

TRACE ELEMENT CONCENTRATIONS IN IRON TYPE COSMIC SPHERULES DETERMINED BY THE SR-XRF METHOD

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Abstract: The X-ray fluorescence method using synchrotron radiation (SR-XRF) was applied to determine trace element abundances in iron type (I-type) cosmic spherules collected at deep-sea sediments. Cr, Co, and Ni were detected from almost all spherules and average concentrations are 1336, 2991 ppm, and 4.0%, respectively. Ga, Ge, and Mn were detected from 20, 30, and 20% of spherules and average concentrations are 4, 4 and 486 ppm, respectively. Spherules containing metallic cores were enriched in Ni and Co and depleted in volatile elements such as Ga and Ge relative to those without cores. The Ni and Co enrichments resulted from high concentrations of the elements in the metallic cores, while the Ga and Ge depletion might indicate that core-bearing spherules have experienced more severe heating during atmospheric entry than the core-lacking ones.

On the basis of Mn concentration we divided spherules into two groups: high and low Mn groups. Trace element abundances of the low Mn group are systematically fractionated relative to those of iron meteorites: volatile elements are depleted and refractory ones are enriched in the spherules. This appears to be consistent with the hypothesis that I-type spherules are ablation products of iron meteorites that have lost volatile elements during melting. Production of the low Mn spherules by ablation of chondritic meteorites is also possible, but chondrite melting should have occurred under a limited range of oxygen fugacity in order to enrich Cr and remove Mn in the spherules. Spherules belonging to high Mn group show a complex trace element pattern when normalized to chondrites. A large Mn excess relative to Cr in this type of spherules can not be explained by any formation process, thus it is difficult to infer the precursor material of the Mn-rich spherules.

1. Introduction

Iron-type spherules are extraterrestrial particles collectable in terrestrial environments. They have a range in size from 10 μm to 2 mm (YAMAKOSHI *et al.*, 1981) and black, smooth, or dull surfaces. Their mineral assemblages and major-element abundances are simple: Fe oxides (wustite, magnetite, and hematite) are predominant and occasionally Fe-Ni metal occurs as a metal core. They are recovered from deep-sea sediments (MURRAY and RENARD, 1891; FINKELMAN, 1970) and Antarctic (*e.g.*, THIEL and SCHMIDT, 1961; YIOU and RAISBECK, 1987) and Greenland (EL GORESY, 1968; MAURETTE *et al.*, 1986) ice fields. They have been studied for more than one century

(*e.g.*, MURRAY and RENARD, 1891; BROWNLEE, 1985) and their extraterrestrial origin was confirmed by the presence of cosmogenic isotopes such as ^{53}Mn (NISHIZUMI, 1983), ^{10}Be , and ^{26}Al (RAISBECK *et al.*, 1986).

The origin of I-type spherules has been controversial for more than three decades: the ablation product of iron meteorites during atmospheric entry (SCHMIDT and KEIL, 1966), or metallic particles separated from metal-rich silicate meteoroids (BLANCHARD *et al.*, 1980). BROWNLEE *et al.* (1983) proposed that I-type spherules are droplets of a metallic melt which has been separated from a chondritic melt consisting of silicate and metallic parts. In their model, the remaining silicate melt becomes stony type (S-type) cosmic spherules. This process explains why S-type spherules are depleted in Ni and Cr and why I- and S-type spherules are found in similar abundance.

Constituents of the I-type spherules are Fe oxides and Fe-Ni metals, so that limited evidence for the formation process can be derived from the mineralogy and the major element chemistry. Origin and the formation process of I-type spherules, therefore, can be elucidated from the signatures of trace element abundance. But small size range of spherules makes it extremely difficult to determine the trace element concentrations. There have been only a few reports on the analyses of trace elements in I-type spherules. CHEVALLIER *et al.* (1987) analyzed trace elements (Ni, Zn, Ga, Ge, Pb, and Se) of two I-type spherules by the X-ray fluorescence method by SR-XRF. They proposed that I- and S-type spherules originated from different meteoroids, because trace element abundances of the two types of spherules are not complementary to each other. NOGAMI *et al.* (1980) determined siderophile element concentrations (Fe, Co, Ni, Ir, Au, and Mn) in I-type spherules by instrumental neutron activation analysis. In their results, Ni and Co contents in spherules are slightly lower than the mean Ni and Co concentrations of iron meteorites. However, heating experiments of an iron meteorite revealed that Ni and Co tend to be enriched in the residues of the experiments (NOGAMI, 1985). Therefore, it was suggested that not only iron meteorites but also other cosmic material must be considered for the sources of these spherules. In this study, we have applied SR-XRF method to determine the trace element concentrations in I-type spherules and discussed on the origin of I-type spherules.

2. Sample Preparation and Experimental Techniques

I-type spherules used in the present study were collected from magnetic fractions separated from the deep-sea sediments that were dredged from a place which is located off the coast of Hawaiian Islands and 5800 m in depth. These spherules range in diameter from 100 to 300 μm . Surfaces of the spherules had been subject to contamination by molecular implantation during passage of atmosphere and alteration by sea water when they were on the sea floor (CHEVALLIER *et al.*, 1987). Degrees of such contamination and alteration are severer on the surfaces than in the interiors of spherules. In order to avoid the effects of contamination and alteration, as much as possible, the spherule samples were washed in a supersonic bath and polished to make thin sections with 30 μm thickness. All spherule samples and standard iron meteorites have a constant 30 μm thickness, which gives an advantage in correction of the absorption effects of X-ray fluorescence. The degree of X-ray absorption depends on

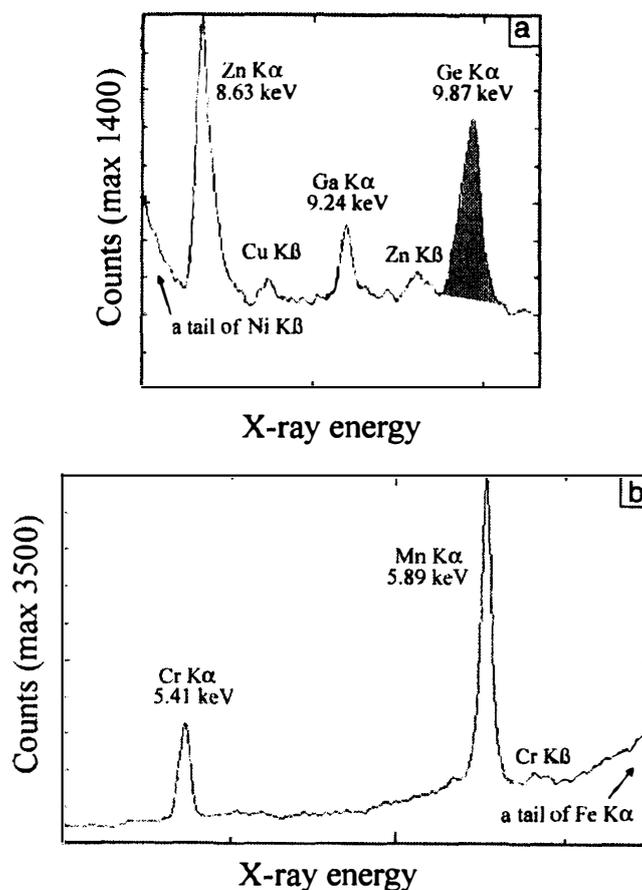


Fig. 1. (a) A synchrotron X-ray fluorescence spectrum of an Odessa (IA) iron meteorite. Ga and Ge concentrations are 76 and 283 ppm, respectively. (b) A synchrotron X-ray fluorescence spectrum of ISPB10 I-type spherule. Cr and Mn concentrations are 183 and 2077 ppm, respectively.

sample's thickness, thus it is determined more simply and precisely when the samples and the standards are the same thickness.

We have determined major element compositions and textural types of spherules by an electron probe microanalyzer (EPMA) JEOL-JCXA733. We performed element mapping to see distributions of Ni, Co, and Mn in the interiors of some spherules using a scanning electron microscope (SEM) JEOL-5800LV. Trace element (Ga, Ge, Cr, Co, and Mn) concentrations of 45 I-type spherules have been measured using a white X-ray microbeam with a beam size approximately $500\mu\text{m} \times 500\mu\text{m}$ at the beam line 4A in the Photon Factory Institute of Materials Structure Science, High Energy Accelerator Research Organization. The samples were attached to nucleopore filters using an acetone-soluble bond. The background concentrations of the trace elements were measured repeatedly and were confirmed to be very low in the filters and the bond. The Odessa IA iron meteorite whose trace element concentrations are well known (CHOI *et al.*, 1995) and two spherule samples whose Mn and Cr concentrations were determined precisely by an EPMA were used for standard samples. We analyzed the standard samples repeatedly in between the sample analyses. A wavelength dispersive spectrom-

eter was used to analyze X-ray fluorescence. X-ray fluorescence from samples was reflected by (001) planes of a graphite crystal and was detected by a position sensitive proportional counter (OHASHI *et al.*, 1993).

Counting time for Co, Cr, Mn, Ga, and Ge was 100, 300, 300, 2000, and 2000 s, respectively. Figures 1a and b show X-ray fluorescence spectra of Ga-Ge and Cr-Mn obtained by the SR-XRF method. Concentrations of the trace elements were quantitatively obtained through X-ray intensity calibrations between spherule and standard samples, and X-ray absorption corrections for differences between surface areas and material matrix of the samples. The concentrations of the elements are given by

$$W_{\text{smp}} = W_{\text{std}} \frac{I_{\text{smp}} \rho_{\text{std}} F_{\text{smp}}}{I_{\text{std}} \rho_{\text{smp}} F_{\text{std}}}, \quad (1)$$

$$F = \frac{\sin\theta}{2\mu} (1 - e^{-2\mu D/\sin\theta}), \quad (2)$$

$$\mu = \rho \sum_i \frac{\mu_i}{\rho_i}, \quad (3)$$

where W is an elemental abundance, I is an intensity of X-ray fluorescence, ρ is a density, F is an absorption factor, θ is an angle between the sample's surface and the X-ray beam that was always 45° , D is thickness of samples and standards ($30\mu\text{m}$), μ is an absorption coefficient of materials, and μ_i/ρ_i is an absorption coefficient per unit mass for element i . Indices 'smp' and 'std' mean sample and standard, respectively. For most elements detection limits are approximately 4–8 ppm in the area of $100\mu\text{m} \times 100\mu\text{m}$, except for Mn and Co whose detection limit were approximately 25 ppm and 360 ppm, respectively.

3. Results

The results of major and trace element analyses of I-type spherules are shown in Table 1. In Table 1, the mean¹ is the lower limit of the mean concentration calculated with an assumption that element concentrations below detection limit are zero. The mean² is the upper limit of the mean concentration calculated with an assumption that element concentrations below detection limit are equal to the detection limit. The differences between upper and lower limits of element concentrations are not significant enough to affect our discussion. Therefore, we will use the mean¹ as the mean value in the following discussion. EPMA analyses indicated that I-type spherules consist entirely of magnetite, wustite, and occasionally Fe-Ni metal. Eight out of 45 spherules contain metallic cores that are enriched in Ni and Co, while others consist entirely of Fe-oxides. All spherules contain variable amounts of Ni ranging typically from 0.1 to 9% and occasionally up to 44%. SEM observations of the Mn-rich spherules revealed that Mn is distributed uniformly in the interior of spherules (Figs. 2a and b). If the spherules were subjected to Mn contamination on the seabed to form Mn-rich surface layers, high concentration of Mn would be detected in peripheries of the cross sections of the spherules. But the SEM image shows homogeneous distribution of Mn (Fig. 2a) which implies that Mn in the spherules could be indigenous, although we cannot completely rule out a possibility of contamination.

Table 1. Elemental abundances of I-type spherules.

	Cr (ppm)	Mn (ppm)	Fe (%)	Ni (%)	Co (ppm)	Ga (ppm)	Ge (ppm)
ISPA10	1683	- ※1	69.7	4.5	-	< 1 ※2	15
ISPA18	817	-	49.7	5.4	-	< 2	< 2
ISPA20	696	-	50.7	44.0	-	< 3	< 3
ISPA21	556	-	68.9	2.8	-	< 1	< 1
ISPA22	1802	-	69.9	3.7	-	12	< 2
ISPA24	159	-	70.1	4.4	-	< 1	< 1
ISPA26	867	-	67.0	2.2	-	< 1	< 1
ISPA27	1093	-	62.6	4.4	-	12	< 1
ISPA28	5020	-	67.3	6.6	-	< 1	< 1
ISPA29	648	-	74.4	0.3	-	< 3	< 2
ISPA30	207	-	65.7	6.3	-	< 2	< 2
ISPA31	580	-	66.8	0.0	-	11	< 3
ISPA32	112	-	53.6	18.5	-	< 3	< 2
ISPB01	545	< 5	70.0	1.7	1109	< 1	< 1
ISPB02	3840	< 10	64.9	1.4	2016	< 1	4
ISPB03	715	< 21	64.8	0.7	4277	< 3	< 2
ISPB04	155	< 18	70.0	6.3	4761	2	3
ISPB05	257	5924	70.6	2.5	3474	< 1	< 1
ISPB06	93	2587	69.4	0.0	< 96	6	4
ISPB07	180	< 9	67.8	3.8	2550	< 1	< 1
ISPB09	994	3505	58.9	1.7	2729	< 2	< 1
ISPB10	183	2077	63.6	1.3	2798	7	< 1
ISPB11	188	< 15	67.8	5.3	18839	< 2	< 1
ISPB12	1167	< 21	64.5	0.0	1242	19	6
ISPB15	571	53	63.4	9.2	3603	< 2	3
ISPB16	446	< 15	65.7	2.1	4461	< 2	< 1
ISPB17	4847	< 17	65.3	1.4	2111	29	4
ISPB18	2075	< 23	74.7	0.4	929	< 3	< 2
ISPB19	10828	< 30	70.0	1.4	-	59	8
ISPB24	1290	< 22	61.6	9.6	4561	< 3	18
ISPB25	373	< 6	62.9	0.3	1266	< 1	< 1
ISPB27	-	-	73.2	2.4	3587	< 3	< 2
ISPB29	194	< 26	73.7	0.7	4073	< 4	7
ISPB40	244	< 19	58.9	1.6	6685	< 3	7
ISPB42	1592	< 28	70.4	1.2	3454	< 4	87
ISPB48	1273	< 25	60.1	2.0	4278	< 4	< 3
ISPB50	1311	< 13	70.3	1.6	189	< 2	2
ISPB51	117	178	64.5	1.6	1534	< 3	< 2
ISPC01	934	< 26	70.3	7.1	4169	-	-
ISPC06	885	< 11	76.2	2.2	1360	-	-
ISPC07	2282	< 16	63.5	2.5	1577	-	-
ISPC08	332	368	62.3	0.8	1088	-	-
ISPC09	111	< 13	65.5	4.6	< 152	-	-
ISPC11	513	377	71.1	1.2	< 157	-	-
ISPC34	5994	< 24	64.8	0.0	< 362	-	-
Mean ¹	1336	486	66.2	4.0	2991	4	4
Mean ²	1336	499	66.2	4.0	3016	6	6
Error#	b	b	a	a	a	c	c

※1 not analyzed

※2 below detection limit

Mean ¹: The lower limit of the mean concentration calculated with an assumption that element concentrations below detection limits are zero.Mean ²: The upper limit of the mean concentration calculated with an assumption that element concentrations below detection limits are equal to the detection limits.

Errors (a: <10 rel.%, b: <20 rel.%, and c: <30 rel.%)

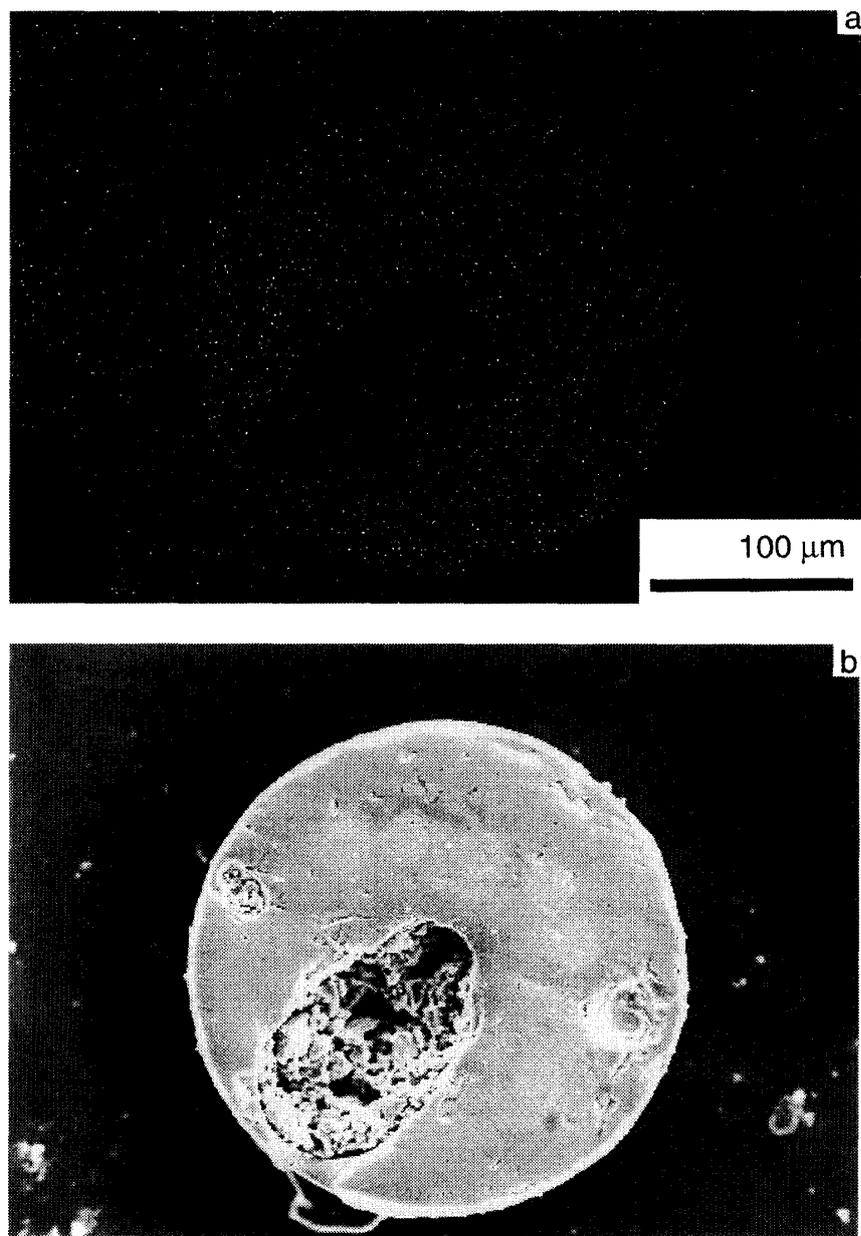


Fig. 2. (a) Mn-K α mapping of ISPBO6 I-type spherule, showing homogeneous distribution of Mn in the interior of the spherule. Bulk Mn concentration of this sample is 0.26 wt%. (b) A SEM image of the same frame as (a). Diameter of ISPBO6 is 250 μ m.

Averages and ranges of trace element concentrations determined by SR-XRF are shown in Fig. 3. Cr and Co were detected from almost all spherules: average concentrations are 1336 and 2991 ppm and range up to 10828 and 18839 ppm, respectively. Ga, Ge, and Mn were detected from 9, 13 and 8 samples and average concentrations of these elements are 4, 4 and 486 ppm, respectively.

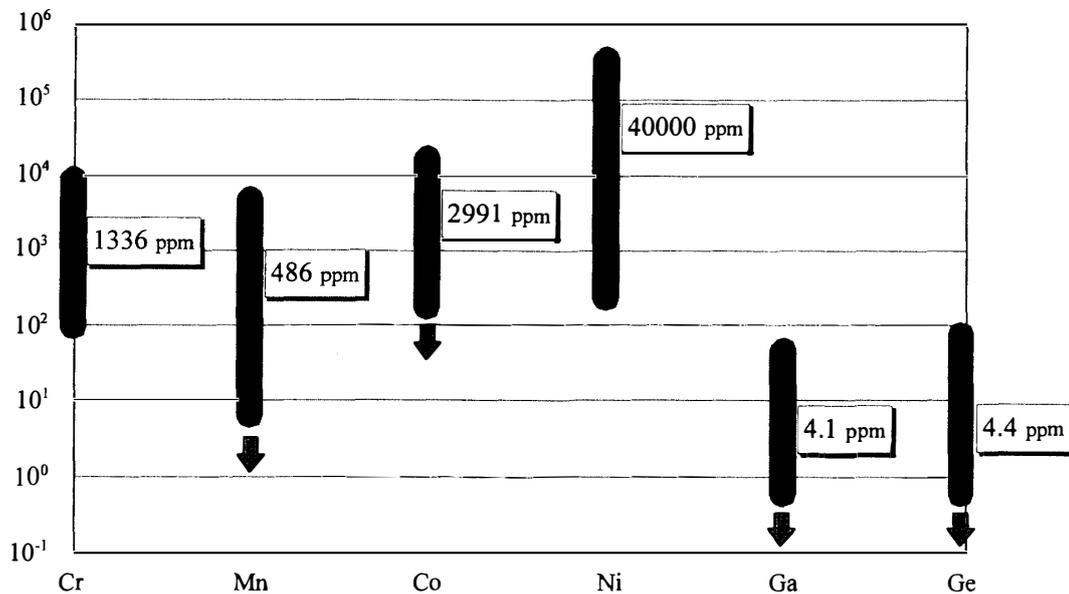


Fig. 3. Elemental abundances of I-type spherules. Gray bars show ranges of concentrations and dark circles show the mean values of all samples. Gray arrows represent the limit of detection. Concentrations of all elements except for that of Ni, which was measured by an EPMA, were determined by the SR-XRF method.

4. Discussion

4.1. Trace element signatures of spherules with Fe-Ni metallic cores

In this section we will discuss the signatures of trace element contents in the spherules having metallic cores. These spherules are enriched in Ni and Co and depleted in Cr, Ga, and Ge relative to spherules without cores (Fig. 4). Ni, Co, and Cr abundances can be explained by the location of these elements in spherules in which Ni and Co are exclusively present in the cores, while Cr is enriched in oxide mantle (e.g., KOSAKEVITCH and DISNAR, 1997). In our analyses elemental signatures of metallic cores strongly inherit to those of thin sections of spherules, since volume ratios of cores to mantles of thin sections of spherules are higher than those of true ratios obtained from bulk spherules. Thus, the lower abundance of Cr and higher abundances of Ni and Co in the spherules with cores are likely due to Ni and Co enrichments and Cr depletion in metallic cores. On the contrary, Ga and Ge are sensitive indicators of heating up on atmospheric entry, since they are volatile enough to be lost from spherules by vaporization. Heating duration of the spherules with cores might have been shorter than those without cores, because oxidation proceeded from surfaces of spherules and prolonged oxidation resulted in total replacement of metallic cores by Fe-oxides. The Ga and Ge depletion observed in core-bearing spherules could be interpreted that these spherules were heated for shorter duration but to higher temperatures than those without cores. An alternative, which is less likely in our model, is that Ga and Ge were already depleted in precursor material of the core-bearing spherules.

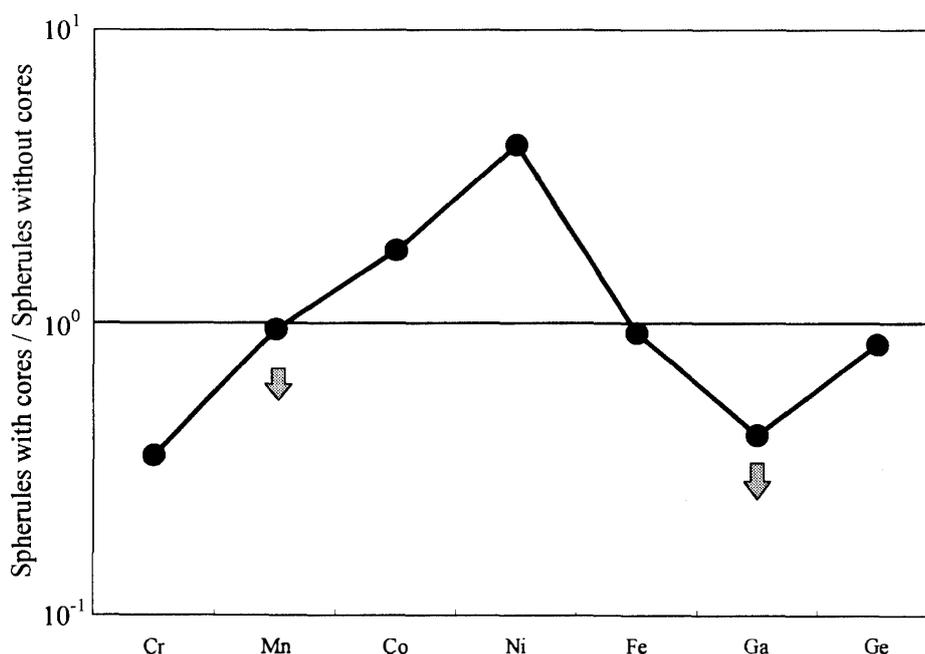


Fig. 4. The mean elemental abundances of spherules with cores normalized to those of spherules without cores. Arrows in the diagram indicate that true concentrations of Mn and Ga are less than the black circles that correspond to the detection limit of the elements.

4.2. Possible precursors of I-type cosmic spherules with low Mn concentration

Mn concentration in I-type spherules is very important to determine whether they have originated from iron meteorites or not, because iron meteorites generally contain little Mn up to 0.1 ppm (HONDA *et al.*, 1990). Thus, we divided spherule samples into two groups based on Mn contents: low Mn group that contains Mn below the detection limit (less than 25 ppm) and high Mn group that contains Mn over the detection limit. Average concentrations of measured elements in low and high Mn groups are summarized in Table 2. The low Mn contents of the low Mn group indicate a genetic relation to iron meteorites. In the next paragraph we will discuss whether trace element signatures of the low-Mn group can be explained by the ablation of iron meteorites or not.

The elemental abundances of low Mn group normalized to Fe and the Cape York IIIAB iron meteorite (WASSON *et al.*, 1989) are shown in Fig. 5. IIIAB iron meteorites are regarded as the most probable candidate for precursors of I-type spherules, because

Table 2. Mean concentration of trace elements in I-type spherules.

	Cr (ppm)	Mn (ppm)	Co (ppm)	Ni (%)	Ga (ppm)	Ge (ppm)
Low Mn group	1803	0	3359	2.5	6	8
High Mn group	383	1884	1903	2.3	2	1

Mean concentrations are calculated with an assumption that element concentration below detection limits are zero.

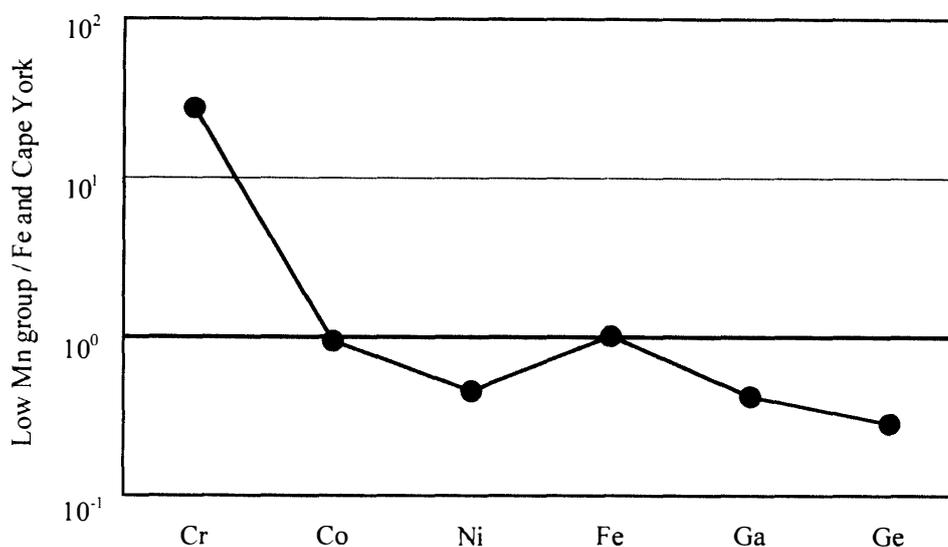


Fig. 5. The mean elemental abundances of low Mn group normalized to Fe and the IIIAB Cape York iron meteorite, showing that relative abundance decreases from left to right in the diagram. Elements are ordered with increasing vapor pressure.

IIIAB is the largest group in iron meteorites. A large excess of Cr, up to 158, is observed in all spherules. Co and Ni abundances in the spherules seem slightly lower than those in Cape York, which are scattering from 0.01 to 5 and from 0.01 to 1.7, respectively. Ga and Ge abundances are lower in the spherules than in Cape York (Fig. 5). Assuming IIIAB iron meteorites as a precursor of I-type spherules, the fractionation of the elements relative to IIIAB meteorites indicates some changes of elemental abundance during ablation in the atmosphere. Vaporization at high temperatures is one of the most effective processes on the elemental fractionation. If iron meteorites were severely heated and partially vaporized, their elemental abundances would be fractionated in accordance with vapor pressures. At oxygen fugacity where liquid magnetite is stable, Cr, Mn, Co, Ni, Ga, and Ge are in the form of Cr_2O_3 , MnO, Co, Ni, Ga_2O_3 , and GeO_2 , respectively, and volatilities of these elements and oxides are calculated to be $\text{Cr}_2\text{O}_3 < \text{MnO} < \text{Ni} \sim \text{Co} < \text{Fe}_3\text{O}_4 < \text{Ga}_2\text{O}_3 < \text{GeO}_2$, using literature data (Fe_3O_4 data from SAMSONOV, 1973; others from JANAF, 1986; LAMOREAUX *et al.*, 1987). Elements are ordered with increasing vapor pressure in Fig. 5. Highly volatile elements such as Ga and Ge are depleted and refractory element, Cr, is enriched (Fig. 5), which is consistent with the model that I-type spherules are ablation products of iron-meteorites. But Ni is more strongly depleted than the value expected from its vapor pressure. One possible explanation for the Ni depletion is ejection of metallic cores, rich in Ni up to 95% (Bi *et al.*, 1993), from spherules during deceleration in the atmosphere (PARKIN *et al.*, 1980; MURRELL *et al.*, 1980; Bi *et al.*, 1993).

Next we consider whether chondrite-derived metallic melts can be precursors of I-type spherules of the low-Mn group. It is expected that during atmospheric ablation of chondritic meteorites the metallic melts were separated from silicate melts due to large density differences upon strong deceleration of meteoroids and the ejected metallic

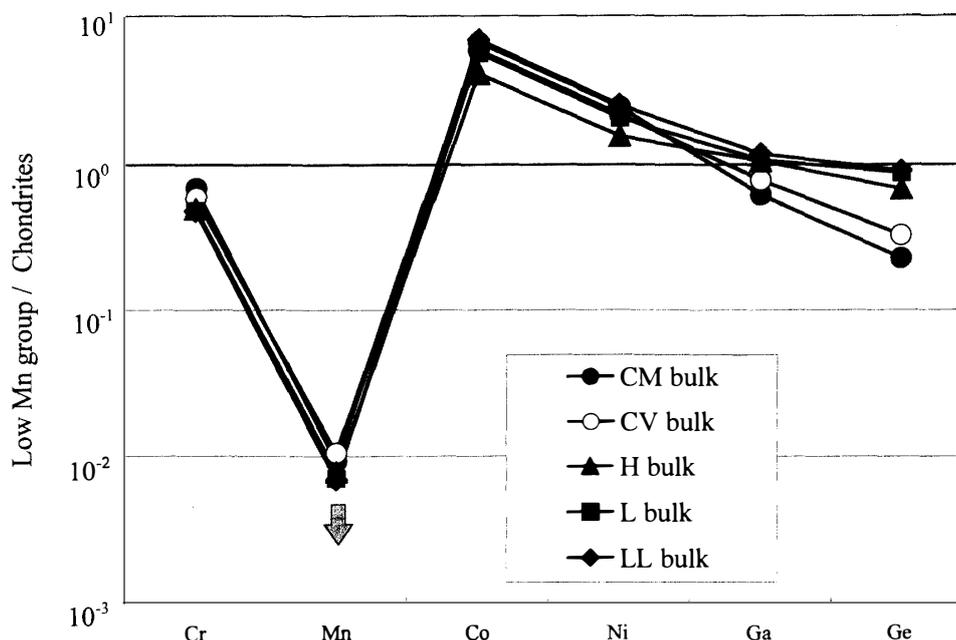


Fig. 6. The mean elemental abundances of low Mn group normalized to those of CM, CV, H, L, and LL chondrite groups (KALLEMEYN *et al.*, 1989; BAEDECKER and WASSON, 1971), showing a large depletion of Mn and excesses of siderophile elements such as Co and Ni. An arrow in the diagram indicates that true concentration of Mn is less than the black circle that corresponds to the detection limit of the element.

melts were later cooled to form I-type spherules, as was outlined by BROWNLEE *et al.* (1983). Element abundances of the low Mn group normalized to those of bulk H, L, LL, and C chondrites (data from KALLEMEYN *et al.*, 1989; BAEDECKER and WASSON, 1971) are shown in Fig. 6. Enrichments of Co and Ni in the spherules resulted from preferential partitioning of the elements into the metallic melt during melting of chondrites, whereas depletions of Ga and Ge might be caused by evaporation loss (Fig. 6). Abundances of Cr and Mn differ greatly (Fig. 6), indicating that they would have behaved differently each other in a chondritic melt.

From here discussion is focused on the different behavior of Cr and Mn. Any type of chondrites including H, L, LL, and C types contains almost equal amounts of Mn and Cr, approximately 3000 ppm (GOLES, 1971a, b), while spherules of the low-Mn group contain Cr 1803 ppm in average but are completely lacking in Mn (Table 2). During atmosphere entry, surface layers of meteorites are molten. In the surface layers, metallic melts coexist with silicate melts as immiscible liquids. Element partitioning should occur between metallic and silicate melts. However, the duration of high temperature is estimated to be very short around 10 s based on the numerical simulation of aerodynamic ablation of I-type spherules (YADA *et al.*, 1996). Diffusion rates of Mn and Cr in liquid metal are very high; at 1600°C Mn and Cr diffuse approximately 600 μm length in 10 s (ONO and MATSUMOTO, 1974), suggesting that partitioning of the elements would be in equilibrium within the metallic spherules with $\sim 300\mu\text{m}$ diameter even for very short time.

Based on the experimental determination of element partitioning between silicate and S-bearing metallic melts at 1260°C (DRAKE *et al.*, 1989), Mn and Cr are lithophile elements that tend to locate in silicate melts under oxygen fugacity higher than 10^{-12} bar, whereas they are siderophile under oxygen fugacity lower than 10^{-15} bar. At an intermediate fugacity from 10^{-12} to 10^{-15} bar, Cr is siderophile and Mn is lithophile (DRAKE *et al.*, 1989). At 85–90 km altitude in the atmosphere where I-type spherules experienced the highest temperatures (LOVE and BROWNLEE, 1991), oxygen fugacity on the surface of meteoroids is estimated to be 10^{-6} bar or higher. When we apply the metal/silicate partition coefficients for Mn and Cr at 1260°C and 10^{-6} bar oxygen fugacity to the elemental partitioning between silicate and metallic melts in molten chondrites, both Mn and Cr are lithophile, locate preferentially in silicate melts, and are absent from metallic melts. This is inconsistent with the presence of abundant Cr in the spherules (Table 2). In order to produce the spherules from chondritic melts, a more reduced condition where Cr is siderophile and Mn is lithophile is required, since Cr is present but Mn is absent in spherules (Table 2). In such condition Cr must behave as a weakly siderophile element that is partitioned equally into metallic and silicate melts, because Cr concentrations in spherules and chondrites are comparable (Fig. 6). BROWNLEE *et al.* (1983) proposed that carbon in chondritic meteorites worked for reduction of oxygen fugacity by reacting with oxygen at high temperatures. But too much reduction would fail in producing elemental abundances of the spherules, because at lower oxygen fugacity both Cr and Mn behave as siderophile (DRAKE *et al.*, 1989) to form Cr- and Mn-rich spherules.

Element partitioning between liquid metal and liquid silicate in molten chondrites is likely to occur at temperature higher than 1260°C. As was mentioned, at 1260°C and 10^{-6} bar oxygen fugacity both Cr and Mn are lithophile, but Cr and Mn tend to become siderophile with increasing temperature (GEBMANN and RUBIE, 1998). Thus, it is probable that at a certain temperature and 10^{-6} bar oxygen fugacity Cr is siderophile and Mn is lithophile. Experimental study is clearly needed to establish the range of oxygen fugacity and temperature of melting chondrites where Cr-rich and Mn-poor metallic melt is stable.

4.3. Clues to a precursor of Mn-rich spherules

Spherules of high-Mn group showed elemental abundances different from those of low-Mn group. Chief differences are Mn and Cr concentrations. In the high-Mn group, concentrations of these elements are 1884 ppm and 383 ppm in average, respectively (Table 2). Homogeneous Mn distribution in a Mn-rich spherule implies that Mn might be indigenous. Therefore we assume that high Mn content in the spherules is primary. Spherules with high Mn concentration would not be originated from iron meteorites that contain very little Mn up to 0.1 ppm. A possible candidate for precursor material that can explain high Mn contents is chondrite-derived metallic melts. Element abundances of the high Mn group normalized to those of bulk H, L, LL, and C chondrites (data from KALLEMEYN *et al.*, 1989; BAEDECKER and WASSON, 1971) are shown in Fig. 7, where Cr is depleted relative to Mn. In metallic melts in a chondritic melt that contains Cr and Mn equally, concentration of Cr must be higher than that of Mn, since a partition coefficient of Cr between liquid metal and silicate is higher than

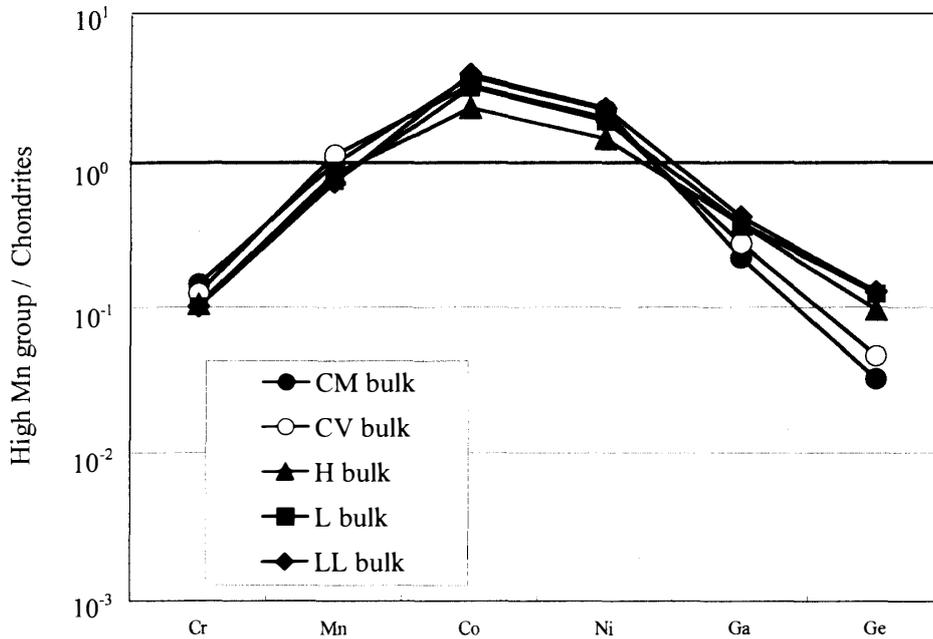


Fig. 7. The mean elemental abundances of high Mn group normalized to those of CM, CV, H, L, and LL chondrite groups (KALLEMEYN *et al.*, 1989; BAEDECKER and WASSON, 1971), showing depletions of Cr, Ga, and Ge and excesses of siderophile elements such as Co and Ni. Unlike elemental abundance in Fig. 6, Mn is enriched relative to Cr.

that of Mn over a wide range of oxygen fugacity (DRAKE *et al.*, 1989). In addition, volatility of Cr is lower than that of Mn at high temperatures, which facilitates enrichment of Cr relative to Mn in the spherules. These requirements are inconsistent with the observation: Mn is richer than Cr in the spherules (Fig. 7). Therefore precursor material of spherules of the high-Mn group may be neither iron meteorites nor metallic melts ejected from chondrites, when assumed that Mn in the spherules is indigenous.

5. Conclusions

(1) Trace element abundances of Mn-poor spherules are systematically fractionated relative to iron meteorites. Refractory elements are enriched and volatile ones are depleted in the spherules, except for a strong depletion of Ni. This is generally consistent with the hypothesis that the spherules are ablation products of iron meteorites. The Ni depletion might be explained by the ejection of Ni-rich metallic cores from the spherules.

(2) Mn-poor spherules could be produced by the ablation of chondritic meteorites, in which metallic melts are separated from chondritic meteoroids to form I-type spherules. But this mechanism is valid only when melting of chondrites occurred at a limited range of oxygen fugacity under which Cr is siderophile and Mn is lithophile.

(3) Unique compositional features of Mn-rich spherules make it difficult to infer a precursor material.

(4) Spherules with Fe-Ni metallic cores are depleted in volatile elements relative to those without cores, suggesting heating at very high temperatures or deficiency of these elements in the precursors.

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