have lower scandium content than the detection limit, as indicated by the inverted triangles in the figure, whereas the magnetic spherules with greater than 1,000 mg/kg Mn tended to have more than a few milligrams per kilogram of scandium, as indicated by the open circles in the figure. In the crustal rock samples with less than 100 mg/kg Mn, the scandium content was lower than 1 mg/kg; in samples with greater than 1,000 mg/kg Mn, the scandium content was more than a few mg/kg. On the contrary, it was found that the scandium against manganese contents in most of the Antarctic spherules were obviously lower than those of sea sediment spherules and crustal rocks. In terms of the correlation between manganese and scandium, it was confirmed that the 37 Antarctic spherules excluding F97BN032 were different from the magnetic spherules that were extraterrestrial in origin [9–11] and from terrestrial rock samples [15]. Therefore, the 37 Antarctic spherules, which were determined to be neither extraterrestrial nor natural and terrestrial in origin, are likely artificial contaminants, as reported by Nakamura et al [6].

3.4. *Origin of the Antarctic spherules*

A plausible origin of the Antarctic spherules analyzed in this study is summarized in Table 2. The following criteria were used in evaluating their origin.

According to the contents of iron and cobalt in the spherules reported in our previous work [9,11], the origin of spherules with greater than 10% iron and greater than 60 mg/kg cobalt is extraterrestrial, and that of less than 10% of iron or less than 60 mg/kg cobalt is other than extraterrestrial.

On the basis of the Co/Fe ratio in the spherules proposed in this paper and considering the criterion of the ratio introduced by Kobayashi and Ebihara [4], the origin of spherules with greater than 2.0×10^{-3} Co/Fe is extraterrestrial; that of 0.085×10^{-3} to 2.0×10^{-3} Co/Fe is extraterrestrial or natural and terrestrial; and that of less than 0.085×10^{-3} Co/Fe is other than extraterrestrial and other than natural and terrestrial.

Table 2 shows that among the 38 spherules, only F97BN032—with greater than 10% iron, greater than 60 mg/kg cobalt, and greater than 2.0×10^{-3} Co/Fe—was judged to be extraterrestrial in origin. Fourteen spherules with greater than 10% iron, greater than 60 mg/kg cobalt, and 0.085×10^{-3} to 2.0×10^{-3} Co/Fe were suggested to be extraterrestrial or natural and terrestrial in origin. One spherule, F97BN030—with greater than 10% iron, less than 60 mg/kg cobalt, and 0.085×10^{-3} to 2.0×10^{-3} Co/Fe—was judged to be natural and terrestrial in origin. Twenty-one spherules with greater than 10% iron, less than 60 mg/kg cobalt, and less than 0.085×10^{-3} Co/Fe were determined to be artificial in origin considering the manganese and scandium contents in the spherules analyzed. The origin of the one spherule with greater than 10% iron, greater than 60 mg/kg cobalt, and less than 0.085×10^{-3} Co/Fe could not be identified at present.

Table 2 – Plausible origin of the Antarctic spherules evaluated in this study.

Fe content	Co content (mg/kg)	Co/Fe ratio	Number of Antarctic spherules	Origin
>10%	>60	$>2.0 \times 10^{-3}$	1	Extraterrestrial
>10%	>60	$0.085 \times 10^{-3} < Co/Fe < 2.0 \times 10^{-3}$	14	Extraterrestrial or natural terrestrial
>10%	<60	$0.085 \times 10^{-3} < Co/Fe < 2.0 \times 10^{-3}$	1	Natural terrestrial
>10%	>60	$<0.085 \times 10^{-3}$	1	Unidentified
>10%	<60	$<0.085 \times 10^{-3}$	21	Artificial

4. Conclusion

The chemical compositions of 38 spherule samples collected from precipitated particles in the water tank at Dome Fuji station in Antarctica were determined by INAA under two different conditions by using the KUR. Only one spherule, F97BN032, was judged to be extraterrestrial in origin on the basis of its iridium and nickel contents. Considering the iron and cobalt contents, the Co/Fe ratio, and the correlation between scandium and manganese, the differences among the remaining 37 Antarctic spherules and sea sediment spherules containing extraterrestrial matter or crustal rocks as terrestrial materials were revealed. Based on the criteria of iron and cobalt contents, the origin of these Antarctic spherules was discussed. Of these, 21 spherules were considered to be artificial in origin.

Conflicts of interest

The authors declare no competing financial interest.

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