CHEMICAL STUDIES ON THE DISTRIBUTION OF GERMANIUM AND GALLIUM IN ANTARCTIC IRON METEORITES

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Abstract: Three Antarctic iron meteorites, Yamato-790517, Y-791076 and Y-791694, were analyzed and Y-790517 was classified as a IIIA meteorite. Elemental distributions of Ge, Ga, P, S, Co and Ni in the six Antarctic iron meteorites, ALH-77263, ALH-77289, Y-790724 and the three meteorites listed above, were examined and mapped by a newly developed computer-aided microanalyzer (CMA) and presented in color printouts.

1. Introduction

Germanium (Ge) and gallium (Ga) in iron meteorites are very important elements for classification and study of their origins (SCOTT and WASSON, 1975). Many scientists have published papers on analytical results for Ge and Ga in iron meteorites. Some meteorites show high concentrations of Ge and Ga according to their analytical studies. However, most of their studies were limited to the determinations of the total amounts of Ge and Ga in iron meteorites. GOLDSTEIN (1966, 1967) studied the distribution of germanium in metallic phases of iron meteorites by using an electron probe microanalyzer (EPMA).

In this second paper of our chemical studies of iron meteorites, we analyze the three new Antarctic meteorites, Yamato-790517, Y-791076 and Y-791694. And we study to find out segregations of Ge, Ga, P, S, Co and Ni in the bulk of these six meteorite samples, including ALH-77263, ALH-77289 and Y-790724, by using the newly developed computer-aided microanalyzer (CMA).

2. Experimental

2.1. Samples

Six samples, ALH-77263, ALH-77289, Y-790517, Y-790724, Y-791076 and Y-791694 were studied here.

2.2. Analytical methods

2.2.1. Elemental analysis

Neutron activation analysis and ordinary chemical analysis were carried out in order to determine the chemical composition of the iron meteorites. Twelve elements, Co, As, Au, Cr, Ga, Ge, Ir, Pt, Re, Ru, Sb and W were determined by neutron activation analysis. Ni was determined by the nickel glyoxime gravimetric method and P by the molybdenum blue spectrophotometric method, according to the Japan Industrial Standard, JIS G 1216–1981 and 1214–1980.

Neutron activation analysis was carried out as follows. A sample of 0.1 g was irradiated for 1 min in F24 irradiation pit (1×10^{12} n/cm^2·s) of the nuclear reactor, TRIGA Mark II, of Atomic Research Laboratory, Rikkyo University, and cooled for 2 h, Gamma rays from the activated Ge was measured by the Ge(Li) solid-state detector (Canberra Ind., 8100 type, measuring time: 5 min). The sample was irradiated again for 15 min, cooled for 24 h and then γ-rays from the other 11 elements were measured by the same detector (measuring time: 15 min).

2.2.2. Distribution analysis

A new analyzer, CMA, is applied for distribution analysis of the elements in the iron meteorites. CMA is an abbreviation of Computer-aided Microanalyzer (TAGUCHI, 1984; TAGUCHI and HAMADA, 1985). It has been developed from a high-grade combination of EPMA (Electron Probe X-ray Microanalyzer) and a computer. The sample surface is irradiated by electron beam in vacuum and the amount of characteristic X-ray emission is measured. By repeating this procedure and processing the analytical data for many points on the sample surface (max.: 1 million points) by a computer, the CMA quantitatively displays the distribution of elements (max.: 5 elements) on the sample surface, and the results are shown in the color displayer. A new large-area scanning system and a data processing system have been applied to the CMA. It has been used for quantitative analysis of elemental segregation of steel slab samples. The CMA was also used for quantitative spot analysis.

3. Results and Discussion

3.1. Elemental composition

The analytical results of the iron meteorites by neutron activation analysis and

Table 1. The analytical results of the six Antarctic ron meteorites.

Element	ALH-77263	ALH-77289	Y-790517	Y-790724	Y-791076	Y-791694
Ni	67800	67900	74200	74700	136000	355000
Co	4700	5200	5800	4500	7600	6000
P	2000	1800	4100	1200	2800	1500
As	10.6	14.0	10.0	4.0	3.2	3.5
Au	1.5	1.7	0.9	0.5	2.6	1.9
Cr	2.8	5.1	7.2	9.7	5.6	3.2
Ga	99.4	97.5	24	15.6	38	14
Ge	409	360	32	48.9	210	17
Ir	3.1	3.5	2.7	10.0	2.9	1.8
Pt	5.5	6.7	38	9.1	76	56
Re	0.06	0.02	0.43	0.14	0.12	1.1
Ru	3.5	4.8	48	9.9	21	67
Sb	2.1	2.7	9.5	14.7	21	11
W	1.3	1.6	8.8	0.5	0.6	4.5

chemical analysis are given in Table 1. From Table 1, Y-790517 was classified as a Group IIIA meteorite by comparison with the information summarized in Table 27 of BUCHWALD (1975), based mainly on the contents of Ni and Ir, but was not typical because Ga, Ge and Pt are somewhat off. CLARKE (Personal communication, 1985) reported that this meteorite was completely reheated preterrestrially and classified as a IIIA meteorite.

Y-791076 and Y-791694 are not classified because their Ni contents are higher than the upper limit of Ni content shown in the information. CLARKE (Personal communication, 1985) reported that Y-791076 was a plessite octahedrite, paired with Y-75031 and that Y-791694 was an ataxite. The other iron meteorites, ALH-77263, ALH-77289 and Y-790724, were classified into Group I, Group I and Group IIIA, respectively in the previous paper (NAGATA *et al.*, 1983). CLARK (1982) classified ALH-77263 and ALH-77289 into Group IA and grouped them with three other meteorites under the name ALH-76002.

3.2. *Elemental distribution*

3.2.1. ALH-77263

ALH-77263 is an Antarctic iron meteorite collected near the Allan Hills in Victoria Land in January 1978. It is a coarse octahedrite composed of a kamacite matrix of about 6.5 wt% Ni and taenite.

Elemental distributions of Ge, Ga, P, S and Ni in ALH-77263 were measured and presented in Figs. 1–5, respectively. An analytical unit spot, the measured area and the scale bar are shown under the figures. The elemental concentrations measured by X-ray detector at each analysis unit spot are equally divided into more than two groups. Each group is colored in different colors, for example, red, blue, green and dark brown according to the concentration (highest concentration: red, lowest: dark brown). Segregations of Ge and Ga in ALH-77263 are clearly shown in Figs. 1 and 2. From the results of Figs. 1 and 2, the segregations of Ge and Ga are almost the same and are related to Ni segregations. Figure 3 shows the existence of the phosphide (schreibersite, $(Fe, Ni)_3P$). Figure 4 shows the sulphide (troilite, FeS).

Table 2 shows the results of quantitative spot analysis of Ge, Ga, Ni, Co, P and S at the seven spots (*cf.* Fig. 5) of ALH-77263. Table 2 also shows almost the same segregation behaviors of Ge and Ga in ALH-77263 and their relationship to Ni concentration. Nos. 1 and 2 in kamacite are spots where Ge, Ga and Ni are in low concentrations. Nos. 3 and 4 show that Ge and Ga concentrations are higher in taenite of high Ni concentration. At the spots Nos. 5 and 6, schreibersite is located and the Ge and Ga concentrations are very low. At spot No. 7, troilite is found and the concentrations of the two elements are also low.

3.2.2. ALH-77289

ALH-77289 is also an Antarctic iron meteorite collected near the Allan Hills and is a coarse octahedrite composed of kamasite matrix of about 6.5 wt% Ni and taenite. Elemental distributions of Ge, Ga, P, S and Ni in ALH-77289 are presented in Figs. 6–10, respectively. Segregations of Ge and Ga in ALH-77289 are shown in Figs. 6 and 7. The segregation trends for Ge and Ga are almost the same as in ALH-77263. Figure 8 shows schreibersite. Figure 9 shows sulphur accumulation to the grain

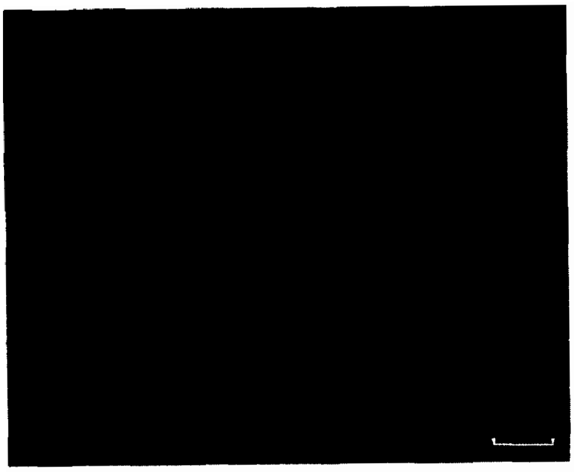

Fig. 1. Ge.

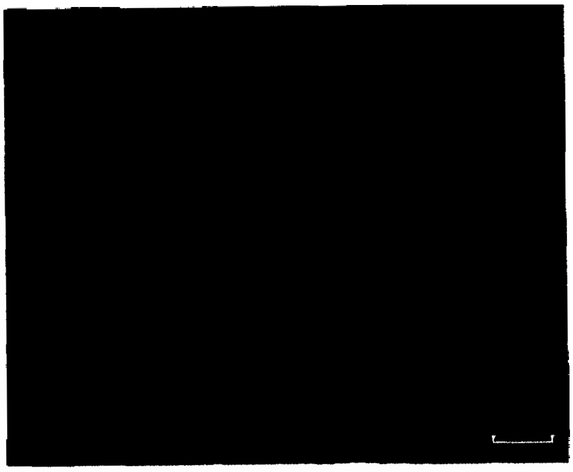

Fig. 2. Ga.

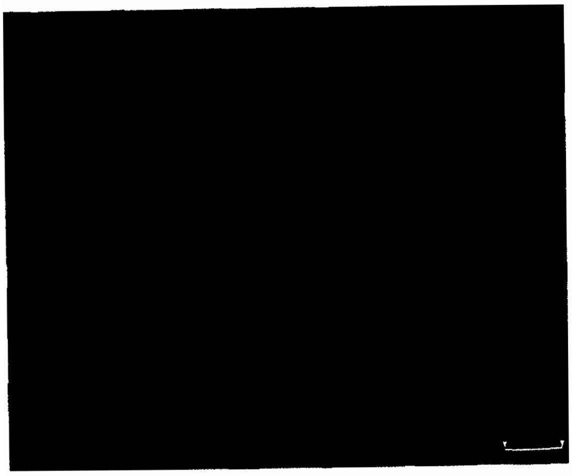

Fig. 3. P.

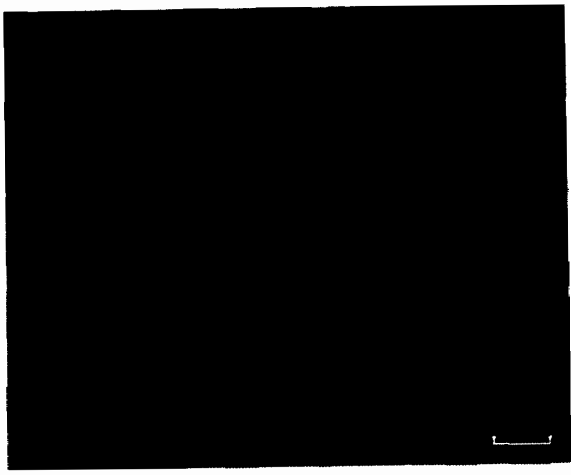

Fig. 4. S.

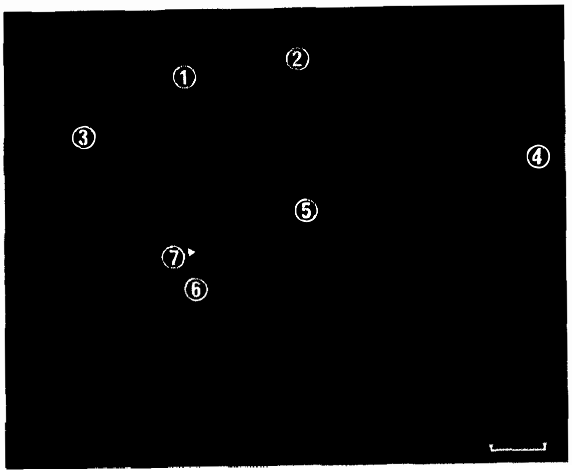

Fig. 5. Ni.

Figs. 1–5. Distributions of Ge (Fig. 1), Ga (Fig. 2), P (Fig. 3), S (Fig. 4) and Ni (Fig. 5) in ALH-77263, studied by CMA. Analytical unit spot: 4×4 μm; measured area: 1.7×2 mm; scale bar: 200 μm.

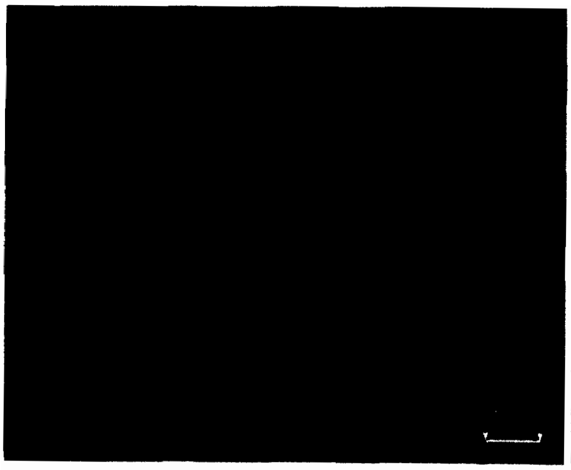

Fig. 6. Ge.

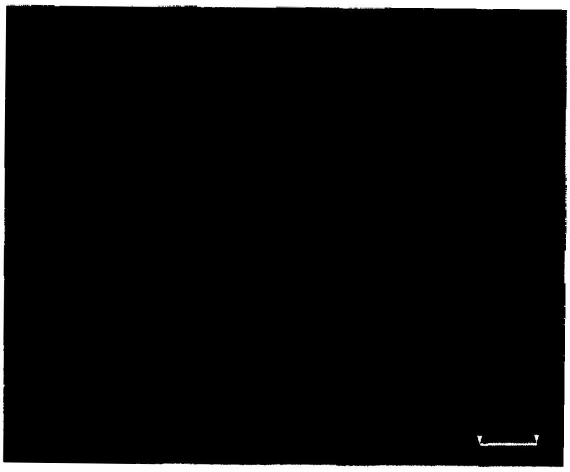

Fig. 7. Ga.

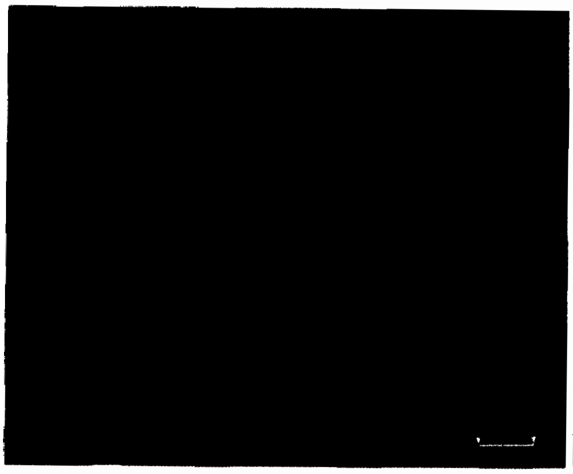

Fig. 8. P.

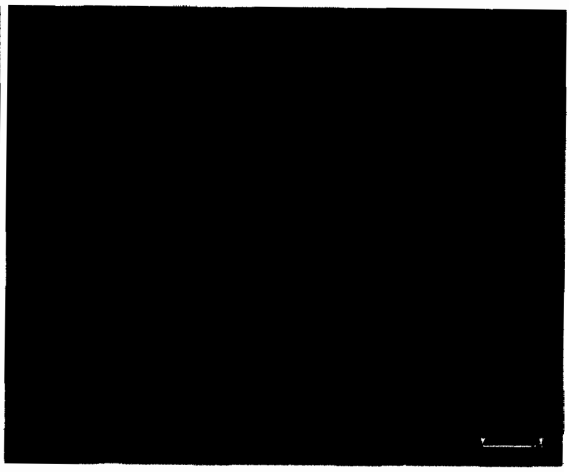

Fig. 9. S.

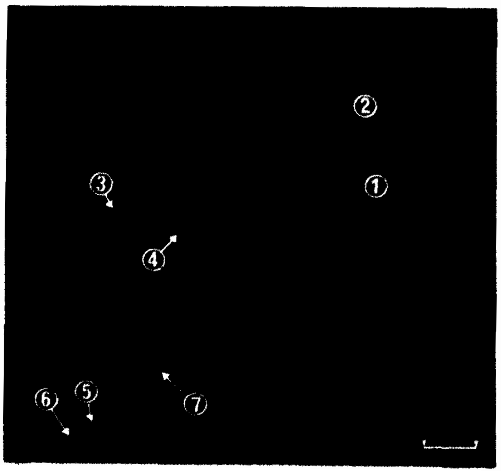

Fig. 10. Ni.

Figs. 6–10. Distributions of Ge (Fig. 6), Ga (Fig. 7), P (Fig. 8), S (Fig. 9) and Ni (Fig. 10) in ALH-77289, studied by CMA. Analytical unit spot: 4×4 μm; measured area: 1.8×2 mm; scale bar: 200 μm.

Table 2. Quantitative spot analysis of ALH-77263 (wt%).

No.	Ge	Ga	Ni	Co	P	S
1	0.046	<0.002	6.89	0.366	0.068	<0.002
2	0.041	0.012	6.48	0.405	0.107	<0.002
3	0.079	0.065	34.68	0.090	0.011	<0.002
4	0.093	0.043	34.86	0.067	0.005	<0.002
5	0.002	<0.002	33.52	0.113	15.71	0.002
6	0.006	0.008	33.86	0.085	15.85	0.002
7	<0.002	<0.002	0.63	0.046	0.005	30.92

Table 3. Quantitative spot analysis of ALH-77289 (wt %).

No.	Ge	Ga	Ni	Co	P	S
1	0.030	<0.002	6.69	0.367	0.059	<0.002
2	0.037	0.005	6.48	0.406	0.088	<0.002
3	0.075	0.067	34.84	0.082	0.013	<0.002
4	0.061	0.052	29.60	0.092	0.009	<0.002
5	<0.002	0.007	38.06	0.066	15.93	0.012
6	0.010	<0.002	37.03	0.072	15.90	0.013
7	0.009	<0.002	1.93	0.117	0.018	30.49

Table 4. Quantitative spot analysis of Y-791076 (wt %).

No.	Ge	Ga	Ni	Co	P	S
1	0.009	0.003	5.22	0.682	0.020	0.005
2	0.023	0.022	4.99	0.685	0.018	<0.002
3	0.034	0.007	36.47	0.287	0.008	<0.002
4	0.052	0.014	31.40	0.326	0.010	<0.002
5	0.049	0.014	21.51	0.411	0.012	0.003
6	0.025	0.014	29.50	0.260	0.010	<0.002
7	0.028	<0.002	6.97	0.705	0.031	0.004
8	0.045	<0.002	7.02	0.692	0.054	0.004
9	0.012	<0.002	40.56	0.110	15.62	0.009
10	0.005	<0.002	42.36	0.107	15.56	0.004

boundaries.

Quantitative spot analysis at seven spots (*cf.* Fig. 10) of ALH-77289, shown in Table 3, reveals the same segregation tendencies of Ge and Ga in ALH-77289 as in ALH-77263. Nos. 1 and 2 are the spots of low concentrations of Ge, Ga and Ni in kamacite. Nos. 3 and 4 are the spots of high concentrations of Ge, Ga and Ni in taenite. At the spots No. 5 to 7, where phosphide and sulphide exist, Ge and Ga are in very low concentrations.

The same behaviors of the elements of ALH-77263 and ALH-77289 probably suggest that the two iron meteorites represent the same fall. The two meteorites were analyzed by CLARKE (1980), DAODE *et al.* (1982) and the three of the present authors (NAGATA *et al.*, 1983). They presented similar analyses and came to the same conclusion that the two meteorites were paired from the viewpoint of total elemental analysis.

3.2.3. Y-791076

Y-791076 is a plessite octahedrite and consists of kamacite of 7.3 wt% Ni and

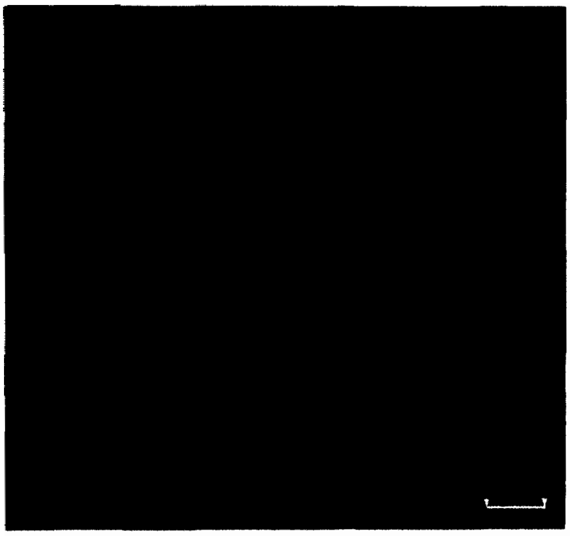

Fig. 11. Ge.

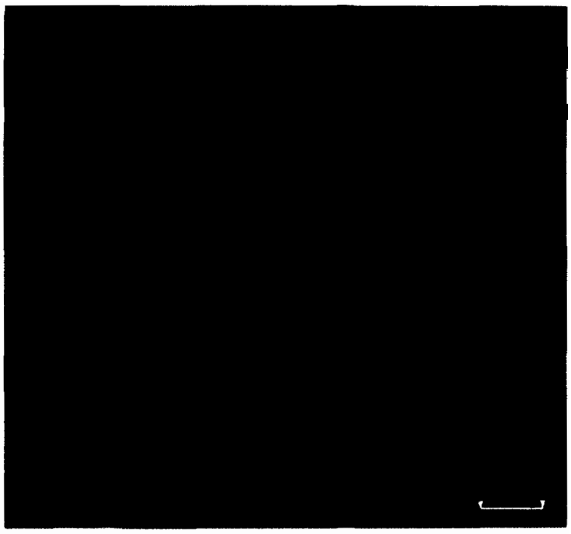

Fig. 12. P.

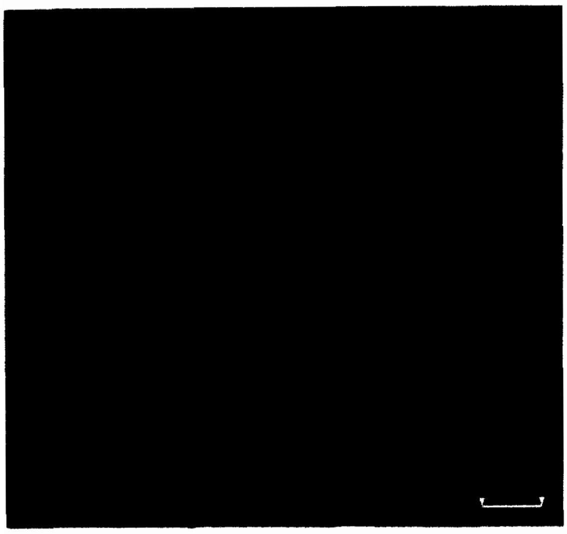

Fig. 13. Co.

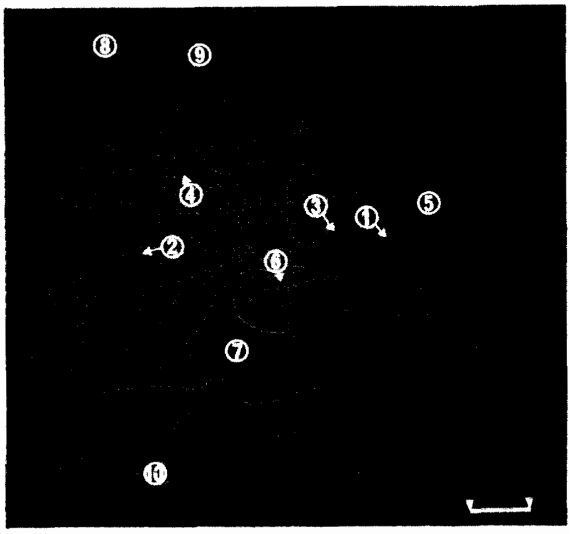

Fig. 14. Ni.

Figs. 11–14. Distributions of Ge (Fig. 11), P (Fig. 12), Co (Fig. 13) and Ni (Fig. 14) in Y-791076, studied by CMA. Analytical unit spot: 1×1 μm; measured area: 0.5×0.5 mm; scale bar: 50 μm.

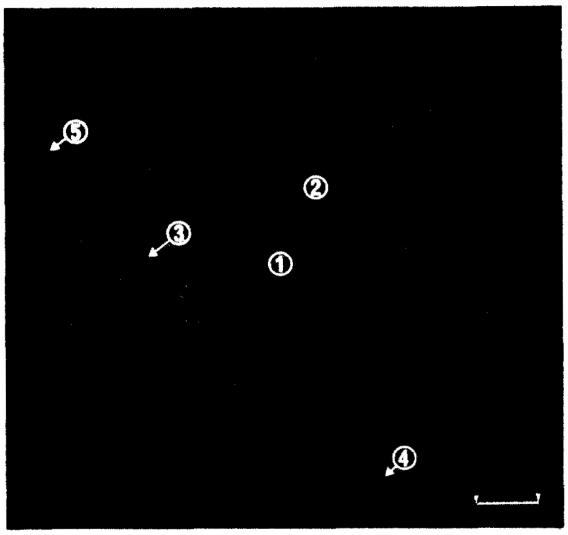

Fig. 15. Distribution of Ni in Y-790724, studied by CMA. Analytical unit spot: 4×4 μm; measured area: 2×2 mm; scale bar: 200 μm.

plessite of about 12 wt% Ni. Elemental distributions of Ge, P, Co and Ni in Y-791076 were measured and are presented in Figs. 11–14, respectively. The results of spot analysis are presented in Table 4 (*cf.* Fig. 14). Segregation of Ge in Y-791076 was detected but not clearly demonstrated, as shown in Fig. 11. The segregation of Ga was almost the same as that of Ge. Figure 12 shows the distribution of schreibersite. Comparing the Ge distribution (Fig. 11) with the phosphide (Fig. 12), it is revealed that Ge is not concentrated at the spots where phosphide exists. Figures 13 and 14 show the distributions of Co and Ni. The Co concentration is high at the spots where the Ni concentration is low.

3.2.4. The other meteorites

Chemical studies were also conducted in order to investigate the distributions of the elements in Y-790517, Y-790724 and Y-791694. Y-790517 consists of kamacite matrix of 6.4 wt% Ni, another kamacite of about 12 wt% Ni and taenite. Y-790724 is a coarse octahedrite of kamacite matrix of 7.0 wt% Ni and taenite. Y-791694 is an ataxite consisting of taenite of about 40 wt% Ni and a small amount of kamacite. Remarkable segregations of Ge and Ga of the three Yamato meteorites were not detected because of the low total concentrations. For example, Ni distribution of Y-790724 is shown in Fig. 15 with the analytical results of the five marked spots. The results are presented in Table 5. Remarkable segregations of Ge and Ga are not

Table 5. Quantitative spot analysis of Y-790724 (wt %).

No.	Ge	Ga	Ni	Co	P	S
1	<0.002	<0.002	6.97	0.458	0.107	<0.002
2	<0.002	<0.002	7.02	0.448	0.122	0.004
3	0.012	0.010	28.22	0.138	0.027	<0.002
4	<0.002	0.034	32.70	0.107	0.015	<0.002
5	<0.002	<0.002	29.06	0.118	15.97	0.008

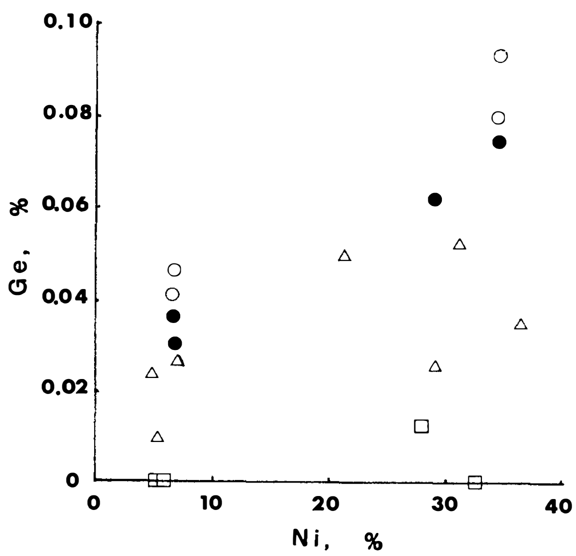

Fig. 16. Relationship between Ge and Ni. ○ ALH-77263, ● ALH-77289, △ Y-791076, □ Y-790724.

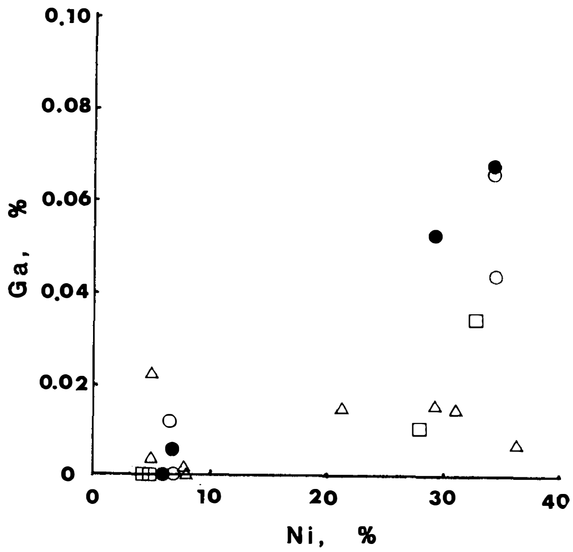

Fig. 17. Relationship between Ga and Ni. Symbols as in Fig. 16.

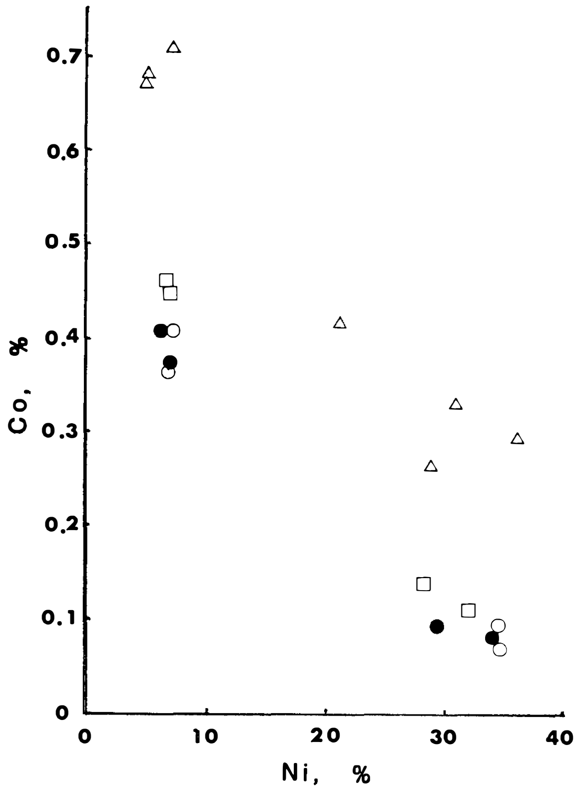

Fig. 18. Relationship between Co and Ni. Symbols as in Fig. 16.

detected from Table 5.

3.2.5. Others

The relationship between the two elements (Ge/Ni, Ga/Ni, Co/Ni) was plotted from the analytical results of Tables 2–5 and are shown in Figs. 16–18. The concentrations of Ge and Ga are largely related to the concentration of Ni. The concentrations of Ge and Ga increase with the concentration of Ni, as shown in Figs. 16 and 17. This tendency is clearly noticed in ALH-77263, ALH-77289 and Y-791076, but cannot be noticed in Y-790724. All the analytical data from Tables 2–5 were plotted, except the data measured at the spots where phosphide and sulphide were located. Figure 18 shows the relationship between Co and Ni. The concentrations of the two elements are closely related. The Co concentration is high at the spots of low concentration of Ni.

4. Summary

(1) Three Antarctic iron meteorites, Y-790517, Y-791076 and Y-791694, were analyzed and Y-790517 was classified as a IIIA meteorite.

(2) Distributions of the elements, Ge, Ga, P, S, Co and Ni, in the six Antarctic iron meteorites, ALH-77263, ALH-77289, Y-790724 and the three meteorites listed in (1), were examined and mapped by using the newly developed computer-aided microanalyzer (CMA). The results were presented in color printouts.

Acknowledgments

We wish to express our gratitude to Dr. K. AOKI, senior managing director and central R & D bureau director of Nippon Steel Corporation, for his interest and support.

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(Received October 1, 1984; Revised manuscript received January 14, 1986)